Properties and Photodefinition of Poly(aromatic diacetylenes)

Timothy M. Miller,* Elizabeth W. Kwock, Teaster Baird, Jr., and Arturo Hale

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

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Diacetylene copolymers prepared by oxidative coupling of 4,4′-diethynyldiphenyl ether and *m*-diethynyl benzene and 4,4′-diethynyldiphenyl ether and 4,4′-bis(3-ethynylphenoxy)-2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl can be photochemically cross-linked with a dose of 30 and 60 mJ/cm^2 μm (λ = 365 nm), respectively. Patterns in films up to 10 μm thick have been produced with features as small as approximately 12 μm with a contrast of ca. 2. The diethynylbenzene-containing polymer is oxidized slowly at temperatures above 200 °C in air. The fluorinated polymer is quite stable to oxidation at high temperatures in air and can be stretched 90% before it breaks. Both polymers are quite hydrophobic and absorb less than 1% of their weight in water, coefficients of thermal expansion are about 50 ppm/°C in the plane of thin films, and adhesion to Au, Ag, Al_2O_3, and Si is good. Dielectric constants for the series of poly(aromatic diacetylenes) are found to range from 2.82 for the fluorinated polymer to 3.34 for a copolymer of 4,4′-diethynylbenzophenone and *m*-diethynylbenzene.

Introduction

The microelectronics industry needs polymers as dielectric materials in multichip modules (MCM) having a combination of properties including: high toughness and thermooxidative stability, good insulating capability and adhesion, low-temperature processing, low moisture absorption, low dielectric constant, low coefficient of thermal expansion, and simple photodefinability. It is easiest to apply polymers from solution which requires high solubility in, preferably, environmentally acceptable solvents. Photodefinability requires that there be a mechanism for significantly changing solubility on exposure. It is possible to imagine mechanisms in which the solubility of a polymer increases or decreases upon exposure giving rise to positive or negative tones, respectively. In practice, polymers for dielectrics are exclusively negative tone.[1] Polyimides are the main candidate materials for interlayer dielectrics in MCMs because of their high-temperature stability, good processability, mechanical properties, and manufacturer's extensive experience with them.[2] Polyimides have several disadvantages including the evolution of water on thermal curing at high temperatures (ca. 300 °C) and high moisture absorbance which makes their dielectric constant vary with humidity. Considerable effort has been expended to mitigate the latter problem by incorporation of fluorine.[3-6] There are several commercially available photodefinable polyimides which work on two different principles. In one a polyamic acid is esterified or made into a salt with a polymerizable group such as an acrylate. Incorporation of a photoinitiator in a film of the resulting polymer allows it to be gelled in the exposed areas.[7] Unexposed areas remain soluble and can be washed away after which the cross-linkable moieties are volatilized upon thermal curing leaving polyimide. The problem with this approach is that a significant fraction of the mass of the original film must be volatilized, resulting in considerable shrinkage and less than ideal properties. The second approach utilizes an intrinsically photochemically reactive polyimide with carbonyl groups in the backbone which on photoexcitation abstract hydrogen atoms from benzylic positions of alkyl groups incorporated in the polymer.[8,9] The resulting radicals couple yielding cross-links. These materials are soluble in their fully imidized state, have lower T_g values, are less solvent resistant than typical polyimides, are not very sensitive to UV light, and are rather opaque because of the high concentration of chromophores required. Several other classes of polymers are in use or in development for insulators in

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MCMs, or as solder masks or barrier layers.[10] It should be stated that, the patterning of polymer dielectrics does not demand the resolution required of photoresists in IC manufacture. Formation of 20 μm features in 20 μm thick films would be quite adequate for present MCMs.

