

Formation of Phenoxynorbornane Pendant Groups by Acid-Catalyzed Hydroalkoxylation of Poly(hydroxystyrene) and Its Application to Photopatterning

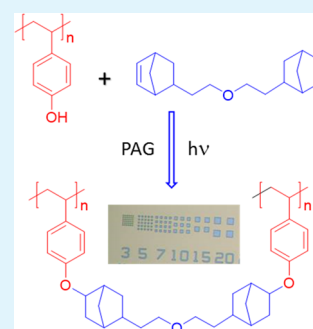
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Supporting Information

ABSTRACT: Poly(hydroxystyrene) (PHS) reacts with norbornene in the presence of acid to form a phenoxynorbornane pendant group through the hydroalkoxylation of the norbornene double bond by the phenol –OH group of PHS. Films of PHS, an aqueous base soluble polymer, containing norbornene derivatives and a photoacid generator (PAG) create a negative tone photopatternable composition. Acid generated in the exposed regions of the film promotes the hydroalkoxylation reaction generating the phenoxynorbornane pendant group, rendering the film insoluble in an aqueous base developer. Both dinorbornene and mononorbornene-functional additives were evaluated. In the case of the mononorbornene additive, a unique example of a negative tone photopatterned film that can be reworked after patterning by dissolution in a mild solvent at room temperature was demonstrated. Polymers containing aliphatic alcohol and carboxylic acid pendant functionalities could be photopatterned in the presence of dinorbornene additives showing the generality of this method.

KEYWORDS: poly(hydroxystyrene), photopatterning, hydroalkoxylation, dinorbornene, *exo*-phenoxynorbornane



INTRODUCTION

Photopolymer compositions can be classified as either positive tone or negative tone, acting depending on whether the exposed region of a film cast from said composition is dissolved away or remains intact upon development, respectively.¹

Typically upon exposure, a positive tone photopolymer undergoes a reaction that increases its solubility in a developer. Examples include diazonaphthoquinone/novolac resins, which act based on a dissolution rate suppression mechanism² and protected poly(hydroxystyrene) (PHS)/photoacid generator (PAG) systems that are rendered soluble in aqueous base developer by an acid-catalyzed, thermally-driven deprotection step.³

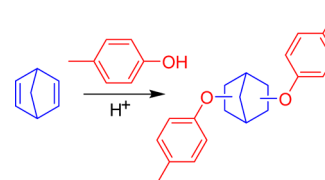
A negative tone photopolymer typically undergoes a reaction such as cross-linking that decreases its solubility in developer after exposure. An exemplary system is the cross-linking of cyclized poly(*cis*-1,4-isoprene) binder resins by difunctional nitrenes formed from the photochemical degradation of bis(diazides) such as BAC-E.⁴

Addition of alcohols or carboxylic acids to olefins is a well-known reaction that is typically acid catalyzed.⁵ Specifically, the hydroalkoxylation and hydrocarboxylation of strained norbornene rings with alcohols, phenols, and carboxylic acids in the presence of strong acids such as triflic acid have been reported by Hartwig et al.⁶ and Tschan et al.⁷

In 2008, Mathers et al. reported that polymers could be created by employing the acid-catalyzed addition reaction of alcohols, phenols, and carboxylic acids to the olefinic

functionalities of norbornene.⁸ A model reaction reported by Mathers et al. in which 2 equiv of 4-methylphenol was shown to add to norbornadiene in the presence of triflic acid (Scheme 1) without the substantial cationic polymerization of

Scheme 1. Acid-Catalyzed Addition of 4-Methylphenol to Norbornadiene



norbornadiene or electrophilic aromatic substitution was especially intriguing to us. This result suggested that dinorbornenes should react with the phenol substituents in PHS in the presence of acid. In a photopolymer composition, the acid for this reaction could be provided by photochemical decomposition of a photoacid generator in the exposed regions of the photopolymer film. If sufficient reaction between the polymer and the dinorbornene occurred, a three-dimensional, negative tone pattern should result after dissolution and removal of the unexposed regions of the film.

