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Photopatterning of Low Dielectric Constant Cycloolefin Polymers Using Azides and Diazirines

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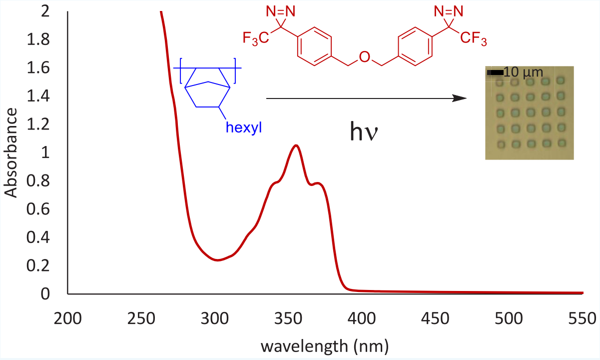
ABSTRACT: Polymers are widely used as insulators in electronic devices. Low dielectric constant polymers are desirable since this lowers the potential for unintentional crosstalk and inductive coupling between conductors. Attempts to photopattern a low dielectric constant polymer, poly(5-hexyl-2-norbornene) (poly(**1**)), with a bis(azide) were unsuccessful. Incorporation of butenyl pendent groups improved patterning, but the dielectric constant of the cross-linked film was relatively high (2.60). A difunctional bis(diazirine) (compound **4**) was synthesized and characterized by NMR and MS. Compound **4** rendered unreactive, aliphatic cycloolefin polymers such as poly(**1**) photopatternable, yielding negative tone patterns with good resolution. The dielectric constant of films cross-linked with compound **4** was substantially lower than the films cross-linked with bis(azide) (2.09 for poly(**1**)).



KEYWORDS: *bis(azide), bis(diazirine), polynorbornene, photopatterning, low dielectric constant*

INTRODUCTION

The manufacturing of state-of-the-art electronic devices requires a myriad of materials ranging from conductors to semiconductors to insulators. Polymeric materials are especially well-suited as insulators and are found to dominate the packaging segment of electronics. General classes of materials that are most prevalent commercially include polyimides, polybenzoxazoles, and polybenzocyclobutenes. These materials are readily applied to substrates as thin films by deposition (typically spin coating) from organic solvents followed by a baking step to remove residual solvent. Each of these material classes offers, as a subset, compositions that are photopatternable, either positive or negative tone. For negative tone compositions, after image-wise exposure to light, the areas of the exposed film undergo a chemical reaction that results in a cross-linked polymer that is no longer soluble in a developer solvent. Thus, an image produced by a two-dimensional mask through which the light is projected results in a three-dimensional relief pattern in the exposed negative tone film after development.

Early commercial negative tone polyimides were based on methacrylate esters of poly(amic acid) or methacrylate ammonium salts of poly(amic acid). During exposure to light free radical cross-linking of the film occurs. After cure, typically at 350 °C, the amic acid functionality ring closes, and the methacrylate cross-linking group is decomposed and volatilized, leaving a polyimide film. The dielectric constants for several varieties of commercially available negative tone photosensitive polyimides are ≥2.8.[1]

While the vast majority of commercial polybenzoxazoles are positive tone materials, there is at least one report of a negative tone composition.[2] The aqueous base-developed film exhibited a similar dielectric constant to polyimide, 2.78, after cure at 350 °C in air.

An aqueous base developed, positive tone poly(benzocyclobutene) has been reported with a dielectric constant of around 3.0.[3] The commercially available resins developed by Dow Chemical are negative tone, solvent developed and are sold under the CYCLOTENE trademark. After cure, the dielectric constant of these compositions is 2.65 according to technical data sheets.[4]

Low dielectric constants for insulators are desirable for wiring applications in electronics since such materials lower the potential for unintentional crosstalk and inductive coupling between two wires.[5] In that regard, cycloolefin polymers as a general class of materials would seem to be a logical choice for such applications. There are three basic types of cycloolefin

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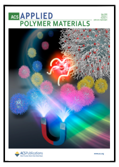
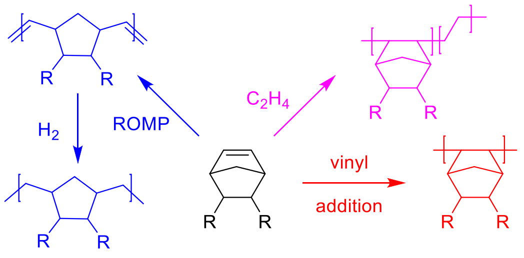


polymers available on the market: hydrogenated ring-opened metathesis polymers (ROMP/H_2), copolymers of norbornene-type monomers with ethylene, and vinyl addition polymers of norbornene-type monomers (see Scheme 1). The dielectric constant of this family of materials is low as expected given their aliphatic nature. For example, the dielectric constant of Zeonex polymers (ROMP/H_2) is reported to be 2.3,[6] while the dielectric constant of Topas polymers (norbornene/ethylene copolymers) is as low as 2.19.[7] A dielectric constant of 2.2 was found for vinyl addition poly(norbornene).[8] However, in order for such materials to be easily integrated into electronics applications, it would be advantageous if they were photo-patternable at imaging wavelengths that are typically used in the industry (for example 365, 405, and 435 nm emission lines from a mercury lamp).