We sought to design an intrinsically photochemically cross-linkable polymer possessing many of the above properties for potential use in multichip modules. The diaryl diacetylene moiety appeared to be a good building block because it is known to have photochemical and thermal reactivity without evolving volatiles. The thermally cured materials are quite stable; the requisite diethynyl aromatic monomers are prepared relatively easily, and their polymerizations proceed very easily. Finally, if the aromatic moieties are chosen correctly, the polymers should have low dielectric constants and moisture uptakes. The thermal reactivity of poly(aromatic diacetylenes) has been described by several authors, as has the photochemical reactivity of block copolymers containing mainly alkyldiacetylenes.[11-15] The thermal reactivity of diacetylenes is believed to involve their transformation to mainly polycondensed aromatic rings.[12] The photochemical reactions of diacetylenes are probably similar to the topochemical polymerization of crystalline diacetylenes although the number of chains linked together by a single photon is very small compared with the chain polymerization which occurs in crystalline diacetylenes. The difficulty with the known poly(aromatic diacetylenes) is that their thermal reactivity is too high and solubilities are too low. We have reduced these problems by preparing monomers having greater flexibility and copolymerizing these.[16] Here are described some of the properties of these materials relevant to MCM manufacture and a study of their photodefinability.

Results and Discussion

Film Preparation. The copolymers **1**–**4** (Scheme 1) used in this study are random and were prepared as previously described.[16] These copolymers do not possess measurable glass transitions or melting points but exhibit thermally induced cross-linking at 225–275 °C. Three of these are deliberately endcapped with phenylacetylene to keep the solubilities high and viscosities of solutions reasonable. Cyclohexanone dissolved **1**, **2**, and **4** easily, permitting the spinning of 6 μm thick films in a single coating. Solutions of up to 15 wt/wt % of **1** and **2** could be prepared after brief heating and filtration. Concentrated (>10%) solutions of polymers **1** and **2** are unstable and gelation occurs in 4–6 h; however, dilute (5%) solutions in cyclohexanone are stable for many weeks. We do not understand what causes gelation of these concentrated solutions, but it does not appear to be caused by either light or atmospheric oxygen and is irreversible. Solutions of up to 25 wt/wt % **4** can be prepared in cyclohexanone and are stable for several weeks at room temperature even in ambient lighting. Polymer **3** is not appreciably soluble in cyclohexanone but stable 20 wt/wt % solutions in *N*-methylpyrrolidone (NMP) could be prepared and were stable to gelation. NMP is not an ideal solvent for spinning however adequate films of **3** could be prepared. Immediately after spinning polymers on substrates, the films were placed in an oven for soft baking to remove most of the solvent yielding smooth, optically transparent, tack-free films.

Scheme 1

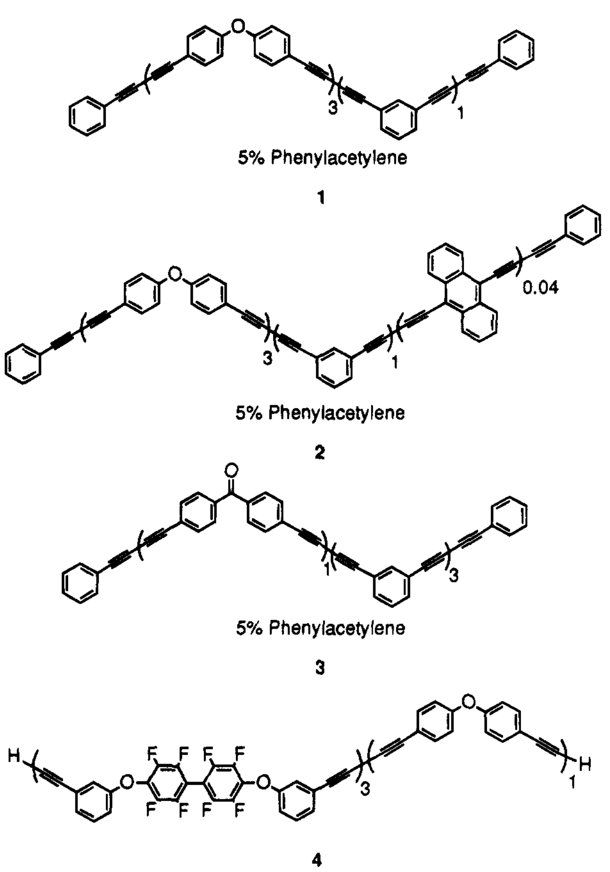

Table 1

polymer	dielectric constant[a] ε′	loss[a] ε″
1	3.12	0.0024
2	3.19	0.0019
3	3.34	0.0034
4	2.82	0.0063

[a] Measured at 1 kHz.

