ACS Macro Letters

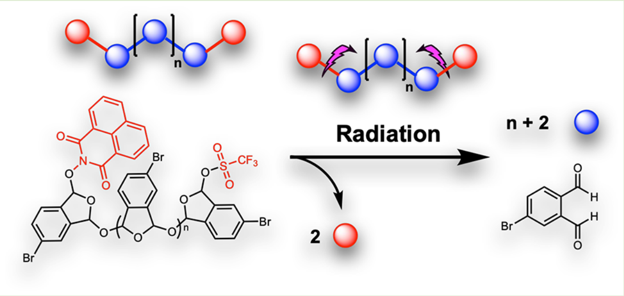
pubs.acs.org/macroletters Letter

Synthesis of End-Cap Enabled Self-Immolative Photoresists For Extreme Ultraviolet Lithography

Jingyuan Deng,* Sean Bailey, Ruiwen Ai, Anthony Delmonico, Gregory Denbeaux, Shaoyi Jiang, and Christopher K. Ober*

Cite This: *ACS Macro Lett.* 2022, 11, 1049−1054 **Read Online**

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Conventional chemically amplified resists (CARs) rely on the usage of photoacid generators to serve as the source of chemical amplification. However, acid diffusion inevitably accompanies CARs and has led to the resolution, line edge roughness, and sensitivity (RLS) trade-off, which is the most challenging technical problem for modern photoresists. Herein, we take advantage of the self-immolative property of polyphthalaldehyde (PPA) derivatives to create end-cap enabled chain scissionable resists for extreme ultraviolet (EUV) lithography. The feasibility of this strategy was demonstrated under UV photodegradation experiments. The dose-to-clear (DTC) under EUV radiation was 90 mJ/cm^2 for the most promising resist, representing more than a 100-fold improvement over previous PPA resists. Density functional theory (DFT) calculations were conducted to understand the structural origin of end-cap EUV sensitivity.

Photodegradable materials have witnessed numerous advances in the past decades in a variety of areas, including implant materials,[1−3] delivery systems,[4] and transient electronics,[5] but most notably in photoresists.[6] Extreme ultraviolet (EUV) lithography, which utilizes 13.5 nm radiation, currently serves as the state-of-the-art production technology for transistors with sub-7 nm nodes.[7] Chemical amplification is a central requirement for polymer-based resists to achieve the high sensitivity mandated by the EUV exposure process. This requirement has been satisfied through the development of photoacid generators (PAGs), which have undergone significant improvements since their original formulation by IBM.[8] Unfortunately, the ability of new PAGs to further enhance resist performance has become limited due to the difficulty in simultaneously optimizing a resist's resolution, line edge roughness, and sensitivity (RLS).[9] As one of the primary causes of the RLS barrier is acid diffusion,[10] which is inherent to all PAGs, nonchemically amplified resists have garnered increased attention. Examples include chain-scissionable polymers,[11−13] metal-oxide nanoparticles,[14−16] and cross-linkable, inorganic compounds.[17] Despite improvements in resolution, these novel resists are markedly below current sensitivity demands.

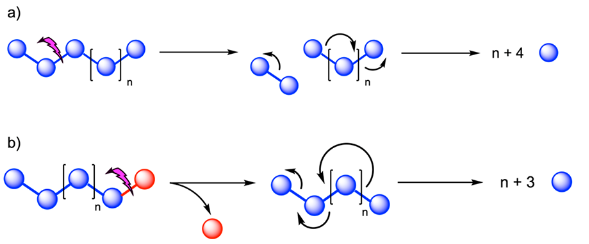
Circumventing the usage of PAGs does not necessarily need to result in the elimination of chemical amplification, and depolymerization has proven to be a viable alternative amplification mechanism. These self-immolative resists predate[18] the employment of PAGs but have long been neglected due to their instability[19] and propensity to contaminate[20] the optics of lithography tools. Recently, we reported the synthesis of a remarkably stable poly(phthalaldehyde) (PPA) derivative that did not suffer from monomer outgassing associated with the original PPA resist.[21−23] This brominated derivative (Br-PPA) was studied with various PAGs to create a resist system that was ultimately limited by acid diffusion and the stochastics of mixing the two components. In this work, we sought to synthesize an improved resist based on Br-PPA that did not require the usage of separate small molecule PAGs to achieve high EUV sensitivity.