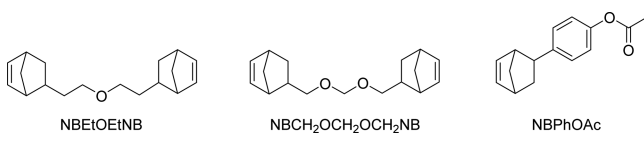
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In this contribution, we show that phenol-functional polymers such as PHS react with norbornene to create phenoxynorbornane pendent groups. On the basis of this hydroxyalkoxylation reaction, PHS can be patterned to give negative tone images when formulated with a photoacid generator and dinorbornene additives. The ability to form negative tone patterns with PHS is not limited to the dinorbornenes NBEOEtNB and NBCH₂OCH₂OCH₂NB. We also demonstrate that the mononorbornene (5-norbornene-2-phenylacetate, NBPhOAc) can yield negative tone patterns with PHS also (Chart 1).

Chart 1. Structures of Norbornene Additives Used To Make Negative Tone Formulations



EXPERIMENTAL SECTION

General Procedures. Poly(hydroxystyrene) (PHS, nominal $M_w = 27,400$) was purchased from Sigma Aldrich Company. Irgacure 290 was sourced from BASF. TMAH (tetramethylammonium hydroxide, 0.26 N, Microposit MF-CD-26 from Dow) was purchased from MicroChem. NBCH₂OCH₂OCH₂NB was prepared previously.⁹ 5-Norbornene-2-ethanol (NBEOH) was prepared as previously published¹⁰ as 5-norbornene-2-phenylacetate (NBPhOAc).¹¹

NMR spectra were recorded at 298 °K on a Bruker Avance III HD spectrometer operating at 500.15 (¹H) MHz and 125.78 (¹³C) MHz. Chemical shifts are reported relative to tetramethylsilane (¹H, ¹³C, 0 ppm) recorded at the same temperature.

FT-IR spectra were recorded using a Nicolet iS50 instrument. Samples were analyzed using a diamond cell from High Pressure Diamond Optics.

GPC data were obtained using a Polymer Labs GPC50 instrument with a refractive index detector. The data was collected at 40 °C using PL 5 μ m Guard and PLgel 5 μ m Mixed-C \times 2 columns with stabilized tetrahydrofuran as the solvent. Poly(styrene) standards of known molecular weight were run using the same conditions and column set to create a calibration curve.

GC-MS data were obtained using a 1% solution of analyte in tetrahydrofuran (Fisher, Optima) using an Agilent 6890N gas

chromatograph fitted with an Ultra-1 methyl siloxane column (Agilent, 0.33 μ m film thickness, 200 μ m \times 25 m) and an Agilent 5975B quadrupole mass spectrometer. A 1 μ L injection was made (1:20 split ratio) with helium carrier gas at 1 mL/min. The MS conditions were: electron impact mode, 70 eV, MS source 250 °C, MS quadrupole at 150 °C, electron multiplier 1235 volts, with masses scanned from 46 to 405 amu. The postcolumn eluent was also connected to a flame ionization detector (FID) using a two-way splitter. FID conditions were a hydrogen flow of 40 mL/min, an air flow of 400 mL/min, and a nitrogen flow of 30 mL/min. The purity of the analyte was determined from the integrated peak areas in the FID chromatogram.