Dielectric Constants of Polymers. The dielectric constants and dissipation factors for the four polymers were measured on thin films (1.5–7 μm) sandwiched between aluminum electrodes at 1 kHz and are summarized in Table 1. The dielectric constants are all rather low as one would expect for materials lacking strong dipoles, and they increase with increasing polarities of the constituent groups. The low dielectric constant (2.82) for the fluorinated polymer is noteworthy. For comparison, the values for polyimides used in

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microelectronic applications are 3.0–3.5.[2]

Thermooxidative Stability. Polymer **1** gains about 8 wt % mass during thermal gravimetric analysis at 10 °C/min under air presumably due to incorporation of oxygen. The mass increase begins around 220 °C and peaks at about 370 °C at which point degradative processes overtake oxygen incorporation and the material rapidly oxidizes completely. When **1** is subjected to isothermal analysis at 200 and 250 °C it gains about 4 and 10 wt %, respectively, over 12 h. The latter appears to be the limit of uptake but at 200 °C the weight was still increasing after 12 h. Oxidation of **1** is also inferred from its darkened appearance and from IR spectra of films heated to 190 °C (15 h) in air. The bands due to the polymer are observed to broaden and broad new bands between 1636 and 1830 cm^{-1} grow in. The latter are particularly evident in thin (0.5 μm) films but less evident in thick (5 μm) films, implying preferential surface oxidation.

Polymer **4** is more thermally stable than **1**. It gains only 1.9% mass by TGA at 10 °C/min under air. The mass increase begins around 250 °C and peaks at around 400 °C where the polymer begins to degrade rapidly. When **4** is subjected to isothermal analysis at 200 °C for 12 h, it loses only 0.4% of its mass. At 250 °C, **4** gains about 2.5% of its mass over ca. 2 h and is followed by a slow mass loss of ca. 1% over 10 h. Analysis of a thin (0.5 μm) film heated at 200 °C in air for 17 h by IR spectroscopy shows negligible incorporation of oxygen, as observed in the 1700 cm^{-1} region of the spectrum, and very little darkening.

Mechanical Properties. Materials in integrated circuits and their packages must withstand being cycled through numerous temperature changes without cracking or delaminating both during subsequent manufacturing steps, testing, and in use. Polyimides are superior in this respect which is attributed to their high elongations to break, and in some cases low coefficients of thermal expansion (CTE).[3,7a] We have carried out a preliminary assessment of the elongation to break and CTE of **1** and **4**. Films (5–12 μm thick) were prepared as described above, blanket exposed with UV light, and then briefly (10 min) heated to 165 °C, below where major thermal cross-linking reaction occurs, and then removed from the Si wafer. Polymer **1** could be stretched 7–9% before it failed and had a CTE of 51 ppm over the temperature range 0–150 °C. For reference we also evaluated the elongation to break of **1** before irradiation and postexposure bake and found that it could be stretched 20% before breaking. Polymer **4** could be stretched 90% and had a CTE of 52 ppm over 0–25 °C. Polymers **1** and **4** were heated to 225 and 250 °C under Ar where they cross-link as previously observed by DSC.[16] After this treatment, **1** is too brittle to even attempt a mechanical measurement. Polymer **4** is also quite brittle after thermal cross-linking and has an elongation to break of only ca. 1%.

Moisture Uptake. Insulators should absorb as little moisture as possible to minimize changes in properties, particularly dielectric constant, as a function of humidity. We have determined the amount of moisture taken up by **1** and **4** by passing water saturated air over samples in a TGA at 30 °C and by monitoring weight loss from polymer saturated with water. We expected from the low polarity of their constituents that these materials would not absorb very much moisture and our expectation was confirmed. Polymers **1** and **4** absorb 0.9 and <0.5 wt % water, respectively.