The depolymerization of PPA can be triggered either by radiation-induced end-cap or backbone cleavage, as shown in Scheme 1. Significantly enhancing the rate of backbone cleavage under EUV radiation did not seem practical, as the bond dissociation energy (BDE) of the acetal linkages could not be lowered via aromatic substitution without losing the desired thermal stability of the polymer. Instead, we modified the end-cap to control EUV sensitivity, concentrating on three different end-capped PPA derivatives for study (Figure 1). We learned from previous work[21] that PAGs based on aryl sulfonates were chemically active under both UV and EUV radiation. We therefore selected a triflate group to serve as the end-cap for PPA **2**. As the triflate group could only be

Received: July 7, 2022
Accepted: August 8, 2022

https://doi.org/10.1021/acsmacrolett.2c00395
ACS Macro Lett. 2022, 11, 1049−1054

Scheme 1. Depolymerization Reaction Triggered by (a) Polymer Backbone Cleavage and (b) End-Cap Cleavage



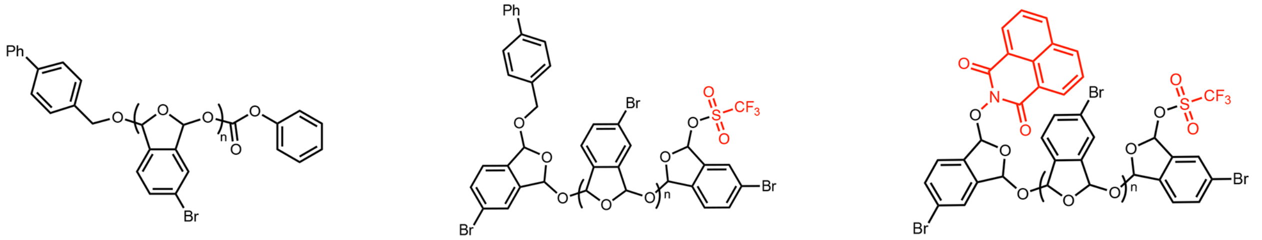
incorporated using an electrophilic reagent that terminated polymerization, this left the end-cap of the opposite terminus of the polymer unused. Fortunately, inclusion of this end-cap was made possible through the naphthalimide group, another moiety previously shown to be susceptible to UV and EUV radiation, as it could be easily added as a nucleophilic initiator. This resulted in PPA **3**, which possessed two responsive end-caps at the head and tail of the polymer. For comparison, PPA **1** was constructed to bear a phenyl carbonate end-cap known to be inactive[22] under UV radiation. TGA analysis (SI) demonstrated that PPA **2** and **3** still enjoyed good thermal stability, with degradation temperatures of 143 and 147 °C, respectively. The number average molecular weights of PPA **1**−**3** were assessed by gel permeation chromatography and found to be 4730, 4250, and 3970 g/mol, respectively.

We first conducted photodegradation experiments under UV irradiation to discern if the well-known effectiveness of triflate and naphthalimide groups in UV-sensitive PAGs would translate to end-cap removal. PPA **1**−**3** were dissolved in DMSO-d_6 and transferred to quartz NMR tubes. The NMR tubes were exposed to UV irradiation at a wavelength of 254 nm (20 mW/cm^2) for 30 min followed by heating to 110 °C for 5 min. The degradation processes of PPA **2** and **3** were studied by NMR and the spectra are shown in Figures 2 and 3, respectively. The spectrum of PPA **1** was unchanged over the course of the photodegradation experiment. Figure 2b illustrates the beginning of dialdehyde formation in PPA **2**, as indicated by the NMR signal at 10.5 ppm, which becomes more intense upon heating, as shown in Figure 2c. Figure 2c also reveals that a significant amount of polymer residue is left in solution, suggesting that most polymers are still end-capped. This experiment demonstrates that while the triflate group is capable of undergoing O−S bond cleavage under UV radiation and initiating depolymerization, likely via the photodegradation pathway given in the SI (Figure S13), its activity as an end-cap is significantly limited compared to its capability as a PAG.[24−26]