Scheme 1. Three Different Types of Norbornene Monomer Polymerization: Ring-Opening Metathesis Polymerization (ROMP), Ethylene Copolymerization, and Vinyl Addition Polymerization



In this contribution, the photopatterning of heretofore unreactive, low dielectric constant cycloolefin polymer formulations with photoactive compounds such as bis(azides) and bis(diazirines) is described.

EXPERIMENTAL SECTION

General. All synthetic manipulations were performed under an atmosphere of nitrogen by using standard airless or glovebox techniques. Anhydrous grade solvents were deoxygenated by sparging with nitrogen prior to use.

Materials. 5-Hexyl-2-norbornene (HexNB), 5-decyl-2-norbornene (DecNB), and 5-(3-buten-1-yl)-2-norbornene (ButenylNB) were obtained from Promerus LLC. The synthesis of (η^6-toluene)Ni-$(C_6F_5)_2$ has been described previously.[9] The synthesis of (allyl)-palladium(trinaphthylphosphine)(trifluoroacetate) followed published literature.[10] $[Li(Et_2O)_{2.5}][B(C_6F_5)_4]$ (LiFABA) was purchased from Boulder Scientific. 2,6-Bis(4-azidobenzal)-4-ethylcyclohexanone (BAC-E) was purchased from Toyo Gosei. 4-[3-(Trifluoromethyl)-3*H*-diazirin-3-yl]benzyl alcohol, 4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]benzyl bromide starting materials, and 3-phenyl-3-(trifluoromethyl)-3*H*-diazirine were purchased from TCI America and used without further purification. Ethylnorbornane was supplied by Sigma. Zeonex 480 is a Nippon Zeon product, and Topas 6013S-04 is offered by Topas Advanced Polymers.

Characterization. NMR spectra were recorded at 298 K on a Bruker Avance III HD spectrometer operating at 500.15 (^{1}H), 470.55 (^{19}F), and 125.78 MHz (^{13}C) (unless otherwise specified). Chemical shifts are reported relative to tetramethylsilane (^{1}H, ^{13}C, 0 ppm) or trifluorotoluene (^{19}F, −63.72 ppm).

GPC data were obtained by using a Tosoh EcoSEC HLC-8320GPC with an RI detector. The data were collected at 40 °C by using one PLgel 5 μm guard and two PLgel 5 μm Mixed-C columns with stabilized THF as the solvent. Polystyrene standards of known molecular weight were run by using the same conditions and column set to create a calibration curve.

Differential scanning calorimeter (DSC) measurements were performed on a TA Instruments DSC Q-200 instrument operated from room temperature to 250 °C at a scan rate of 10 °C/min.

Glass transition measurements were done with a Mettler Toledo TMA STARe+. Scans were run in tension mode from room temperature to 350 °C at 10 °C/min with a force of 0.03 N.

Tensile properties were measured with an Instron Mdl. 5564 tensile tester. Strips with a thickness of 10 μm and 5 mm in width were mounted in jaw clamps set at a separation of 20 mm. The jaw speed was 5 mm/min. No extensometer was used for this measurement.

UV−vis measurements were made using an Agilent Cary 100 spectrometer. Compounds were dissolved in cyclohexane.

FT-IR spectra were recorded by using a Nicolet iS50 instrument.

The liquid chromatograph−mass spectrometry data were obtained by using 1% of the analyte, bis(diazirine) solution in methanol (Fisher Optima), using a Shimadzu high performance liquid chromatograph in tandem with an ion trap−time-of-flight mass spectrometer (LCMS-IT-TOF). One microliter injection was made on the LC with methanol and water as the eluent in a gradient elution on the column; the analyte was ionized under positive mode atmospheric pressure (APCI), and afterward masses were analyzed in the IT-TOF with a mass accuracy of 0.05 amu for 15 min. The LC (LC-20ADXR) conditions were as follows: Phenomenex column 3.0 mm × 150 mm C18 Kinetex 2.6 μm; column temperature = 35 °C; flow rate and eluent = 0.6 min/mL, 10% methanol (8.5 *m*), 95% methanol (2.5 *m*), and 10% methanol (4 *m*). MS and ionization conditions were as follows: interface temperature = 400 °C; CDL temperature = 200 °C; nebulization gas (N_2) flow rate = 2.5 L/min; heat block temperature = 200 °C; scanning mass range = 200−600 amu; and a loop time of 0.4 s at detector voltage = 1.65 kV.