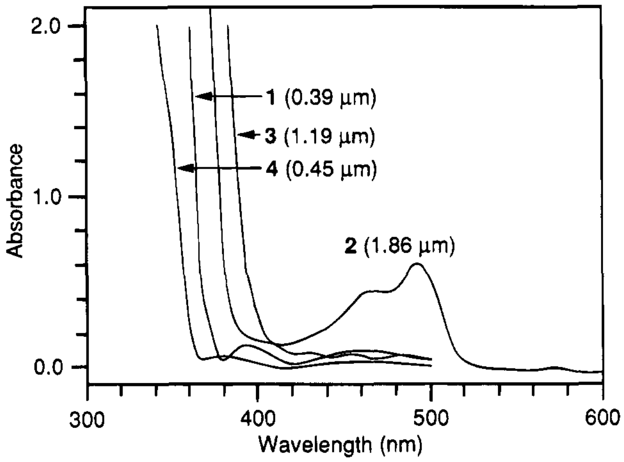


Figure 1. UV/vis spectra of thin films of polymers **1**–**4**.

Adhesion. The adhesion of photochemically cross-linked **1** and **4** to various substrates was evaluated by immersion in cyclohexanone and EtOAc, respectively. Qualitatively, polymer **1** adhered to Al, Si, Au, and Al_2O_3. Polymer **4** adhered to Al, Au, and Al_2O_3 but did not adhere to Si wafers. Pretreatment of Si wafers with aqueous (3-aminopropyl)triethoxysilane considerably improved adhesion.

Photodefinition of Polymers. The UV absorbance spectra of thin films of **1**–**4** are shown in Figure 1. The spectra resemble the diphenylbutadiyne chromophore and, with the exception of **2**, are not ideal for carrying out photochemistry. Polymers **1**, **3**, and **4** have rather sharp absorption onsets and are thus either too strongly absorbing ($\lambda < 360$ nm) to get light through a reasonable thickness for photochemistry to take place throughout the film or absorb too little light at longer wavelengths for significant reaction to occur. Polymer **2** was designed to have, and does have, absorbance properties much closer to ideal for a photoimageable material since it has a weak absorbance at longer wavelengths. Unfortunately, exposure of films of **2** to light of wavelengths longer than 425 nm did not result in insolubilization, thus it has no advantages over **1**. Films of **3** cross-linked when exposed to UV light, but NMP is the only solvent which dissolves them at an appreciable rate and visibly cracked the exposed regions. The wavelength that is probably most practical for imaging is the 365 nm (*g*-line) emission of a mercury lamp because of the intensity available and the absorbance characteristics of polymers likely to have the desired mechanical and thermal properties. We used the outputs of either a Tamarac Scientific exposure tool or a medium pressure mercury lamp as light sources. Both emit broad-band UV light with emission maxima at 365 nm.

The sensitivities to UV light were determined by measuring film thickness remaining as a function of dose after development (Figure 2). A dose of approximately 200 mJ/cm^2 is required to gel a 7 μm thick film of **1** whereas only 100 mJ/cm^2 gels a 6.5 μm thick film of **4**. The contrast ratio as defined by the initial slope of the sensitivity curve is about 1.8 for **1** and 2 for **4**. At the largest doses examined 100% of the original thicknesses of **1** are retained but only about 85% of the original thicknesses of **4** are retained. Exposure of a 1

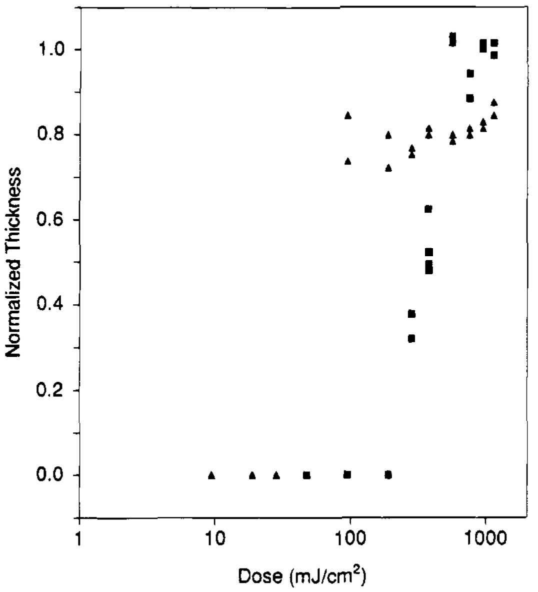
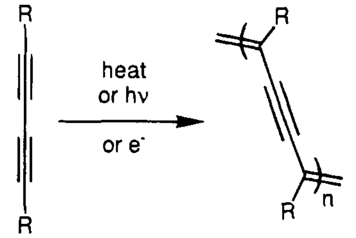


Figure 2. Dosimetric response of approximately 6 μm thick films of polymers **1** (■) and **4** (▲).