In contrast, PPA **3** underwent complete depolymerization, as seen in Figure 3c. Significant color change accompanied this process (Figure 3), with the yellow color indicating the formation of the monomer. The photodegradation pathway of PPA **3** is almost identical to Figure 2 with the exception that depolymerization can also be initiated via homolytic N−O bond cleavage from the polymer head. While the increased sensitivity of PPA **3** compared to **2** is not unexpected given that naphthalimide PAGs have higher acid yields[24] under UV radiation than triflate PAGs, it is surprising that the extent of depolymerization between **2** and **3** is substantially different.

Applying the same postexposure bake temperature as employed in the UV photodegradation experiments, EUV contrast curves were collected for each PPA derivative (Figure 4) using isopropanol as the developer. PPA **1** did not exhibit any noteworthy decrease in film thickness, indicating that its carbonate end-cap was unreactive to the secondary electrons generated by EUV radiation (considered to be the primary reaction mechanism[27] of polymers with EUV photons). PPA **2** possessed considerably higher sensitivity, but its thickness decreased linearly, suggesting a lack of amplification. PPA **3** had sharp contrast for doses in the range of 0 to 20 mJ/cm^2 before becoming linear. To understand this behavior, we examined the likely depolymerization pathway (SI, Figure S14) initiated by the addition of a secondary electron to PPA **3** to form a radical anion. Chain scission ensuing from loss of the end-cap generates multiple monomers and resulted in clear evidence of amplification in the contrast curve. However, as the dosage increases and the monomer concentration goes up, the anionic species at the chain end reacts reversibly with monomers to form a hemiacetal. The linearization of the contrast curve therefore arises from an in situ equilibrium established in the exposed region. This equilibrium did not form during the UV photodegradation experiments as depolymerization occurs via a radical mechanism (Figure S13) that can be effectively quenched in air due to oxygen coupling, preventing monomers from reacting with the chain end of the polymer. Despite this undesirable effect, the dose-to-clear (DTC) of 90 mJ/cm^2 for PPA **3** far exceeds recent attempts[20] to utilize PPA as a PAG free EUV photoresist where DTC measurements exceeded 10000 mJ/cm^2. Furthermore, the absence of PAGs in this resist is likely to significantly improve the resolution and line edge roughness beyond the previously developed two component system[22] by eliminating the deleterious effects of acid diffusion.

Our experimental observations were also supported by DFT calculations. We used two model molecules to imitate both chain ends as shown in Figure 5. As the proposed EUV degradation pathway occurs with the formation of a radical anion species followed by bond cleavage in the end-cap,



1 **2** **3**

Figure 1. End-cap functionalized polyphthalaldehyde synthesized in this work.

