Acid-Labile, Chain-Scission Polymer Systems Used as Positive-Tone Photoresists Developable in Supercritical CO_2

Nelson Felix[†] and Christopher K. Ober[*,‡]

School of Chemical and Biomolecular Engineering and Department of Materials Science and Engineering, Cornell University, Ithaca, New York

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A new type of acid-catalyzed, chain-scission polymeric system is reported based on main-chain acetal linkages and designed for solubility selectivity in supercritical (sc) CO_2. These low-molecular-weight polymer segments, formed by the stepwise polymerization of divinyl ethers and dihydroxy-based monomers, are linked together to render these individually soluble components insoluble in scCO_2. Upon exposure to an acid, the linkages are cleaved and result in a system soluble in both aqueous base and scCO_2, two widely disparate solvents. This fact is utilized to make a positive-tone photoresist system developable in scCO_2 as well as aqueous developer. This represents to the best of our knowledge the first known report of an intrinsically positive-tone photoresist developable in pure scCO_2. Excellent solubility contrasts are shown and feature sizes below 200 nm can be obtained with this system.

Introduction

Recent years have seen a dramatic increase in the study and practical use of supercritical CO_2 (scCO_2) as a high-performance, environmentally friendly solvent.[1] This increase has occurred in both materials synthesis and processing[2–4] and is primarily due to the unique properties of scCO_2 as a solvent. Combining liquidlike densities with gaslike diffusivities, scCO_2 is able to penetrate structures on the nanoscale while being able to selectively dissolve nonpolar components.[5–7] In this way, scCO_2 has been identified as a solvent that enables gentle processing of delicate structures on the scale of a few nanometers. However, when one considers typical matrix solubility, most polymeric materials are insoluble in scCO_2 under moderate conditions. In fact, only nonpolar oligomers and small molecules are significantly soluble in scCO_2.

One area where scCO_2 has been studied in some detail is as a development solvent for photoresist patterning.[8,9] Because of its lack of surface tension, scCO_2 is an ideal solvent for developing dense, high-aspect-ratio features without these features collapsing inward as the solvent dries.[10] However, traditional patternable photoresist materials are not intrinsically scCO_2-soluble. Organic materials that have been shown to be soluble in scCO_2 are primarily nonpolar silicone or fluorinated materials. These concepts were demonstrated in the first reports of scCO_2-developable photoresists ("resists"), where fluorinated methacrylates were copolymerized with monomers containing acid-cleavable groups, which undergo a nonpolar to polar switch when exposed in the presence of a photoacid generator.[8] These types of systems would be positive-tone (exposed/reacted regions more soluble) when developed in aqueous base, but they are negative-tone when developed in any nonpolar solvent such as scCO_2.

This report describes efforts to create new polymeric materials free from fluorinated or silicone containing groups that can be used, in contrast to prior efforts, to produce high-resolution, scCO_2 processed positive tone (sub-100 nm) patterns. The material depends on light-activated, acid-catalyzed cleavage of acetal linkages to depolymerize a polymer and make the scissioned components more soluble in scCO_2.

There have been no previous reports of an intrinsically positive-tone photoresist system developable in pure scCO_2. Multistep systems do exist that render the system positive-tone in final development.[11] Although feasible, these multiple processing steps are not as desirable as intrinsically positive-tone systems. However, solubility changes can be affected by changes in molecular weight. Recent reports on scCO_2-soluble small molecules have shown that size plays an

* Corresponding author. E-mail: cober@ccmr.cornell.edu. Address: 310 Bard Hall, Cornell University, Ithaca, NY 14853.
† School of Chemical and Biomolecular Engineering, Cornell University.
‡ Department of Materials Science and Engineering, Cornell University.