μm thick film of **4** to 1 J/cm^2 and development results in retention of 94% of the film thickness. Several factors may account for the differences in the photosensitivities of the two polymers. Polymer **4** is higher in molecular weight (M_w of 82 000 vs 34 000) than **1** which should lead to greater sensitivity, but the difference seems too great to ascribe simply to molecular weights.[17] We believe that the diacetylene moieties are responsible for gelation because structurally similar poly(phenylenes) and poly(phenylene ethers) lacking diacetylenes are not photochemically reactive in this wavelength region.[18,19] Gelation is due presumably to cross-linking of polymer chains and the significantly lower density of diacetylenes moieties in **4** led us to expect that it should be less sensitive. The greater sensitivity of **4** may be related to its higher solubility, indicating greater chain flexibility, and as a result a larger fraction of reactive diacetylenes. The significantly greater transparency of **4** may also contribute to its sensitivity since exposure at the active wavelengths is more uniform throughout the film thickness.

Several caveats should be mentioned concerning the photodefinition of **1** and **4**. Development of **1** is highly sensitive to the temperature of the developer and the temperature at which the film is baked after spinning. The time required to dissolve a 6 μm thick film of unexposed polymer increases from 3.5 to 7 min when the temperature of the cyclohexanone developer is lowered from 30 to 25 °C. Following soft-bake temperatures of >80 °C, 6 μm thick films cannot be completely dissolved in room-temperature cyclohexanone. We are uncertain whether the difficulty in dissolving films of **1** baked at higher temperature is caused by densification of the film due to driving out more of the spinning solvent or due to a thermally induced cross-linking reaction. A soft-bake temperature of 65 °C and a development temperature of 22 °C have been found to provide the best images in **1**. Polymer **4** is much less sensitive to the bake and developer solvent temperatures and the development times for **4** in EtOAc are found to be much shorter. Ten μm is the thickness of films of **1** or **4** through which enough light of short enough wavelength can pass to permit reaction throughout.

Several experiments were carried out in order to attempt to delineate the mechanism of the photoreaction. Irradiation of films of **1** under Ar as opposed to air did not affect its gelation. This result indicates that the gelation reaction is not caused by photooxidation resulting in an insoluble polymer. IR spectra of exposed and unexposed films were compared and were not measurably different. An ideal photodefinable material bleaches during exposure, permitting definition of optically thick layers. The absorbances of films of **1** and **4** at wavelengths where they are initially less than 1 and greater than 0 are observed to increase slightly on exposure. This result is consistent with our hypothesis that the gelation reaction is related to the topochemical polymerization of crystalline diacetylenes and cross-linking reactions of alkyl-substituted diacetylene-containing polymers.[15,20] In these reactions diacetylene moieties are converted to more conjugated poly(eneynes) (eq 1). As mentioned above, the number of chains linked together by a single photon is very small here, and the resulting increase in absorbance is small compared with the chain polymerization which occurs in crystalline diacetylenes.



(1)

Figure 3a shows a scanning electron micrograph (SEM) of a pattern in an approximately 2 μm thick film of **1** produced by contact printing using a dose of 280 mJ/cm^2. Features are resolved down to approximately 6 μm. The silicon wafer is quite clean and the top of the polymer film quite smooth. The sidewalls of the features are rather shallow. Figure 3b shows a SEM of a pattern in an approximately 10 μm thick film of **1** using a dose of 590 mJ/cm^2. The smallest features in this figure correspond to lines and spaces of 9.8 μm on the mask. The tops of these features are 11 μm wide and the spaces are 8 μm wide at the tops. The sidewalls here are rather steep, giving an aspect ratio (width/thickness) for these features of approximately one and leaving bare silicon between polymer. Parts a and b of Figure 3 give the impression that the patterns are underdeveloped because of the sloping sidewalls. Further development does not improve the shapes of the features, and the symmetry of lines that have large open plateaus beside them suggests that underdevelopment is not a problem. Because of the optical density of the films, it might be expected that lines would have an inverted pyramid shape because less cross-linking should take place at the bottom of the film. We do not fully