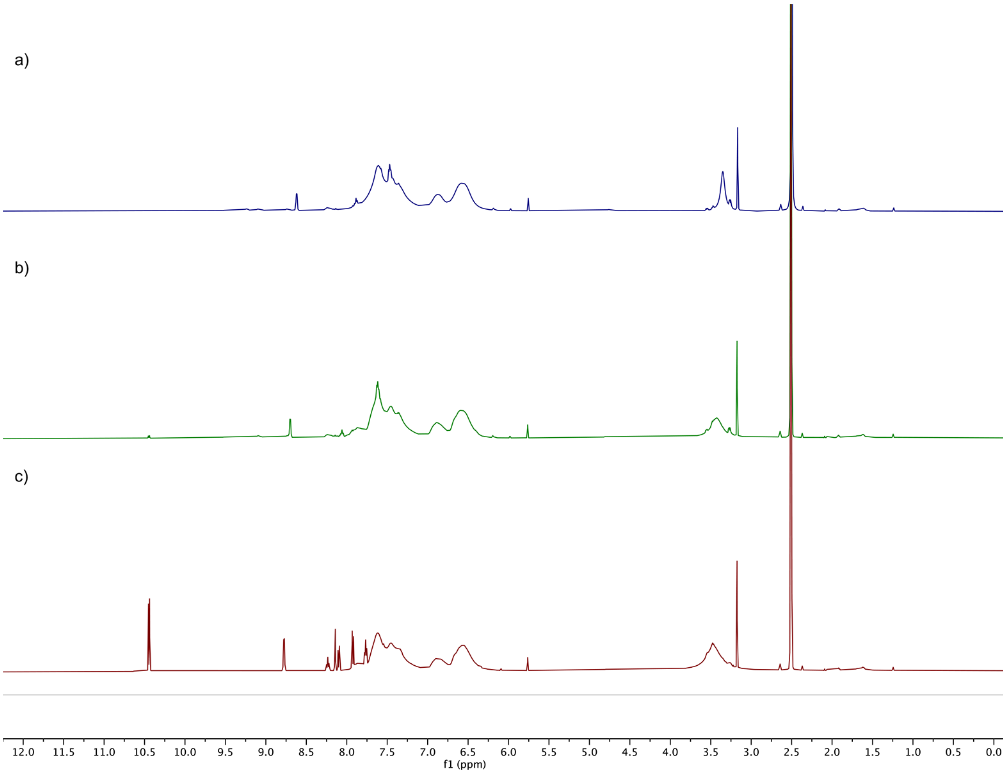


Figure 2. ^{1}H NMR spectra of **2** (a) before UV irradiation and (b) after UV irradiation for 30 min and (c) after UV irradiation for 30 min and heated at 110 °C for 5 min.

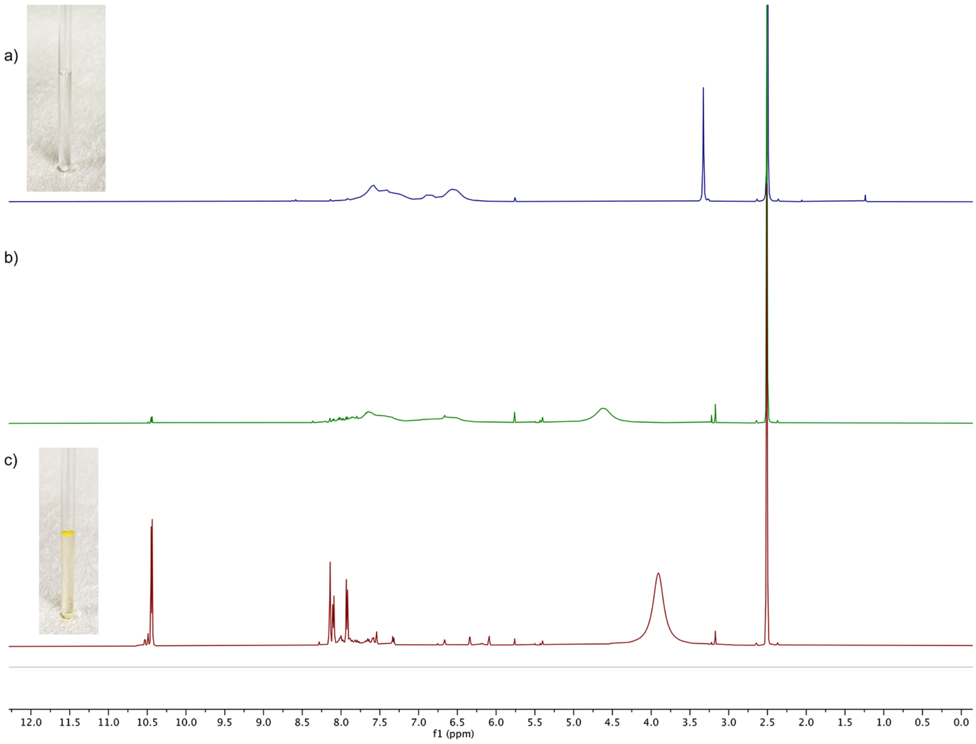


Figure 3. ^{1}H NMR spectra of **3** (a) before UV irradiation, (b) after UV irradiation for 30 min, and (c) after UV irradiation for 30 min and heated at 110 °C for 5 min. The embedded picture shows the change of color before and after the photodegradation experiment.