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Scheme 1. Method for Creating Acetal Bonds Using Divinyl Ether and Dihydroxy Precursors; These Bonds Can Subsequently Undergo Acid-Catalyzed Cleavage in the Presence of Water

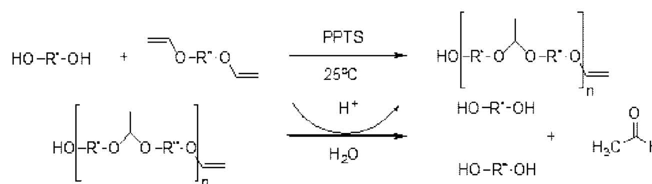
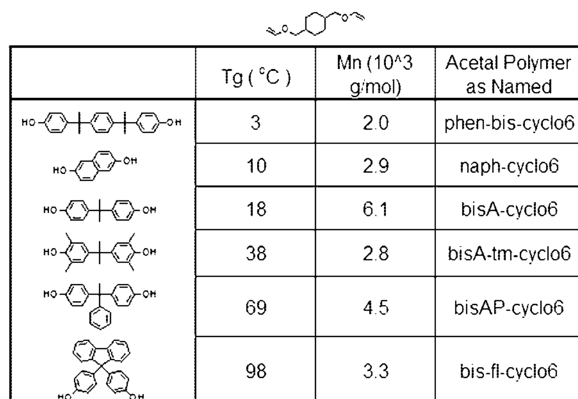


Table 1. Glass-Transition Temperatures and Molecular Weights of the Polymers Obtained by the Combination of Dihydroxy and Divinyl Ether Compounds; Corresponding Short Names Used in This Paper Are Also Shown



	Tg (°C)	Mn (10^3 g/mol)	Acetal Polymer as Named
	3	2.0	phen-bis-cyclo6
	10	2.9	naph-cyclo6
	18	6.1	bisA-cyclo6
	38	2.8	bisA-tm-cyclo6
	69	4.5	bisAP-cyclo6
	98	3.3	bis-fl-cyclo6

important role in determining solubility.[12,13] The solubility of nonpolar molecules will decrease predictably as molecular weight increases. Nevertheless, molecules larger than 1000 g mol^{-1} are still soluble. This suggests that photoresists that undergo chain scission upon exposure have the potential to be intrinsically positive tone, where the small molecular weight fragments in the exposed regions are more soluble than the surrounding larger molecular weight regions.

The chain scission process is the basis of the mechanism of positive-tone electron beam (e-beam) resists such as poly(methyl methacrylate) and poly(methyl-α-chloroacrylate-*co*-αmethylstyrene).[14,15] However, the solubility of these resists is inadequate for $scCO_2$ processing and the required doses for chain scission e-beam resists are relatively high when compared to chemically amplified resists that take advantage of a photoacid generator to lower the activation energy of reaction. To make these types of resists more sensitive would require the inclusion of acid-labile bonds in the polymer backbone.

Along these lines, there have been examples of linear polymers that contain acid-cleavable backbones.[16–20] In general, this type of system is fairly effective in producing low-molecular-weight fragments upon exposure to catalytic amounts of acid, and some types of systems undergo complete polymer "unzipping" back to their volatile monomer species.[19] However, if one is to consider these polymers as photoresists for $scCO_2$ development, the chain fragments themselves must be soluble in $scCO_2$. Small molecules with up to two hydroxyl functionalities also possess some solubility in $scCO_2$,[13] suggesting that monomers based on bisphenol platforms can be soluble in $scCO_2$. This has also been confirmed by other researchers.[21] It has been shown that bisphenol monomers can be polymerized simply using acid-labile acetal linkers.[22] Therefore, scissionable polymer chains from these otherwise $scCO_2$-soluble components would be expected to be positive-tone under $scCO_2$ development conditions.

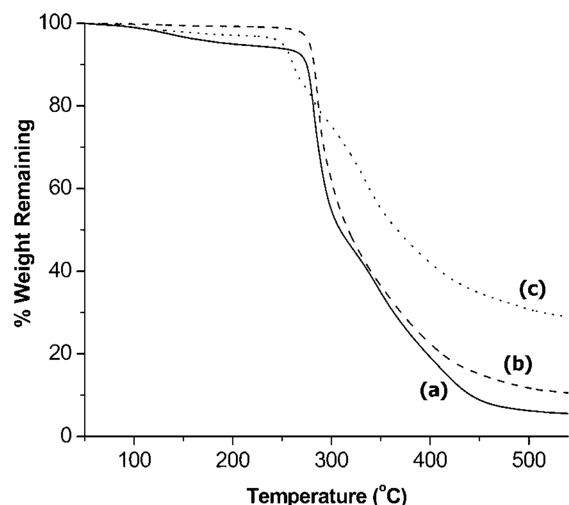


Figure 1. Thermogravimetric data for three representative polymers. All are stable to 250 °C. (a) BisA-cyclo6, (b) bisAP-cyclo6, (c) bis-fl-cyclo6.