Synthesis of 5-Hexyl-2-norbornene Homopolymer, Poly(1). In a representative polymerization, HexNB (1.6 kg, 9.0 mol), cyclohexane (6.2 kg), and ethyl acetate (3 kg) were mixed together, nitrogen sparged for 30 min, and cooled to 20 °C. (η^6-Toluene)Ni-$(C_6F_5)_2$ (12.2 g, 0.0252 mol) dissolved in toluene (250 g) was added to the monomer mixture. The reactor temperature was increased to 40 °C, and the mixture was stirred for 3 h. Residual catalyst was removed, and the polymer was precipitated into isopropanol. After the polymer was isolated by filtration, it was dried in a vacuum oven at 80 °C. GPC: M_w = 183000, M_w/M_n = 2.51. ^{1}H NMR ($CDCl_3$): 3.7−0.1 (m, aliphatic H's).

Synthesis of ButenylNB Homopolymer, Poly(3). In a representative polymerization, a solution of LiFABA (39.2 mg, 0.0450 mmol) and ButenylNB (22.1 g, 150 mmol) in toluene (total solution volume 55 mL) was heated to 70 °C. A solution of [(allyl)palladium (trinaphthylphosphine)(trifluoroacetate)] (10.6 mg, 0.0158 mmol, 0.004 M) in toluene was added to the reaction mixture. The reaction mixture stirred for 5 h at 70 °C. The reaction mixture was allowed to cool to room temperature. The reaction mixture was diluted with toluene (to 275 mL) and then poured into isopropanol (∼6-fold excess). The precipitated polymer was filtered and then dried in a vacuum oven at 50 °C overnight to give a white powder. GPC: M_w = 15100, M_w/M_n = 2.74. ^{1}H NMR ($CDCl_3$): 6.0−5.6 ($-CH{=}CH_2$), 5.2−4.7 ($-CH{=}CH_2$), 3.0−0.5 (m, aliphatic H's). A small amount (∼7%) of the terminal butenyl pendent group isomerized to the internal double bond as shown by a peak at 5.40 ppm in the ^{1}H NMR spectrum.

Synthesis of DecNB/ButenylNB Copolymers, Poly(2/3). In a representative polymerization, DecNB (11.7 g, 0.0500 mol), ButenylNB (22.05 g, 0.150 mol), and toluene (112 g) were added to a 250 mL crimp cap bottle equipped with a magnetic stir bar in the glovebox. LiFABA (0.052 g, 0.060 mmol) was added to the solution. The solution was heated to 60 °C, and [(allyl)palladium (trinaphthylphosphine)(trifluoroacetate)] (0.014 g, 0.021 mmol) in a small volume of toluene was added to the solution. After 20 h, the solution was cooled and was added to MeOH to precipitate the polymer. The polymer was filtered and dried at 60 °C overnight in a vacuum oven. GPC: M_w = 32300, M_w/M_n = 2.94. ^{1}H NMR ($CDCl_3$): 5.9−5.7 ($-CH{=}CH_2$), 5.1−4.8 ($-CH{=}CH_2$), 2.9−0.5 (m, aliphatic H's).

The molar ratio of DecNB to ButenylNB (26/74) was determined by ^{1}H NMR spectroscopy.

Synthesis of 3,3′-[Oxybis(methylene-4,1-phenylene)]bis(3-(trifluoromethyl)-3*H*-diazirine (4). All of the procedures described below were performed in the dark. To an oven-dried 60 mL crimp cap vial equipped with a magnetic stir bar was added NaH (60% dispersion in mineral oil, 0.158 g, 3.95 mmol). The vial was sealed with a septum cap. The septum was pierced with a vent needle (20 gauge), and the vial was placed in a room temperature water bath. Anhydrous THF (10 mL) was added by syringe with stirring. A solution of 4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]benzyl alcohol (0.77 g, 3.6 mmol) in THF (10 mL) was added slowly to the vial by syringe (gas evolution was observed as vigorous bubbling). This mixture stirred for 10 min followed by addition of neat 4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]benzyl bromide (1.0 g, 3.6 mmol) by syringe. The reaction mixture was allowed to stir at room temperature overnight (20 h).