vertical electron affinity (VEA) and bond dissociation energy (BDE) were calculated for these model compounds to study the reason why the naphthalimide end-cap outperforms the triflate end-cap. The molecular geometries were optimized at FT-TPSS/def2-SVP (T_{el} = 5000 K) theoretical level[28−32] with the gCP empirical counterpoise correction,[33] D4 dispersion correction,[34] and the final electronic energies were calculated at FT-B97M-V/def2-TZVPP (T_{el} = 5000 K) level.[32,35,36]

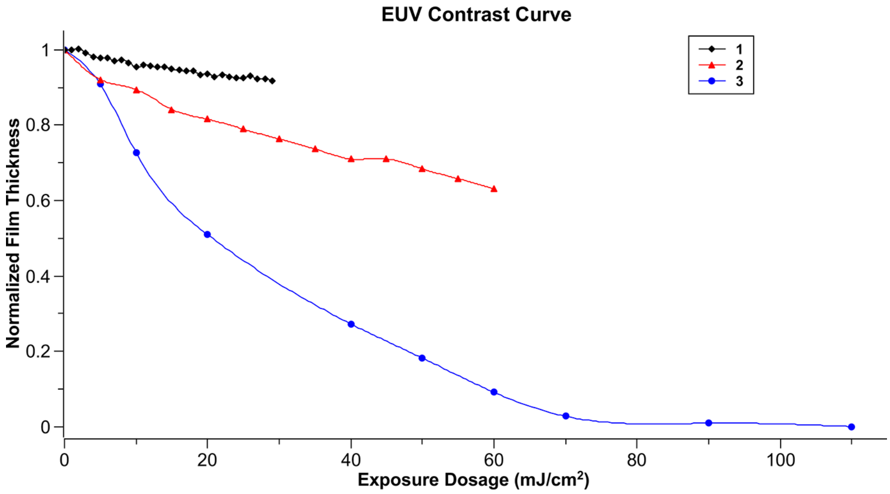
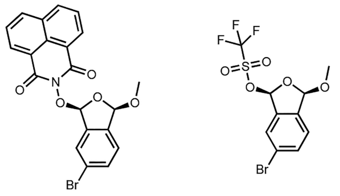


Figure 4. EUV contrast curves for **1**–**3**.



SEC 1 SEC 5

Figure 5. Model compounds SEC **1** and **5** used for DFT calculations.

There are four different isomers for each of the model molecules. Calculation results of the different isomers are summarized in Table S2. As no significant differences existed between the calculated values for each isomer, SEC **1** and **5** were chosen for comparative purposes.

As shown in Table S1, calculations revealed that the N–O BDE was 20 kcal/mol smaller than the S–O BDE, indicating N–O bond cleavage is preferred. VEA results demonstrated that electron attachment was much more thermodynamically favorable for SEC **1** compared to SEC **5**. Both the VEA and BDE calculations reinforce the superior EUV sensitivity of the naphthalimide end-cap.

In summary, we have successfully developed one of the first polymeric resists that is chemically amplified directly by EUV radiation and without using free PAGs. Its DTC of 90 mJ/cm^2 is in the range[37] of commercial viability. Both UV and EUV experiments highlighted that the naphthalimide and triflate moieties possessed far greater differences when employed as end-caps in comparison to their performance as PAGs. This result was explained using DFT calculations to demonstrate the overwhelming advantage of the naphthalimide group under EUV exposure, which was magnified by the absence of catalytic acid. The primary limitation of the newly developed resist was identified as the formation of an equilibrium between monomer and polymer. We are currently developing a single component photoresist by tethering EUV active groups to the polymer backbone to prevent establishment of the equilibrium by driving monomer formation using cleavage of these EUV active side chains to initiate depolymerization via a cascade mechanism.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.2c00395.