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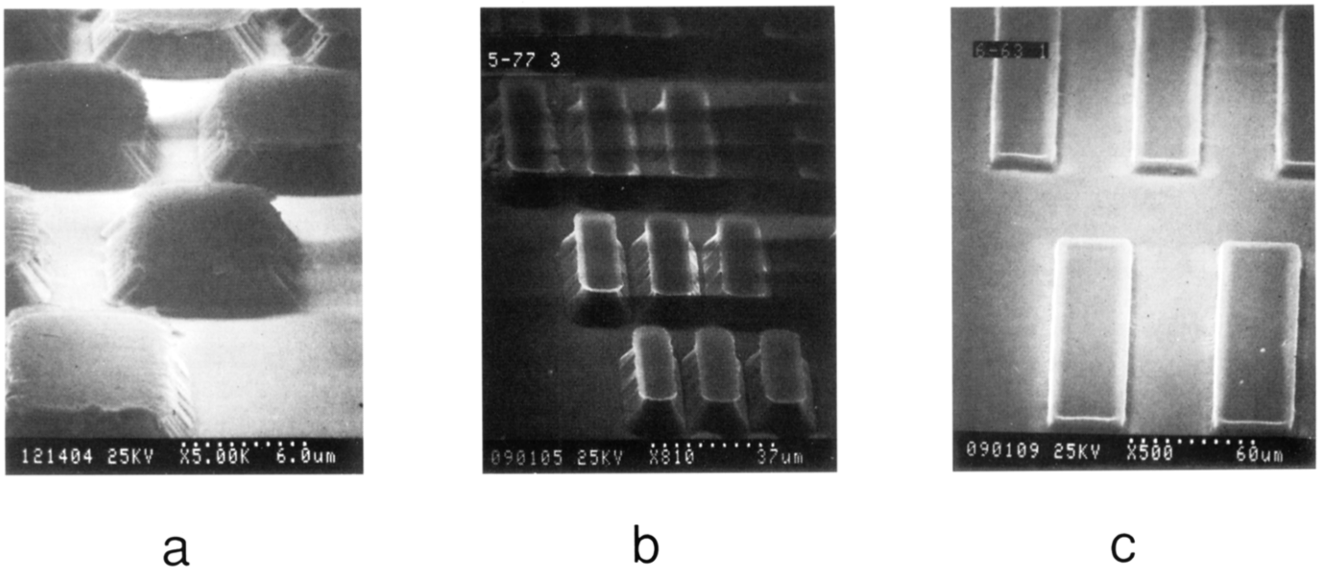

Figure 3. Scanning electron micrographs of patterned films of **1** in a and b and **4** in c. Details provided in the text.

understand the shapes of the features produced here. Figure 3c shows a SEM of a pattern in a 6 μm thick film of **4** produced with a dose of 760 mJ/cm^2, with features resolved down to about 33 μm. Smaller features have residual polymer in the spaces, which does not dissolve on further development. Although it is not evident in this SEM, cross-linked **4** has microscopic cracks in its surface which are visible under an optical microscope. A variety of developer solvents and bake temperatures have been tried to mitigate this problem without success. Thin (1 μm) films that have been exposed to 1 J/cm^2 and developed are free of cracks. Resolution in negative tone photoresists is generally limited by swelling of exposed polymer in developer solvent.[21] This effect does not appear to occur in **1** for reasons which are not entirely clear but may have to do with its high opacity and the broad-wavelength exposure sources we used. The uppermost layer of polymer absorbs all the short-wavelength light which may make it especially resistant to solvent diffusion. The SEM (particularly Figure 3b) of images produced in **1** shows evidence for this in the table-like thin plateau of polymer that sits on top of a base.

Conclusions

Two of the diacetylene containing polymers we have examined are photodefinable in thicknesses up to 6 μm yielding features with aspect ratios of nearly 2 (feature size/thickness), are moderately sensitive, and have good mechanical properties. These and other polymers based on poly(aromatic diacetylenes) may be useful alternatives to better established photodefinable polyimides.