The crude reaction mixture slurry was filtered through a bed of Celite filter aide followed by concentration of the filtrate to a small volume affording the crude product as a yellow oily solid mixture. The crude material was purified by silica gel column chromatography (Davisil, grade 633 high purity 60A, 200−425 mesh) starting with 100% hexanes until the remaining bromide starting material eluted off the column followed by 5−10% ethyl acetate in hexane until the target material eluted. Target material fractions were combined and concentrated under vacuum, and the remaining reaction byproduct was removed by placing the partially purified material under a high vacuum for 2 h to afford the title compound as a yellow oil (0.75 g, 46% yield). ^{1}H NMR (methylene chloride-d_2): 7.41 (d, 4 H), 7.21 (d, 4 H), 4.57 (s, 4 H) ppm. ^{13}C NMR (methylene chloride-d_2): 140.27, 128.18, 127.88, 126.51, 122.19 (2 C, q, J_{CF} = 272.9 Hz), 71.54 (2 C), 28.35 ppm (2 C, q, J_{CF} = 40.2 Hz). ^{19}F NMR (methylene chloride-d_2): −65.7 ppm. LCMS: 415.0655 $(M + 1)^+$, 387.0651 $(M + 1 - N_2)^+$, 359.0690 $(M + 1 - 2N_2)^+$. FT-IR (neat): 3043 (m), 2861 (s), 1614 (s), 1520 (s), 1345 (vs), 1232 (vs), 1192 (vs), 1156 (vs), 1099 (s), 1053 (s), 939 (s), 811 (s), 735 (m), 539 (m).

Caution: an assessment of the shock sensitivity and explosive risk of compound **4** *has not been made.*

Photoactive Composition Formulation. Poly(1) and BAC-E. In a typical formulation, poly(**1**) (1.29 g) was dissolved in 11.65 g of decane. To this solution was added 0.065 g of BAC-E in 1.3 g of toluene. 5.0 g of this formulation was diluted with 4.5 g of decane and 0.5 g of toluene.

Photoactive Composition Formulation. Poly(1) and Compound 4. In a typical formulation, poly(**1**) (0.55 g) and compound **4** (0.11 g) were dissolved in decane (5 g). A portion of this solution (2.5 g) was further diluted with a 2.5 g of a 10 wt % solution of poly(**1**) in decane.

Wafer Processing, Exposure, and Development Details. The photoactive formulation solution was filtered through a 0.45 μm PTFE syringe filter and then coated onto a 4 in. thermal oxide silicon wafer. The wafer was spun at 300 rpm for 40 s and then post apply baked to remove residual solvent (at 120 °C for 2 min for BAC-E formulations and 80 °C for 2 min for compound **4** formulations). The film thickness was determined by using a Dektak profilometer.

The film on the silicon wafer was image-wise exposed through a 365 nm band-pass filter by using an ABM mask aligner at an exposure dose of 1000 mJ/cm^2 (at 365 nm) through a variable density mask. The exposed film was developed with solvent for the prescribed time. The film thickness was determined once again by using the profilometer, and the quality of the resulting three-dimensional relief images was determined by inspection of the wafer under a microscope as a function of exposure dose. The exposure dose at which the minimum feature size with the minimum film thickness loss occurred was the minimum exposure dose reported.

Dielectric Constant Determination. Metal/insulator/metal capacitors were prepared as follows: the photoactive formulation solution was filtered through a 0.45 μm PTFE syringe filter and then coated onto a 1 in. indium tin oxide (ITO)-coated glass substrate to yield a dry film of ∼1 μm in thickness. Residual solvent was driven off the film by a post apply bake at 120 °C for 2 min. Silver contacts of surface area 19.63 mm^2 were subsequently deposited onto the dielectric to a thickness of ca. 60 nm. The capacitance *C* of the structure was measured by using an Agilent 4294A precision impedance analyzer at 1 kHz, with a modulation voltage of 50 mV. From this, the dielectric constant *k* of the material was determined via eq 1

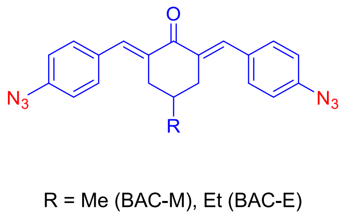
$$C = \frac{k\varepsilon_0 A}{d} \tag{1}$$

where ε_0 is the permittivity of free space, *d* is the exact dielectric thickness as determined using a Dektak profilometer, and *A* is the capacitor area.

■ RESULTS AND DISCUSSION

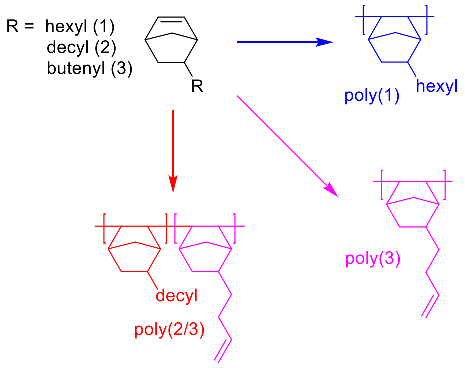
Development of Photosensitive Compositions Based on Bis(azide). The initial approach chosen to engender photopatternability in cycloolefin polymer films was based on the early work by Kodak in which cyclized poly(isoprene) was transformed into a photopatternable composition by addition of bis(azides) such as 2,6-bis(4-azidobenzal)-4-methylcyclohexanone (or BAC-M, Chart 1).[11] According to the literature, the BAC system exhibits an absorption maximum at 355 nm.[12,13] Exposure to light of such systems generates highly reactive nitrenes by extrusion of dinitrogen. Such nitrenes can participate in a number of reactions including rearrangements, coupling, or even C−H insertion.[14] Azides can be engineered to enhance the C−H insertion reaction.[15] However, in the case of the BAC system the cyclized poly(isoprene) cross-links primarily by either inserting into activated allylic C−H bonds, addition to residual C−C double bonds, and/or formation of polymeric centered radicals.