Experimental and computational details (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Jingyuan Deng – *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853, United States; Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0002-0858-9919; Email: jd966@cornell.edu

Christopher K. Ober – *Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0002-3805-3314; Email: cko3@cornell.edu

Authors

Sean Bailey – *Department of Materials Science and Engineering and Department of Biomedical Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0002-0792-210X

Ruiwen Ai – *College of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, New York 12203, United States*

Anthony Delmonico – *College of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, New York 12203, United States*

Gregory Denbeaux – *College of Nanoscale Science and Engineering, SUNY Polytechnic Institute, Albany, New York 12203, United States*

Shaoyi Jiang – *Department of Materials Science and Engineering and Department of Biomedical Engineering, Cornell University, Ithaca, New York 14853, United States;* orcid.org/0000-0001-9863-6899

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmacrolett.2c00395

Author Contributions

CRediT: **Jingyuan Deng** conceptualization (lead), data curation (lead), formal analysis (lead), funding acquisition (supporting), investigation (lead), methodology (lead), project administration (lead), resources (supporting), software (lead), supervision (lead), validation (lead), visualization (lead), writing-original draft (lead), writing-review & editing (lead); **Sean Bailey** data curation (supporting), formal analysis (supporting), investigation (supporting), writing-original draft (supporting), writing-review & editing (supporting); **Ruiwen Ai** data curation (supporting), writing-original draft (supporting), writing-review & editing (supporting); **Anthony Delmonico** data curation (supporting), writing-original draft (supporting), writing-review & editing (supporting); **Gregory Denbeaux** data curation (supporting), resources (supporting), writing-original draft (supporting), writing-review & editing (supporting); **Shaoyi Jiang** resources (supporting), writing-original draft (supporting), writing-review & editing (supporting); **Christopher K. Ober** conceptualization (supporting), funding acquisition (lead), project administration (lead), resources (lead), supervision (lead), writing-original draft (supporting), writing-review & editing (supporting).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by Intel Corporation through the SRC Research Project (Task ID: 2885.001). Exposures were performed at the Intel research facility and SUNY POLY institute. This work made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF MRSEC Program (DMR-1719875). In addition, characterization was performed at the Cornell NanoScale Facility, an NNCI member supported by NSF Grant NNCI-2025233. This work also made use of the Cornell NMR Facility, which was supported, in part, by the NSF through MRI Award CHE-1531632. The authors gratefully acknowledge the help from Intel collaborators, Dr. Grant Kloster, Dr. Patrick Theofanis, and Dr. Marie Krysak. In particular, we thank Dr. James Blackwell for very helpful discussion and also helping with various aspects of this work. S.J. and S.B. acknowledge start-up support from Cornell University, including the Robert S. Langer Professorship and the Cornell NEXT Nano Initiative.

■ REFERENCES

(1) Kloxin, A. M.; Kasko, A. M.; Salinas, C. N.; Anseth, K. S. Photodegradable hydrogels for dynamic tuning of physical and chemical properties. *Science* **2009**, *324* (5923), 59−63.

(2) Azagarsamy, M. A.; McKinnon, D. D.; Alge, D. L.; Anseth, K. S. Coumarin-Based Photodegradable Hydrogel: Design, Synthesis, Gelation, and Degradation Kinetics. *ACS Macro. Lett.* **2014**, *3* (6), 515−519.

(3) Lunzer, M.; Shi, L.; Andriotis, O. G.; Gruber, P.; Markovic, M.; Thurner, P. J.; Ossipov, D.; Liska, R.; Ovsianikov, A. A Modular Approach to Sensitized Two-Photon Patterning of Photodegradable Hydrogels. *Angew. Chem., Int. Ed. Engl.* **2018**, *57* (46), 15122−15127.

(4) Kitayama, Y.; Takeuchi, T. Photodegradable Polymer Capsules Fabricated via Interfacial Photocross-linking of Spherical Polymer Particles. *Acs Applied Polymer Materials* **2020**, *2* (9), 3813−3820.

(5) Shi, C.; Leonardi, A.; Zhang, Y.; Ohlendorf, P.; Ruyack, A.; Lal, A.; Ober, C. K. UV-Triggered Transient Electrospun Poly(propylene carbonate)/Poly(phthalaldehyde) Polymer Blend Fiber Mats. *ACS Appl. Mater. Interfaces* **2018**, *10* (34), 28928−28935.