The interest in this type of polymer system lies in the fact that the thermal, mechanical, and thermodynamic properties of the polymer can be fine-tuned without having to change their basic chemical functionality. In this way, the thermal properties of these polymers can be tailored to enable their use in other applications such as patternable dielectric layers[23] and other applications needing good film-forming materials[24] with patternable functionality. Given a sufficiently high glass-transition temperature, these polymers can be processed in $scCO_2$ while withstanding the plasticizing nature of the solvent.[25] This paper describes our studies of bisphe-

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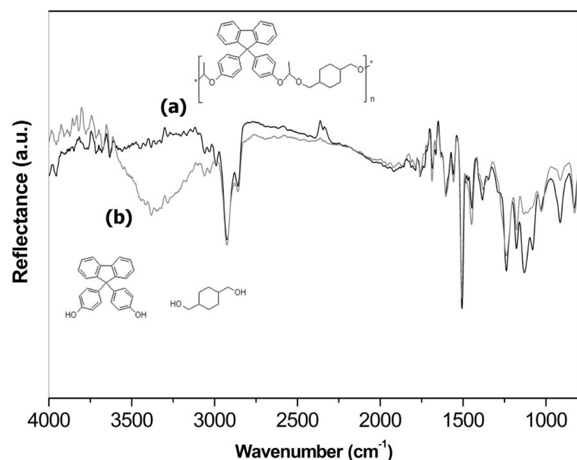

Figure 2. Reflectance FTIR data from a representative (a) unexposed and (b) exposed film. The acetal peaks from 1140 to 1080 cm^{-1} disappear, whereas the hydroxyl stretch appears at 3600–3100 cm^{-1}, indicating that acid-catalyzed cleavage has taken place.

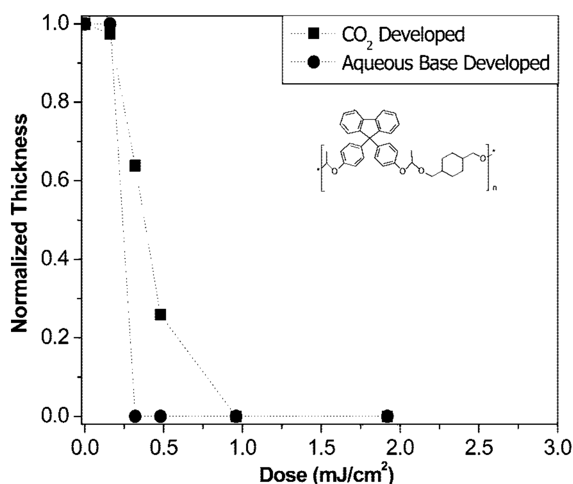

Figure 3. Contrast curve for the bis-fl-cyclo6 photoresist system with (a) aqueous base and (b) supercritical CO_2 development. The photoresist is fairly sensitive and positive-tone in both cases.

nol-based acetal polymers and their processing in $scCO_2$ as well as their investigation as high-resolution photoresists.

Experimental Section

Materials. Histological grade methanol was purchased from Fisher Scientific and used as received. Anhydrous tetrahydrofuran, 1,4-cyclohexanedimethanol divinyl ether, 4,4′-(1,4-phenylenediisopropylidene)bisphenol ("phen-bis"), 2,6-dihydroxynaphthalene ("naph"), 2,2-bis(4-hydroxyphenyl)propane ("bisA"), 4,4′-isopropylidenebis(2,6-dimethylphenol) ('bisA-tm'), 4,4′-(1-phenylethylidene)bisphenol ("bisAP"), 9,9-bis(4-hydroxyphenyl)fluorene ("bis-fl"), pyridinium *p*-toluenesulfonate (PPTS), and sodium ethoxide solution (21% in ethanol) were purchased from Aldrich and used as received. Triphenylsulfonium perfluoro-1-butanesulfonate (TPS-Nf) and propylene glycol monomethyl ether acetate were also purchased from Aldrich and used as received.