Chart 1. Structure of Photoactive Compounds BAC-M and BAC-E



The ability of BAC-E to photo-cross-link a hydrocarbon polymer with unactivated C−H bonds was tested by using poly(**1**) made with a nickel catalyst (Scheme 2). A mixture of poly(**1**) and BAC-E in toluene and decane was spin-coated

Scheme 2. Polymerization of Norbornene Monomers



onto silicon wafers and image-wise exposed by using 365 nm UV light through a variable density mask after baking to remove residual solvent. Most of the film washed off the wafer after development with decane.

To enhance the imaging performance of the BAC-E formulation, homo- and copolymers containing an olefin pendent group were synthesized. Copolymers of DecNB and ButenylNB were made by using a palladium compound, (allyl) palladium (trinaphthylphosphine)trifluoroacetate, in the presence of LiFABA. The lithium compound abstracts the trifluoroacetate from the palladium complex, generating a cationic catalyst in situ initiating vinyl addition polymerization of norbornene monomers.[16]

The ButenylNB polymerization results are found in Table 1. The polymerization yields for all the polymerizations were fair to good, and the ratio of the monomers in the copolymers was similar to the molar feed ratio. The molecular weights obtained were moderate to low, ranging from ~40000 to ~15000. It is noteworthy that the trinaphthylphosphine catalyst allows polymerization of ButenylNB with minimal isomerization of the pendent double bond despite the sensitivity of this class of catalysts to olefin chain transfer agents like 1-hexene.[16]

Table 1. Polymerization of DecNB (**2**) and ButenylNB (**3**)

run	ratio of **2**/**3** in feed	yield (%)	M_w	M_w/M_n	ratio of **2**/**3** in product
1	75/25	86	40400	3.25	76/24
2	50/50	53	24100	2.87	43/57
3	25/75	78	32300	2.94	26/74
4	0/100	70	15100	2.74	0/100

The polymers from runs 1, 3, and 4 in Table 1 were formulated with BAC-E at 10 wt %. The formulations were then spin-coated onto silicon wafers and image-wise exposed by using 365 nm UV light through a variable density mask. The exposed wafers were then developed, and the minimum resolution of the features was determined as a function of dose by optical microscope evaluation. The results of this investigation, along with the results for a poly(**1**)/BAC-E formulation, are presented in Table 2. As noted above, the poly(**1**) formulation does not photo-cross-link very effectively, and therefore no features were observed since most of the film washed off the wafer during development. However, incorporation of ButentylNB into a copolymer with DecNB resulted in images after exposure to light and development. As the fraction of ButenylNB increases in the copolymer, the film thickness loss after development goes down and the minimum feature size observed decreases as well. These results are shown graphically in Figures S14 and S15. A photomicrograph of the features observed for poly(**3**) is shown in Figure 1, in which 5 μm lines and 15 μm spaces are resolved. The trends observed in Figures S14 and S15 indicate the photo-cross-linking of the film improves as the amount of pendent vinyl groups increases. This is consistent with the cross-linking mechanism proposed for cyclized poly(isoprene) in which the photogenerated nitrene from the azide either adds to C−C double bonds or inserts into allylic C−H bonds.

Table 2. Photoimaging Results of BAC-E Formulations

polymer	composition	wt % BAC-E on polymer	exposure dose (mJ/cm^2)	% film thickness loss after development	min feature size (μm)
poly(**1**)	100	5	1000	100[a]	
poly(**2**/**3**)	76/24	10	720	91[b]	50
poly(**2**/**3**)	26/74	10	72	23[c]	25
poly(**3**)	100	10	72	0[d]	5

[a] Developed for 15 s in decane. [b] Developed for 30 s in decane. [c] Developed for 20 s in decane. [d] Developed for 15 s in decane.

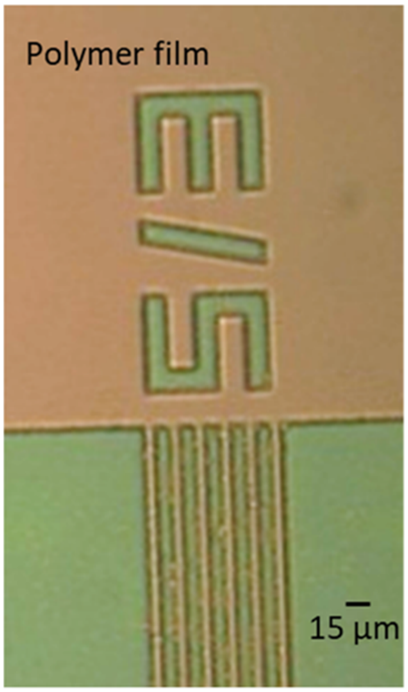


Figure 1. Photomicrograph of bright-field imaging results for poly(**3**)/BAC-E formulation in Table 2 (5 μm lines and 15 μm spaces).