(6) Chatterjee, S.; Ramakrishnan, S. A novel photodegradable hyperbranched polymeric photoresist. *Chem. Commun.* **2013**, *49* (94), 11041−3.

(7) Li, L.; Liu, X.; Pal, S.; Wang, S.; Ober, C. K.; Giannelis, E. P. Extreme ultraviolet resist materials for sub-7 nm patterning. *Chem. Soc. Rev.* **2017**, *46* (16), 4855−4866.

(8) MacDonald, S. A.; Willson, C. G.; Frechet, J. M. J. Chemical Amplification in High-Resolution Imaging Systems. *Acc. Chem. Res.* **1994**, *27* (6), 151−158.

(9) Itani, T.; Kozawa, T. Resist Materials and Processes for Extreme Ultraviolet Lithography. *Jpn. J. Appl. Phys.* **2013**, *52* (1R), 010002.

(10) Kozawa, T.; Tagawa, S. Radiation Chemistry in Chemically Amplified Resists. *Jpn. J. Appl. Phys.* **2010**, *49* (3), 030001.

(11) Yu, A.; Liu, H.; Blinco, J. P.; Jack, K. S.; Leeson, M.; Younkin, T. R.; Whittaker, A. K.; Blakey, I. Patterning of tailored polycarbonate based non-chemically amplified resists using extreme ultraviolet lithography. *Macromol. Rapid Commun.* **2010**, *31* (16), 1449−55.

(12) Lawrie, K. J.; Blakey, I.; Blinco, J. P.; Cheng, H. H.; Gronheid, R.; Jack, K. S.; Pollentier, I.; Leeson, M. J.; Younkin, T. R.; Whittaker, A. K. Chain scission resists for extreme ultraviolet lithography based on high performance polysulfone-containing polymers. *J. Mater. Chem.* **2011**, *21* (15), 5629.

(13) Deng, J.; Ratanasak, M.; Sako, Y.; Tokuda, H.; Maeda, C.; Hasegawa, J.-y.; Nozaki, K.; Ema, T. Aluminum porphyrins with quaternary ammonium halides as catalysts for copolymerization of cyclohexene oxide and CO2: metal-ligand cooperative catalysis. *Chemical Science* **2020**, *11* (22), 5669−5675.

(14) Luo, C.; Xu, C.; Lv, L.; Li, H.; Huang, X.; Liu, W. Review of recent advances in inorganic photoresists. *RSC Adv.* **2020**, *10* (14), 8385−8395.

(15) Xu, H.; Sakai, K.; Kasahara, K.; Kosma, V.; Yang, K.; Herbol, H. C.; Odent, J.; Clancy, P.; Giannelis, E. P.; Ober, C. K. Metal-Organic Framework-Inspired Metal-Containing Clusters for High-Resolution Patterning. *Chem. Mater.* **2018**, *30* (12), 4124−4133.

(16) Li, L.; Chakrabarty, S.; Spyrou, K.; Ober, C. K.; Giannelis, E. P. Studying the Mechanism of Hybrid Nanoparticle Photoresists: Effect of Particle Size on Photopatterning. *Chem. Mater.* **2015**, *27* (14), 5027−5031.

(17) Rathore, A.; Pollentier, I.; Cipriani, M.; Singh, H.; De Simone, D.; Ingolfsson, O.; De Gendt, S. Extreme Ultraviolet-Printability and Mechanistic Studies of Engineered Hydrogen Silsesquioxane Photoresist Systems. *ACS Applied Polymer Materials* **2021**, *3* (4), 1964−1972.

(18) Ito, H.; Willson, C. G. Chemical amplification in the design of dry developing resist materials. *Polym. Eng. Sci.* **1983**, *23* (18), 1012−1018.

(19) Wang, F.; Diesendruck, C. E. Polyphthalaldehyde: Synthesis, Derivatives, and Applications. *Macromol. Rapid Commun.* **2018**, *39* (2), na.

(20) Rathore, A.; Pollentier, I.; Kumar, S. S.; De Simone, D.; De Gendt, S. Feasibility of unzipping polymer polyphthalaldehyde for extreme ultraviolet lithography. *Journal of Micro/Nanopatterning, Materials, and Metrology* **2021**, *20* (03), na.