Experimental Section

General Techniques. UV/vis and IR spectra were recorded on a Hewlett-Packard 8452A diode array and Biorad FTS 60 spectrometers, respectively. Scanning electron micrographs were obtained on a Hitachi microscope. Film thicknesses and image profiles were obtained on a Dektak 3030 surface profile measuring system with a 12.5 μm stylus. Thermal gravimetry was carried out on a Perkin-Elmer TGA 7 using air, water-saturated air, or Ar as the sample purge. Films were exposed to the output of a 200 W Hanovia medium pressure mercury lamp having an output of 1.1 mW/cm^2 or a Tamarac Scientific Co. Model 162 projection printer with an output of 19 mW/cm^2 as measured with an International Light 1400A radiometer equipped with a XRL 140B photoresist probe sensitive to 300−400 nm light. Elongations to break were evaluated on a Polymer Laboratories Minimat at a strain rate of 10%/min and thermal coefficients of expansion on a Perkin-Elmer 7 Series thermal analysis system. Water uptake was measured by two methods using a TGA. In the first, the increase in mass of a dried (150 °C) sample of polymer using water saturated air as the purge gas at 30 °C was determined. In the second, the decrease in mass of a water saturated (stirred in water for more than 24 h, filtered and pulled air through for 1 h to remove bulk water) sample was determined by heating from 30 to 180 °C at 1 °C/min.

Film Preparation. Polymers were prepared as described previously and used after one precipitation.[16] They were dissolved in cyclohexanone in concentrations of 5−20 wt/wt % except for **3**, which was dissolved in NMP. Films of **1** and **4** of 5−7 μm thickness were obtained from 15 and 20 wt/wt % solutions, respectively, spun at 800 rpm on a Headway Research, Inc., photoresist spinner. Dissolution of the polymers required brief (ca. 2 min) heating with a heat gun. After complete dissolution, the viscous solutions were passed through a Millipore syringe prefilter (Cat. No. AP20 013 00) and stored in vials. Thinner films were obtained by decreasing the concentration or increasing the spinning rate. After spinning, the films were immediately placed in an oven under air to remove more of the spinning solvent. Films of **1** and **4** were generally baked at 65 and 70 °C, respectively, to obtain the best images. Films for dose measurements, dissolution rate studies, and patterning were spun on Si wafers. Films for UV/vis and IR spectroscopy were spun on quartz and NaCl disks. For mechanical measurements, films were spun on Si wafers using the highest polymer concentrations possible. The films were baked to remove solvent, flood exposed, and baked again at 165 °C. The films were then peeled off the Si wafer, cut into strips, and mounted in the tensiometer.

Dielectric constants of the polymers were measured on films spun on Al-coated glass microscope slides. After baking the films at 100 °C, a second circular Al electrode 6.35 mm in diameter was evaporated on the film and the resulting capacitor evaluated with a dielectric spectrometer.

Photodefinition. Sensitivities were evaluated by exposing small areas (5 × 5 mm) of a film to the output of the Tamarac exposure tool equipped with a shutter for various lengths of time. Films were developed as described below and the exposed film thicknesses measured. Exposures were carried out with resolution targets as masks obtained from Oriel

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(21) Reiser, A. *Photoreactive Polymers: The Science and Technology of Resists*; Wiley: New York, 1989; p 56.

corporation (part numbers 13803 and 13804) in contact with the polymer films. The masks have line and space patterns of varying sizes and are transparent to 340−800 nm light. Following exposure, films were immersed in a Petri dish of developer solvent, cyclohexanone for **1** and EtOAc for **4**, until unexposed polymer was completely dissolved. Developer was agitated with a pipette for 3−5 min for **1** and 0.5−1 min for **4**. Patterned films of **1** were rinsed in methoxyethylacetate for 30 s and dried with a flow of warm air. Patterned films of **4** were rinsed with clean EtOAc for a few seconds and dried in warm air. Exposures in the absence of air were carried out on a small film on a Si wafer in a quartz cuvette sealed and purged with Ar.

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