Reaction of PHS with Norbornene. A solution of norbornene (2.35 g, 25.0 mmol), PHS (3.00 g), and Irgacure 290 (0.180 g, 0.133 mmol) in 2-heptanone (10.0 g) was made. The solution was exposed with broadband UV light using an Electro-lite UV curing system equipped with a medium-pressure Hg lamp for 60 s. The solution was then heated to 100 °C for 24 h. A portion of the solution (1.48 g) was added to 8.1 g of methanol to give a milky emulsion. The emulsion was centrifuged for 10 min at 4000 rpm to give a pale yellow oily product. The solvent was decanted from the oil, and the oil was dissolved in acetone (0.88 g). To this solution was added methanol (6.7 g) to give a white emulsion. The emulsion was centrifuged for 10 min at 4000 rpm to give a pale yellow oily solid. The solvent was decanted, and the resulting solid was washed with methanol (~ 8 g \times 2) and then dried in a vacuum oven at 50 °C for 24 h to give a very pale yellow solid (0.26 g). GPC: $M_w = 42,400$; $M_n = 24,700$. GPC, FT-IR and NMR results can be found in the Supporting Information, Figures S1–S9.

Synthesis of NBEOEtNB. 2-Norbornene ethanol (NBEOH, 1360 g, 9.85 mol), anhydrous tetrahydrofuran (6590 g), and sodium *tert*-pentoxide (95%, 540 g, 4.91 mol) were added to a 20 L glass reactor. The jacketed glass reactor was equipped with an agitator and fitted with a water-cooled overhead condenser and a 10 L glass overhead receiver vessel. Oxygen was removed from the reactor system using three pressure/vent swings with nitrogen. The reactor was placed under a nitrogen atmosphere and cooled to 0 °C. *para*-Toluenesulfonyl chloride (940 g, 4.93 mol) was slowly added to the reaction mixture while maintaining temperature in a range of 0–10 °C. The reaction mixture was then heated to 50 °C and maintained at this temperature for 92 h. The crude product was then distilled under vacuum to obtain a liquid ($\geq 99.5\%$ assay by GC). NMR and MS results can be found in the Supporting Information, Figures S10–S12.

Photoactive Composition Formulation, Wafer Processing, Exposure, and Development Details. In a typical formulation, PHS (0.50 g), NBEOEtNB (0.055 g), and Irgacure 290 (0.011 g)

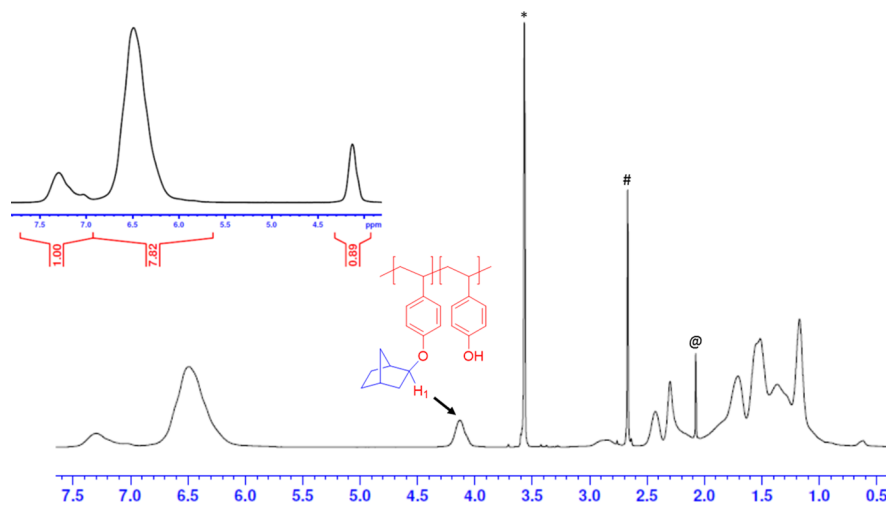


Figure 1. ¹H NMR of the reaction product of PHS and norbornene after exposure and heating in the presence Irgacure 290. Inset shows the integration of the downfield region of the spectrum. * = protio impurity in dioxane-*d*₈, # = water, @ = residual acetone.

were dissolved in PGMEA (4.5 g) and filtered through a 0.45 micron PTFE syringe filter. The solutions were spin-coated onto 4 in thermal silicon oxide wafers. The wafers were baked for 2 min at 100 °C to remove residual solvent from the films. The films on the wafers were image-wise exposed through a 365 nm band-pass filter using an ABM mask aligner at an exposure dose of 113 mJ/cm² at 365 nm. The wafers were then baked for 2 min at 100 °C. The wafers were then developed by immersion in TMAH. In all cases where images were observed, the images were negative tone. The minimum feature size was determined by optical microscopy, and the film thickness loss during development was determined by profilometry before and after development.