Once the imaging capability of the poly(**3**)/BAC-E composition had been established, the dielectric constant of this film with and without exposure to light was measured.

While the photopatterning of BAC-E formulations of poly(**3**) was good, the dielectric constant of the unexposed film was higher than poly(**3**) alone, and it rose upon exposure to light (experiment 2 in Table 3). It is likely that the higher dielectric constant was due to the formation of nitrogen-based functionalities remaining in the cross-linked polymer after photogeneration of the nitrene from BAC-E. To lower the dielectric constant but retain the good imaging performance, we sought alternative cross-linking chemistries that did not involve the formation of nitrenes and did not rely upon unsaturation in the polymer for effective cross-linking.

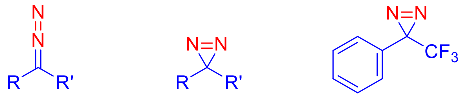
Table 3. Dielectric Constant of Poly(**3**) Compositions with and without BAC-E and Exposure to Light

		dielectric constant	
expt	sample	unexposed	exposed
1	poly(**3**)	2.30	
2	poly(**3**) + BAC-E	2.40	2.60[a]

[a] 3 J/cm^2 at 365 nm.

Development of Photosensitive Compositions Based on Bis(diazirine). Conceptually, the most direct route to a low dielectric constant cross-linked film was to replace the photogenerated nitrene with a carbene. While carbenes can be readily generated from precursors such as diazoalkanes (see generic structure in Chart 2), these compounds are known to undergo explosive decomposition under certain conditions.[17] Diazirines, cyclic isomers of the diazo compounds (Chart 2), can also be explosive depending on the structure.[18,19] The challenge was to develop a di- or even multifunctional carbene precursor that reacts upon exposure at the desired wavelength (i.e., 365 nm), does not suffer from unproductive, intramolecular rearrangements of the carbene, and was safe to handle.

Chart 2. Structures of Diazo and Diazirine Compounds



Diazo Diazirine TPD

In 1980, Brunner et al. reported the synthesis of 3-trifluoromethyl-3-phenyldiazirine (TPD).[20] TPD was found to have reasonable stability; it could be stored at room temperature for weeks in the absence of light or heated to 75 °C for 30 min with little or no change. It was also inert to basic and acidic conditions. In addition, the compound absorbed light in the desired region with a maximum at 353 nm, i.e., near the i-line emission of a mercury lamp. With regard to reactivity with a cycloolefin polymer, it was interesting to find that photolysis of TPD in cyclohexane solvent yielded a product consistent with insertion of the photogenerated carbene into the C−H bond of cyclohexane. In 2006, Simonton and Fewkes reported the synthesis of an ester-linked bis(diazirine) based on TPD and photoinduced cross-linking of an aliphatic urethane acrylate oligomer.[21] Unfortunately, synthetic details were sparse. In 2008, Blencowe et al. disclosed the photo-cross-linking of poly(ethylene oxide) using 1,3-bis(3-(trifluoromethyl)diazirin-3-yl)benzene.[22] On the basis of these reports, we synthesized a bis(diazirine) derivative of TPD, formulated the bis(diarizine) with an unfunctionalized hydrocarbon poly(norbornene), and tested its photopatterning performance.[23,24]

Commercially available starting materials were employed in the synthesis of the difunctional bis(diazirine) compound **4**. As outlined in Scheme 3, sodium hydride was used to deprotonate 4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]benzyl alcohol followed by addition of the 4-[3-(trifluoromethyl)-3*H*-diazirin-3-yl]benzyl bromide to form the ether-linked bis(diazirine) compound **4**.

Compound **4** was characterized by NMR and MS techniques (Figures S7−S10). Noteworthy ^{13}C NMR resonances include a quartet at 28.35 ppm (J_{CF} = 40.2 Hz) due to the diazirine carbons and a quartet at 122.19 ppm (J_{CF} = 272.9 Hz) due to the carbons of the CF_3 groups, both of which are coupled to the three fluorine atoms. A singlet in the ^{19}F NMR spectrum at −65.73 ppm was observed due to the CF_3 moieties. Similar resonances were reported for 1,3-bis(3-(trifluoromethyl)diazirin-3-yl)benzene.[22] The molecular ion for compound **4** was observed in the LC-MS along with fragments due to loss of one N_2 and two N_2 as well as cleavage of the ether linkage.[25]

The thermal stability of compound **4** was evaluated by using differential scanning calorimetry (DSC). The DSC experiment was conducted at a ramp rate of 10 °C/min from room temperature to 250 °C. A broad exothermic transition was observed starting at about 65 °C with a peak at about 132 °C. The total heat evolved was 93 kcal/mol (Figure S12).