Polymer Synthesis. Polymer synthesis was carried out by catalyzed stepwise addition of the dihydroxy (bisphenol) compounds and the divinyl ether compound to form acetal linkages. This is following established literature procedures.[22] The adapted scheme is shown in Scheme 1. Equimolar amounts of bisphenol and divinyl ether were dissolved in anhydrous tetrahydrofuran to a concentration of 1.0 M. A catalytic amount of PPTS was then added, and the solution was allowed to stir at room temperature. After 20 h, the solution was neutralized with a sodium ethoxide solution (21% in ethanol) and then poured into 100 mL of cold methanol; the polymer precipitate was collected and washed with methanol. The solid was then dried in vacuo overnight at 50 °C. Molecular weight was characterized using size-exclusion chromatography with a Waters 486 UV detector and a Waters 2410 differential refractive index detector and tetrahydrofuran as the eluent, and molecular weights compared to a polystyrene standard are reported in Table 1. Thermogravimetric analysis was performed using a TA 500 TGA with a heating rate of 10 °C/min under dry nitrogen atmosphere. Glass transition temperatures were measured on a TA 1000 DSC using repeated heat/cool cycles at 10 °C/min between −50 and 150 °C.

Lithographic Evaluation. Photoresist films for evaluation were made by dissolving each polymer to 10 wt % in propylene glycol methyl ether acetate. Then, the photoacid generator TPS-Nf was added to the solution at a concentration of 5 wt% with respect to the polymer. Each solution was then spin-cast on a primed, bare silicon substrate at 2000 rpm and baked at 130 °C for 60 s. Film thicknesses were measured using a P10 profilometer, and the obtained films were generally ~200 nm in thickness. FTIR spectra were measured using a Mattson Infinity FTIR spectrometer with the Momentμm microscope attachment (HgCdTg detector, cutoff 650 cm^{-1}) operating in reflectance mode.

Contrast curves were obtained by flood exposing regions of the photoresist film using an HTG contact aligner operating at 254 nm wavelength. Films were then postexposure baked (PEB) at 50 °C for 30 s, and they were developed using either supercritical CO_2 at 40 °C and 140 bar (5 min) or aqueous 0.26N tetramethylammonium hydroxide (TMAH) solution (30 s). High resolution patterning was performed using a Leica VB6HR e-beam operating at 100 keV. Conditions for PEB and development were the same as with the flood exposures. SEM images were obtained using a Zeiss Ultra55 SEM with a thin layer of Au/Pd sputtered on top of the film.

Results and Discussion

Patternable acetal-backbone polymeric materials have been previously explored, though in multifunctional forms.[26] Because of the scissioning nature of the material, patterns with relatively low roughness have been shown.[27] In addition, acetal-backbone polymer platforms have a number of other advantages as photoresist materials. When catalyzed by acid in the presence of water, acetal bonds have a relatively low activation energy for cleavage. This translates to a polymer that is very sensitive, and the likelihood of nearly complete chain scission is high. Additionally, this acid catalyzed reaction can take place close to room temperature, reducing the need for a high postexposure bake (PEB) temperature used with most other photoresists. However, since the reaction depends on water,[28] the reaction will not proceed in vacuum exposure systems such as e-beam and extreme ultraviolet (EUV) systems. Because the reaction takes place outside the exposure system during PEB, this reduces the likelihood for outgassing during exposure, which is a key requirement for these systems. Therefore, polymeric acetal