RESULTS AND DISCUSSION

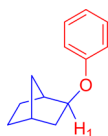
Reaction of PHS with Norbornene. Before embarking on photopatterning experiments, we decided to generate evidence that the pendent phenol functionality of PHS could add across the double bond of norbornene in the presence of acid generated from the exposure of a photoacid generator. Thus, a solution of PHS, norbornene, and Irgacure 290 was exposed to UV light and then heated. Irgacure 290 is a sulfonium salt of tetrakis(pentafluoroborate), which absorbs UV light subsequently generating a strong acid.¹² After heating this mixture, the resulting polymer was isolated as a solid and was characterized.

The average molecular weight of the isolated polymer after reaction with norbornene increased from 23,100 ($M_w/M_n = 1.67$) to 42,400 ($M_w/M_n = 1.72$) based on our GPC measurements. The FT-IR spectrum of the reaction product shows a band around 3400 cm⁻¹ consistent with -OH functionality, albeit in substantially reduced intensity compared to the PHS starting material consistent with the addition of the -OH group across the norbornene double bond (Figure S2). From an overlay of the finger print region of FT-IR spectra of the starting material and reaction product, two new peaks are observed with approximate equal intensity at 1000 and 1078 cm⁻¹. A pair of intense peaks in this region is typical of a mixed aromatic and aliphatic ether moiety.

The ¹H NMR spectrum of the reaction product exhibits a broad resonance at about 7.30 ppm and a larger peak at 6.49 ppm in agreement with the -C₆H₄OH functionality and -C₆H₄- functionality on PHS, respectively (Figure 1). However, the ratio of the integration of the two resonances (7.8 to 1) is greater than expected for the starting material (4 to 1) and is consistent with the disappearance of approximately 50% of the -OH functionality. Concomitant with the disappearance of -OH is the appearance of a new resonance at 4.13 ppm. The intensity of this peak mirrors the loss of the intensity of the peak at 6.40 ppm.

The peak at 4.13 ppm is due to H₁ geminal to the phenoxy linkage between the backbone of PHS and the norbornane pendent group. A similar peak was reported for *exo*-phenoxynorbornane (Chart 2), the reaction product of phenol and norbornene.^{6,13–15}

Chart 2. Structure of *exo*-Phenoxynorbornane Model Compound



Proof of the connectivity of the norbornane pendent group to the aromatic substituent of PHS is found in the HMBC spectrum, which shows a three-bond correlation between the *ipso* carbon of the aromatic ring and H₁ (Figures S8 and S9).

Further, evidence for the addition of norbornene to the -OH functionality is obtained from the aliphatic resonances observed in the HMQC ¹H-¹³C correlation experiment. In Figure 2, 10 peaks are observed in the correlation map because of carbons 2–7 and their associated protons. The carbon resonances at 41.12 (C₄) and 35.43 (C₃) are confirmed to be methine carbons based on the ¹³C-DEPT135 experiment (Figures S3 and S4). Similar resonances are reported in the literature for the *exo*-phenoxynorbornane model compound.^{6,14,15} The remaining carbon resonances are due to methylene carbons; each signal is associated with two proton resonances each in the HMQC spectrum. The carbon resonance at 39.86 is assigned to C₂, the methylene carbon vicinal to the phenoxy linkage, which shifts this signal downfield relative to the other methylene carbons. The remaining carbon resonances are assigned in accordance with those reported by Taylor et al.¹³ Complete assignments of the carbon and proton cycloaliphatic resonances are found in the Supporting Information, Figure S7.