The UV−vis spectrum of compound **4** was recorded in cyclohexane (Figure S13). The maximum absorbance of compound **4** is very close to the imaging wavelength used in i-line exposure units (365 nm). The λ_{max} and ε of compound **4** are compared to those observed for the starting materials in Table S2. As expected, the λ_{max}'s of all three compounds are similar, but the molar absorptivity is higher for compound **4** than the starting compounds since compound **4** has two absorbing units per molecule.

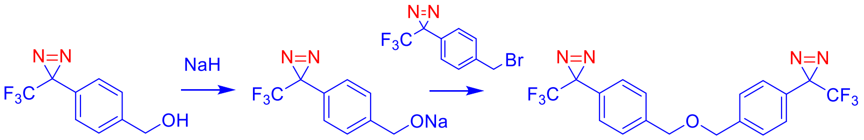
Compound **4** was formulated with three cycloolefin polymers: a vinyl addition norbornene polymer poly(**1**) in decane, a ROMP/H_2 copolymer (Zeonex 480R) in *p*-menthane, and a norbornene/ethylene copolymer (Topas 6013S-04) in *p*-menthane. The solutions were spin-coated onto silicon wafers and then baked at 80 °C for 2 min to remove residual solvent. The films were image-wise exposed by using 365 nm light and then developed according to the protocol in Table 4. The resulting negative tone images were examined by optical microscopy, and the minimum feature size for each film was determined. A representative photomicrograph for the images obtained from the poly(**1**)/compound **4** formulation is shown in Figure 2, revealing resolution of 5−7 μm via holes.

Table 4. Photoimaging Results of Compound 4 Formulations

polymer	wt % **4** on polymer	exposure dose (mJ/cm)[b]	% film thickness loss after development	min feature size (μm)
poly(**1**)[a]	12	255	7.6[b]	7
Zeonex 480R	9	967	12[c]	10
Topas 6013S-04	9	967	1.5[d]	15

[a] M_w: 190000; M_w/M_n: 2.53. [b] Developed with decane for 30 s. [c] Developed with *p*-menthane for 30 s. [d] Developed with *p*-menthane for 20 s.

Scheme 3. Synthesis of Bis(diazirine) Compound 4



4

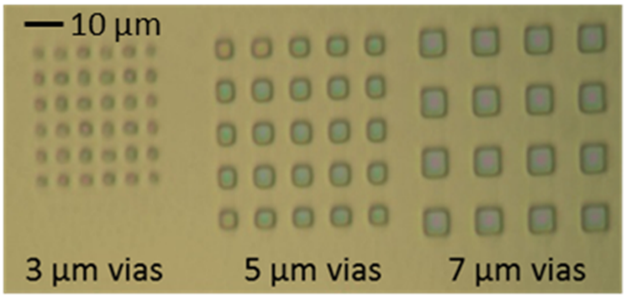
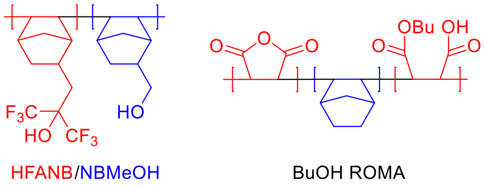


Figure 2. Photomicrograph of bright-field imaging results for poly(**1**)/compound **4** formulation in Table 4.

The data in Table 4 show that, in contrast to the BAC-E formulations in Table 2, compound **4** is effective in forming negative tone features with cycloolefin polymers that contain no carbon−carbon double bond unsaturation. These results are consistent with observations by Brunner et al. that photoactivated 3-trifluoromethyl-3-phenyldiazirine compounds create carbenes that can insert into aliphatic C−H bonds,[20] providing additional support for the type of cross-linking observed by LePage.[24] Similarly, unsaturated poly(arylene ethers) with pendent trifluoromethyldiazirine groups could be cross-linked upon UV exposure and could be photopatterned.[26]

The ability of compound **4** to create negative tone images is not limited to unfunctionalized aliphatic cycloolefin polymers. We tested the photopatterning capability of polymers containing both aliphatic alcohol and carboxylic acid functionalities.[23] Both types of polymer films yielded negative tone, micrometer-sized features after image-wise exposure, postexposure bake, and development with TMAH (Table S1). This proves that aliphatic alcohol (HFANB/NBMeOH) and carboxylic acid-functional (BuOH ROMA, ring-opened maleic anhydride) copolymers can participate in producing a cross-linked film (Chart 3). Brunner et al. reported that upon photolysis 3-trifluoromethyl-3-phenyldiazirine readily reacts with methanol by insertion into the −OH bond.[20] Kanoh and co-workers found that a myriad of products are possible when higher alcohol homologues are used due to insertion into both the −OH and the −CH bonds.[27]