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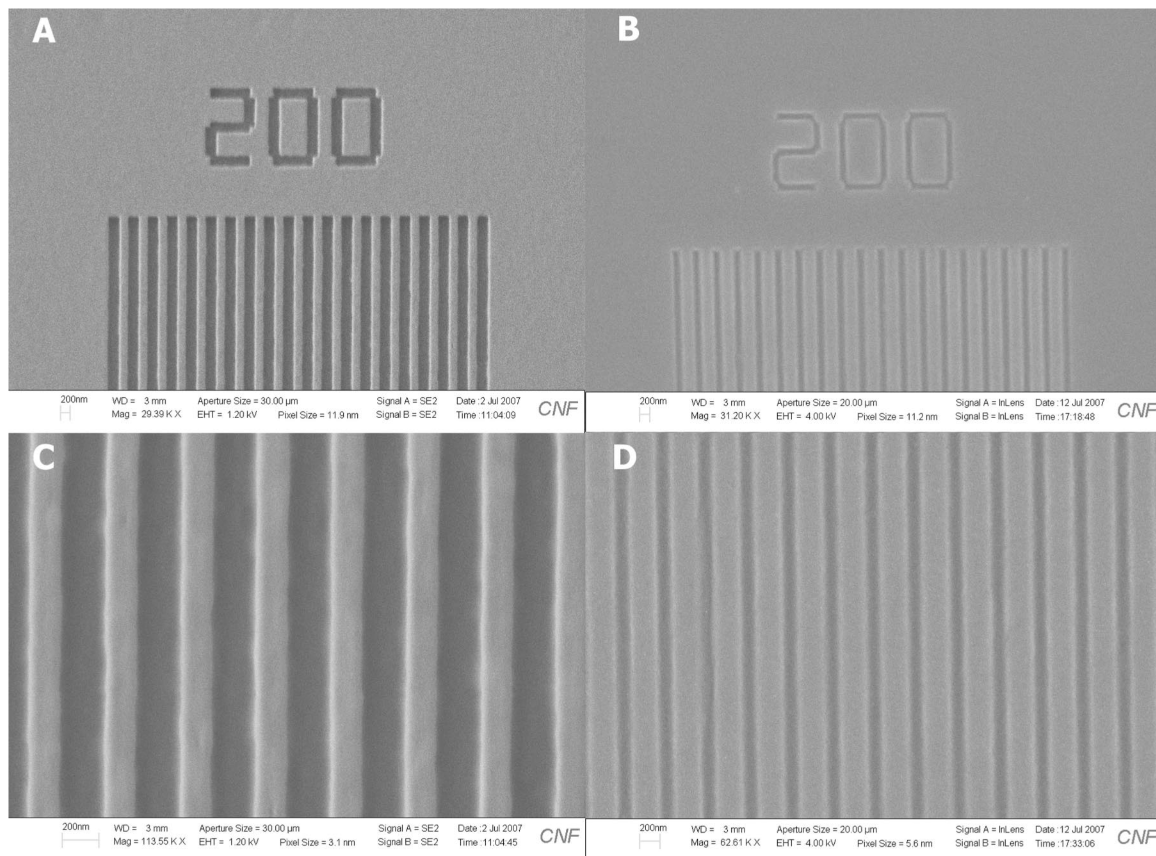

Figure 4. Line and space patterns after e-beam patterning and (A, C) aqueous base or (B, D) supercritical CO_2 development. Trenches in (C) are measured to be 210 nm, whereas trenches in (D) are measured to be 120 nm.

systems have many desirable properties as photoresists in general, with the added benefit that they can be developed using $scCO_2$ as well.

Along with their respective molecular weights, glass-transition temperatures (T_g) for each acetal-linked copolymer combination are shown in Table 1. All polymers comprise commercially available starting materials, and each bisphenol was chosen to enable systematic variation of the central bisphenol linkage in order to determine what factors affected polymer T_g. The results show that T_gs increase for polymers containing bulkier, nonlinear bisphenol monomers, most likely because of the restricted motion and lower free volume of these systems. The highest T_g of 98 °C corresponding to the polymer containing the bulky fluorene moiety. This polymer, bis-fl-cyclo, is the best candidate for $scCO_2$ development as its high Tg will allow it to withstand the plasticizing nature of $scCO_2$ in general. This was the photoresist used for further patterning and $scCO_2$ development. However, all of these polymers can be optimized for other applications by using custom synthesized bisphenols.