Synthesis and Characterization of NBEOEtNB. The synthesis of NBEOEtNB was achieved by deprotonating NBEOH in the presence of one-half equivalence of sodium *tert*-pentoxide and *para*-toluenesulfonyl chloride. High-purity material was obtained after distillation. The compound was characterized by MS and NMR techniques.

The 70 eV electron impact mass spectrum of NBEOEtNB shows a weak parent ion at *m/z* 258. The spectrum is dominated by the base peak ion at *m/z* 66, resulting from reverse Diels–Alder fragmentation.¹⁶ Ions observed at *m/z* 79 and 91 match those previously described for norbornenes.¹⁶ The peak at *m/z* of 121 represents a C–O α -cleavage in NBEOEtNB and formation of the NBEO ion. A peak at *m/z* 193, [M-65+], was reported in other oxygen-substituted norbornenes and interpreted as reverse Diels–Alder fragmentation coupled with hydrogen migration.¹⁷

The NMR spectra collected for NBEOEtNB are consistent with a dinorbornene compound. Assignments of the proton and carbon signals were made with the assistance of the HSQC spectrum (Figures S10 and S11). This compound exhibits an *endo/exo* ratio of 77:23 according to the integration of the olefinic proton resonances in the ¹H NMR spectrum.

Photopatterning Results. The concept of an acid-catalyzed hydroalkoxylation reaction in a photoactive formulation was tested by mixing the phenol-substituted polymer, PHS, with NBEOEtNB (10% by weight on the polymer) in the presence of a PAG (Irgacure 290, 2% by weight on the polymer). The formulation was made in PGMEA, Table 1, formulation 1.

Spin-coated films of formulation 1 on silicon gave excellent negative tone patterns after image-wise exposure, postexposure bake, and development with TMAH. Five microns via holes were resolved in the 1 μ m-thick film (Figure 3). There was no film thickness lost nor was the film swollen during development (formulation 1 in Table 2). The lack of film thickness loss suggests that a sufficient number of phenol functionalities reacted with the dinorbornene additive to prevent dissolution or swelling. Assuming that all norbornene functionality in the formulation reacted, ~10% of the phenol substituents would be involved in cross-linking and not available for dissolution or