(21) Deng, J.; Bailey, S.; Ober, C. Scissionable polymer photoresist for EUV lithography. *SPIE* **2022**, *12055*, na.

(22) Deng, J.; Bailey, S.; Jiang, S.; Ober, C. K. High-Performance Chain Scissionable Resists for Extreme Ultraviolet Lithography: Discovery of the Photoacid Generator Structure and Mechanism. *Chem. Mater.* **2022**, *34* (13), 6170−6181.

(23) Deng, J.; Kaefer, F.; Bailey, S.; Otsubo, Y.; Meng, Z.; Segalman, R.; Ober, C. K. New Approaches to EUV Photoresists: Studies of Polyacetals and Polypeptoids to Expand the Photopolymer Toolbox. *J. Photopolym. Sci. Technol.* **2021**, *34* (1), 71−74.

(24) Martin, C. J.; Rapenne, G.; Nakashima, T.; Kawai, T. Recent progress in development of photoacid generators. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2018**, *34*, 41−51.

(25) Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. Acid formation and deprotection reaction by novel sulfonates in a chemical amplification positive photoresist. *Chem. Mater.* **1990**, *2* (3), 299−305.

(26) Lopez de Pariza, X.; Cordero Jara, E.; Zivic, N.; Ruipérez, F.; Long, T. E.; Sardon, H. Novel imino- and aryl-sulfonate based photoacid generators for the cationic ring-opening polymerization of ε-caprolactone. *Polym. Chem.* **2021**, *12* (28), 4035−4042.
(27) Grzeskowiak, S.; Narasimhan, A.; Rebeyev, E.; Joshi, S.; Brainard, R. L.; Denbeaux, G. Acid Generation Efficiency of EUV PAGs via Low Energy Electron Exposure. *J. Photopolym. Sci. Technol.* **2016**, *29* (3), 453−458.
(28) Kanai, Y.; Wang, X.; Selloni, A.; Car, R. Testing the TPSS meta-generalized-gradient-approximation exchange-correlation functional in calculations of transition states and reaction barriers. *J. Chem. Phys.* **2006**, *125* (23), 234104.
(29) Grimme, S.; Hansen, A. A Practicable Real-Space Measure and Visualization of Static Electron-Correlation Effects. *Angew. Chem., Int. Ed.* **2015**, *54* (42), 12308−12313.
(30) Caldeweyher, E.; Bannwarth, C.; Grimme, S. Extension of the D3 dispersion coefficient model. *J. Chem. Phys.* **2017**, *147* (3), 034112.
(31) Caldeweyher, E.; Ehlert, S.; Hansen, A.; Neugebauer, H.; Spicher, S.; Bannwarth, C.; Grimme, S. A generally applicable atomic-charge dependent London dispersion correction. *J. Chem. Phys.* **2019**, *150* (15), 154122.
(32) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7* (18), 3297−3305.
(33) Kruse, H.; Grimme, S. A geometrical correction for the inter- and intra-molecular basis set superposition error in Hartree-Fock and density functional theory calculations for large systems. *J. Chem. Phys.* **2012**, *136* (15), 154101.
(34) Caldeweyher, E.; Mewes, J. M.; Ehlert, S.; Grimme, S. Extension and evaluation of the D4 London-dispersion model for periodic systems. *Phys. Chem. Chem. Phys.* **2020**, *22* (16), 8499−8512.
(35) Vydrov, O. A.; Van Voorhis, T. Nonlocal van der Waals density functional: the simpler the better. *J. Chem. Phys.* **2010**, *133* (24), 244103.
(36) Hujo, W.; Grimme, S. Performance of the van der Waals Density Functional VV10 and (hybrid)GGA Variants for Thermochemistry and Noncovalent Interactions. *J. Chem. Theory Comput.* **2011**, *7* (12), 3866−3871.
(37) Manouras, T.; Argitis, P. High Sensitivity Resists for EUV Lithography: A Review of Material Design Strategies and Performance Results. *Nanomaterials* **2020**, *10* (8), 1593.

https://doi.org/10.1021/acsmacrolett.2c00395