The TGA traces for 3 representative polymers are shown in Figure 1. In all cases, after initial solvent loss, decomposition does not start until >250 °C. This demonstrates the stability of the polymers in humidity-free environments and indicates the potential for low outgassing in vacuum-based exposure systems such as EUV. Nevertheless, when exposed samples are placed in the controlled-humidity environment of a clean room (40% relative humidity), the acid-catalyzed reaction happens over the course of ~30 min at room temperature. Even though only room temperature "heating" is necessary, samples for lithography testing were baked at 50 °C to increase sensitivity (reaction conversion) and contrast. This reaction was verified by FTIR as shown in Figure 2. After a 5 mJ/cm^2 exposure, the acetal peaks at 1140–1080 and 2990 cm^{-1} almost disappear while the hydrogen bonded −OH stretch appears from 3600 to 3100 cm^{-1}. This indicates the relative completeness of the depolymerization at this dose. However, as shown in Figure 3, this may not be the case at doses lower than 1 mJ/cm^2.

The acetal-based polymers behaved as positive-tone resists with both aqueous base and $scCO_2$ development. This is remarkable, as one solvent is very polar while the other is nonpolar. The aqueous base development of the exposed areas is due to the increased overall polarity/acidity of the exposed regions, while the $scCO_2$ development is due to the much smaller molecular weight of the photoresist in the exposed areas. Contrast curves for the bis-fl-cyclo polymer system are shown in Figure 3. Under both development conditions, the necessary exposure dose is less than 1 mJ/cm^2 at 254 nm wavelength, which is in the typical range for a chemically amplified resist. Development contrast for the $scCO_2$-developed system is qualitatively lower when compared to the aqueous base-developed system. This is a consequence of fragments of different molecular weights existing in the exposed regions, which $scCO_2$ is more selective in dissolving than aqueous base. Therefore, it can be inferred that at doses below 1 mJ/cm^2, small oligomer fragments as well as monomers are present. However, this

is not the case at doses above 1 mJ/cm^2 and dissolution is indeed complete in both cases.

Patterning results are shown in Figure 4. The patterns are shown after e-beam exposure with a dose of 70 μC/cm^2, baking at 50 °C, and development in either aqueous TMAH base or scCO_2. Figure 4 (A) and (C) correspond to aqueous base development, and the obtained trench features are measured to be 210 nm across. Supercritical CO_2 development results are shown in images B and D in Figure 4, where the trench features are measured to be 120 nm across. Features appear different because of the different development contrast and slight plasticization under scCO_2 development, resulting in more sloped pattern sidewalls compared to wet development. These results confirm the patternability of these materials at features of this size and dramatically represent the best results of intrinsically positive-tone materials developable in scCO_2. With future improvements in material T_g, such as with higher molecular weights or bulkier monomers, this plasticization can be mitigated while keeping the same ability to be developed with scCO_2.

The results presented here show the patterning and development performance of acetal-backbone photoresists. The adaptability for both wet and dry processing is a useful attribute for a photoresist system. Materials like these, where an easy transition can be made from wet to dry processing, might increase the likelihood of further introduction of scCO_2 into microelectronics processing. The chemistry contained in these photoresist systems is quite adaptable as well, and different core structures can be explored to use for different applications or photoresist performance optimization for patterning below 100 nm, which will match the performance seen with small molecule resists developable in scCO_2.

Conclusion

Polymers based on acid-cleavable acetal linkages have been shown to achieve high glass-transition temperatures and reactivity for use in photoresist patterning and development. The novelty of this chain-scission type of resist is that it can achieve positive-tone patterning for both aqueous and scCO_2 development. In fact, this is the first known report of an intrinsically positive-tone scCO_2 developable resist. The ability to change the monomer cores for this photoresist system allows for interesting studies to be performed based on the application. The adaptability of this system also allows for further optimization based on thermal, interfacial, and dissolution properties.

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