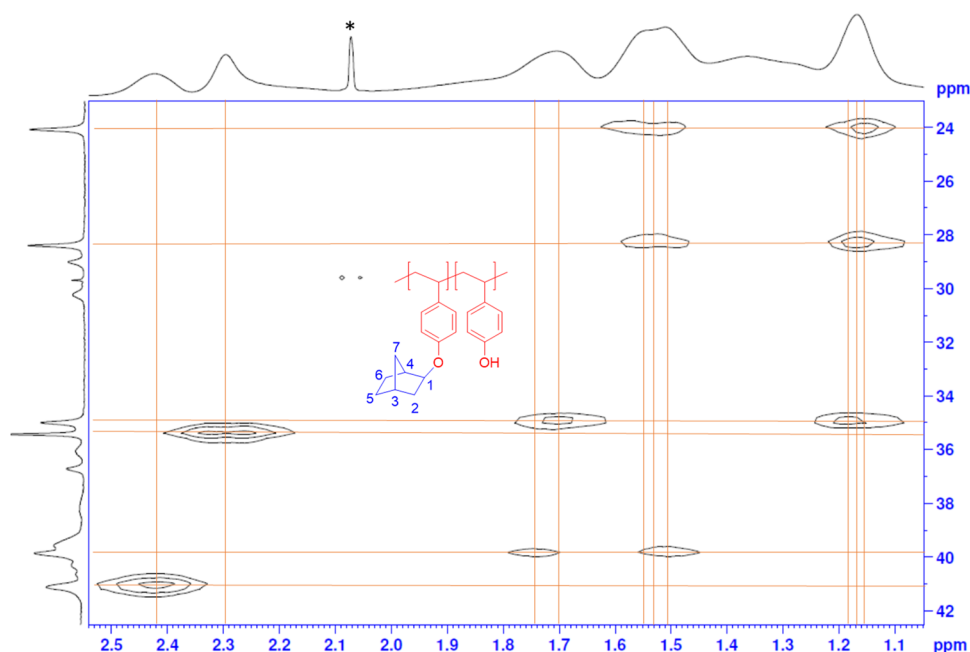


Figure 2. Upfield portion of the HMQC spectrum for the reaction product of PHS and norbornene after exposure and heating in the presence Irgacure 290. * = residual acetone.

Table 1. Photoactive Formulation Details

formulation	polymer (g)	norbornene additive (g)	Irgacure 290 (g)	PGMEA added (g)
1	PHS (0.5)	NBEtOEtNB (0.055)	0.011	4.5
2	PHS (0.5)	NBEtOEtNB (0.055)	0.011	4.5
3	PHS (0.5)	NBCH ₂ OCH ₂ OCH ₂ NB (0.055)	0.011	4.5
4	PHS (1.0)	NBPhOAc (1.0)	0.022	8.0

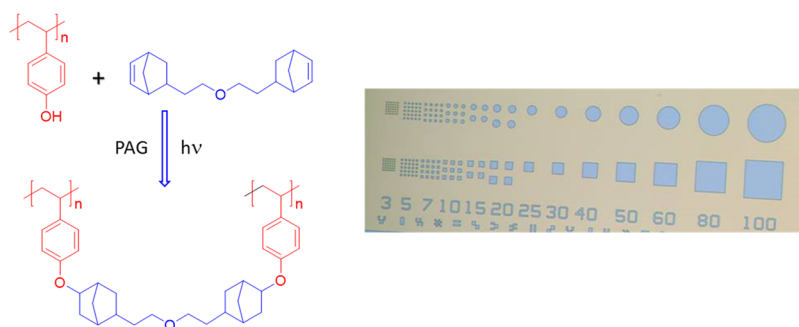


Figure 3. Photochemically-initiated hydroalkoxylation cross-linking reaction and optical photomicrograph of negative tone features resolved after image-wise exposure, postexposure bake, and development of films with TMAH of formulation 1, Table 2.

Table 2. Development Times, Size of Minimum Feature Size Resolved, and Percent Film Thickness Loss during TMAH (or PGMEA) Development for Spin-Coated Films of Photoactive Formulations

formulation	development time	minimum feature size resolved	percent film thickness loss (initial film thickness in μm)
1	10 s in TMAH	5 μm	0% (1.00)
1	10 s in PGMEA	10 μm	0% (0.70)
2	10 s in TMAH		100% (0.80)
3	10 s in TMAH	5 μm	7% (0.94)
4	10 s in TMAH	3 μm	39% (2.11)

swelling because the equivalent ratio of phenol to norbornene functionality is $\sim 10:1$ in formulation 1.

A similar experiment (imaging of formulation 1 with PGMEA development in Table 2) in which PGMEA was used as the developer instead of TMAH, slightly larger via holes (10 μm) were revealed after 10 s development with no film thickness loss.

A control formulation without NBEtOEtNB (formulation 2 in Table 1) gave a 0.8 μm -thick film that completely dissolved in TMAH after image-wise exposure and postexposure bake; no images were observed, and the film thickness loss was 100% (formulation 2, Table 2). This result shows the necessity of the dinorbornene additive for the hydroalkoxylation reaction and resulting photopatterning to occur. It also suggests that no other side reactions are occurring that cross-links the PHS preventing dissolution in TMAH or PGMEA.