Chart 3. Structures of Aliphatic Alcohol- and Carboxylic Acid-Functional Polymers That Can Be Imaged When Formulated with Bis(diazirine) 4



The dielectric constants of films of poly(**1**), Zeonex 480R, and Topas 6013S-04 containing compound **4** were determined before and after exposure to light (Table 5). Compared to the films of poly(**3**), the dielectric constants of films of the aliphatic polymer formulations with compound **4** rose only slightly after exposure to light. It is likely that the increase in dielectric constant is caused by the increase in density of the film due to cross-linking. This hypothesis is supported by the 5% thinner film thickness observed after exposure (11.51 ± 0.10 μm) compared to before exposure (12.07 ± 0.10 μm) by using a substantially thicker film sample.

Table 5. Dielectric Constant of Poly(1) and Cycloolefin Polymer Compositions with and without Compound 4 and Exposure to Light

		dielectric constant	
expt	sample	unexposed	exposed
1	poly(**1**) + compound **4**	2.05	2.09[a]
2	Zeonex + compound **4**	2.23	2.32[a]
3	Topas + compound **4**	2.20	2.36[a]

[a] 1.95 J/cm^2 at 365 nm.

Reaction of 3-Phenyl-3-(trifluoromethyl)-3*H*-diazirine (TPD) with Poly(1) and Ethylnorbornane. The insolubility of the poly(**1**) cross-linked during the photoreaction with compound **4** made it difficult to analyze. To get a better understanding of this reaction, we investigated the ^{19}F NMR spectrum of the reaction products of poly(**1**) and a non-cross-linking diazirine, TPD, after a 16 J/cm^2 exposure. Besides residual unreacted TPD and some of the diazo isomer of TPD (Table S6), which is known to form under irradiation,[22] there are broad peaks in the −63.1 to −64.4 ppm region as well as from the −70.1 to −71.2 ppm region. Similarly, when a small molecule mimic of poly(**1**), ethylnorbornane, is irradiated in the presence of TPD, new resonances are observed in the same region of the ^{19}F NMR spectrum (Figure S20). The ^{19}F NMR of two known compounds from the literature in which the CF_3−C−C_6H_5 fragment has been formally inserted into a C−H bond of cyclohexane and octane, respectively, yielded chemical shifts in the regions of interest, namely ∼−62 and −70 ppm (Table S6). These data and literature comparisons are consistent with the photogenerated carbene from TPD inserting into both the C−H bonds of the norbornane moiety and the hexyl pendant group of poly(**1**).

Effect of Cross-Linking on Thermomechanical Properties of Poly(1). The impact of photo-cross-linking on the thermal properties of poly(**1**) by using compound **4** was negligible. The T_g of poly(**1**) was 191 °C without cross-linking and 193 °C after irradiation of a film containing 10 wt % of the bis(diazirine) **4** as determined by thermomechanical analysis (TMA) in tension.

The mechanical properties from stress−strain curve analysis in tension were found to be mostly consistent with some light cross-linking of the film. Without cross-linking, poly(**1**) exhibited a tensile modulus of 765 ± 41 MPa, a tensile strength of 19.2 ± 0.9 MPa, and an elongation at break of 18.1 ± 3.9%. Irradiation of a film of poly(**1**) with 10 wt % of compound **4** seemed to show a trend toward higher modulus (849 ± 132 MPa) although the error for this measurement was too high to confidently say that the trend is real. The tensile strength increase (24.7 ± 2.3 MPa) and elongation at break decrease (11.5 ± 2.9%) were in accord with light cross-linking of the film by compound **4**.

CONCLUSIONS

The ability to image-wise photo-cross-link and pattern cycloolefin polymers with pendent double bonds by using BAC-E has been demonstrated. Better imaging results were obtained as the concentration of the pendent double bond containing monomer increased. However, the dielectric constant of the cross-linked polymer was higher than desired after exposure to light.

Image-wise photopatterning of unreactive, aliphatic cycloolefin polymers was achieved for films containing the photoactive bis(diazirine), compound **4**. These cross-linked films showed substantially lower dielectric constants compared to films cross-linked with BAC-E. Cross-linking of polymer films is not limited to all cycloaliphatic polymers. Alcohol and carboxylic acid-functional polymers formulated with compound **4** yielded negative tone patterns when image-wise exposed, proving the wide utility of this approach.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.0c00043.

GPC, DSC, TMA, and DSC traces, NMR and UV spectra, photopatterning results, tensile stress−strain curves (PDF)

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Notes

The authors declare no competing financial interest.

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