In formulation 3, NB₂EtNB was replaced by a related dinorbornene additive, the acetal derivative, NBCH₂OCH₂OCH₂NB. As in formulation 1, 10% by weight of the acetal was mixed with PHS along with Irgacure 290 in PGMEA (formulation 3 in Table 1). Under identical processing conditions, films of formulation 3 gave good imaging; 5 μm via holes were resolved in a 0.94 μm-thick film (imaging of formulation 3 results in Table 2). However, in this case, some film thickness loss was observed (7%) after development. This may be an indication of either the slightly lower reactivity of the acetal toward hydroalkoxylation or, more likely, some degradation of the acetal linkage in the presence of acid. Nevertheless, good imaging was observed for this dinorbornene.

We also tested the ability of a mononorbornene additive to create a photopatternable composition with PHS. In this case, a 22% by weight (on polymer) mixture of NBPhOAc on PHS and Irgacure 290 in PGMEA was made, formulation 4 in Table 1. For this formulation, excellent negative tone photopatterning resolution was observed (3 μm via holes resolved), but film thickness loss was quite high (39%) for a 2.11 μm-thick film. Nevertheless, these results prove that a monofunctional norbornene can render PHS negative tone photopatternable when exposed with a PAG. These results are consistent with a hydroalkoxylation reaction across the norbornene double bond that effectively reduces the TMAH solubility of the PHS, creating a sufficient dissolution rate contrast to form patterns after development. This type of dissolution rate contrast mechanism is unique among negative tone photopolymer compositions. Typically, the photopatterning mechanism relies on cross-linking in negative tone materials.

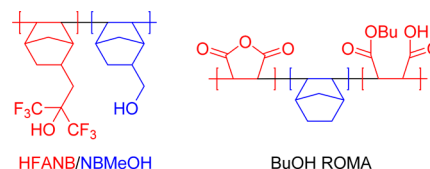
As further proof that a cross-linking mechanism is not responsible for the dissolution rate contrast in a formulation with NBPhOAc, it was discovered that an exposed film (~0.5 μm initial film thickness) of the formulation 4 was readily dissolved and washed off the wafer upon immersion in PGMEA for 1 min. In contrast, when PGMEA is used to develop a film containing NB₂EtNB (i.e., formulation 1), there was no film thickness loss in the exposed regions. The ability to form negative tone patterns by the TMAH development followed by dissolution and removal from the wafer in PGMEA shows that formulations with the monofunctional norbornene additive are a rare example of negative tone compositions that are not cross-linked but can be patterned yet readily removed with mild solvent-like PGMEA at room temperature. Cross-linked photopolymers typically require immersion in strong solvents such as DMF, NMP, or DMSO at high temperatures in order to be removed (i.e., reworked).¹⁸

We also tested the photopatterning capability of polymers containing both aliphatic alcohol and carboxylic acid functionalities with NB₂EtNB and Irgacure 290. Both types of polymer films yielded negative tone, micron-sized features after image-wise exposure, postexposure bake, and development with TMAH (Table S2). This proves that aliphatic alcohol (HFANB/NBMeOH) and carboxylic acid-functional (BuOH ROMA) polymers participate in the acid catalyzed addition to the norbornene functionality yielding a cross-linked film (Chart 3).

CONCLUSIONS

This work has demonstrated that aqueous base-soluble, -OH functional polymers can be prompted to undergo addition

Chart 3. Structures of Aliphatic Alcohol-Functional Polymer and Carboxylic Acid-Functional Polymer that can be Imaged when Formulated with Dinorbornene and PAG Additives



reactions with both di- and mononorbornene additives when exposed in the presence of a photoacid generator. As a result, the polymer can be photopatterned after image-wise exposure and TMAH development. In the case of dinorbornenes, the mechanism of photopatterning is cross-linking. For the mononorbornene, the hydroalkoxylation reaction is the cause of dissolution rate contrast because the acidic -OH from the pendent phenol group adds across a double bond and is no longer available to dissolve the polymer in aqueous base. This composition is a rare example of a negative tone photopatternable, yet reworkable, photopolymer formulation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b03309.

GPC, NMR, and FT-IR spectra for the reaction product of PHS and norbornene; NMR and MS data for NB₂EtNB (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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