Synthesis and Properties of Diazopiperidiones for Use in Nonchemically Amplified Deep UV Photoresists

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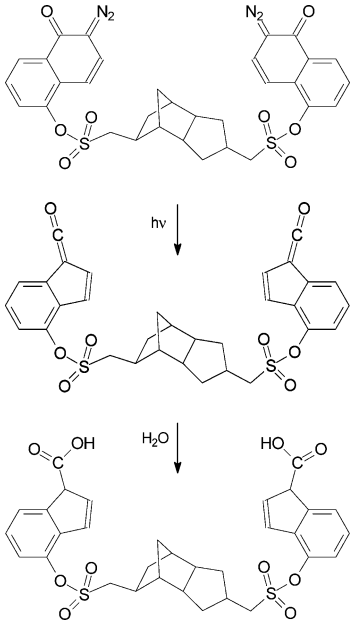
3-Diazopiperi-2,4-diones have been prepared and explored as photoactive substrates for microlithography. Michael addition of primary amines to methyl acrylate, followed by amidation with methyl malonate yielded amides that underwent base-catalyzed cyclization to the corresponding piperi-2,4-diones. The pendant esters of the resultant piperidiones were removed by hydrolysis and decarboxylation and diazotization was carried out by treatment with tosyl azide. The resulting 3-diazopiperi-2,4-diones absorb in the 240−260-nm spectral range, are readily soluble in common solvents, and undergo the Wolff rearrangement with high quantum yield upon exposure in the deep ultraviolet (DUV) (248−257 nm), affording ketenes that react with adventitious water to provide transparent, base soluble photoproducts. These characteristics make them ideal chromophores for the design of nonchemically amplified photoresists for use in the DUV. Bis-diazopiperidione derivatives prepared from 4,8-bis(chlorosulfonylmethyl)tricyclo[5.2.1.$0^{2,6}$]decane and a hydroxyl-functionalized 3-diazopiperi-2,4-dione yielded products that efficiently inhibit novolac dissolution in aqueous tetramethylammonium hydroxide and are therefore useful for formulating advanced resist materials.

Introduction

α-Diazoketones were utilized in early 365 nm (I-line) photolithography formulations because they successively undergo photolysis to the carbene, Wolff rearrangements to the ketene, and hydration to the carboxylic acid, effectively converting the aqueous base insoluble diazoketones into soluble carboxylic acids (Scheme 1).[1] This process of photoinduced solubility switching was the key to designing resist materials for many years. In "modern" photolithography, a polymer is used with pendant functional groups that undergo a chemical change when the resist formulation is exposed to the appropriate wavelength of light, altering the solubility of the exposed regions.[2] These systems function on the basis of acid-catalyzed thermolysis reactions. The catalytic nature of the thermolysis reaction provides high photosensitivity and is often referred to as "chemical amplification.[2]" In the more "classical" dissolution inhibition design, an additive (Figure 1), instead of the polymer itself, undergoes a photochemical reaction that alters the solubility of the bulk material. This design approach is particularly powerful because the solubility switches are small molecule additives, thus simplifying synthesis and optimization of the resist formulation.

Scheme 1. Photochemical Wolff Rearrangement of the Bis-diazonaphthoquinone, TNQ



Chemically amplified resists are useful for many applications because of their high sensitivity, but are also highly susceptible to airborne contamination, requiring establishment of a locally filtered environment. In certain applications, such as laser mask writing, there is no need for the high sensitivity of chemically amplified resist. Because the implementation of carbon-

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(1) Dammel, R. *Diazonaphthoquinone-Based Resists*; SPIE-The International Society for Optical Engineering: Bellingham, WA, 1993.
(2) MacDonald, S. A.; Willson, C. G.; Fréchet, J. M. J. *Acc. Chem. Res.* **1994**, *27* (6), 151.

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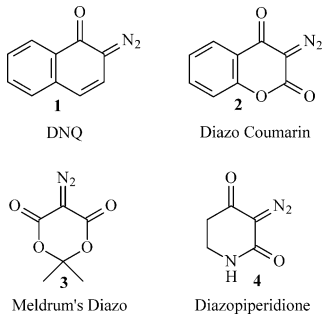


Figure 1. Chemical structure of some diazochromophores investigated for use as dissolution inhibitors.

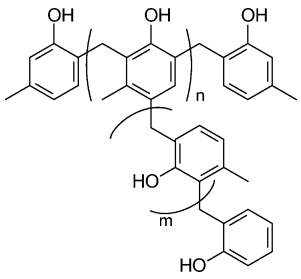


Figure 2. Cresol novolak.

filtered air is unnecessary and extremely expensive, nonchemically amplified resists offer an attractive alternative for these less-sensitive applications.

In an ideal nonchemically amplified system, the unexposed resist must be sparingly soluble in the appropriate developer, while the exposed resist must be freely soluble. The resin typically used, cresol-novolac (Figure 2), is soluble in aqueous base so the photoactive additive must be designed to reduce the solubility of the novolac resin before exposure, but readily solubilize the resist formulation after the photochemical transformation takes place. Effective photoactive additives have generally been constructed by attaching two photoactive chromophores to a central aliphatic polycyclic "ballast" via two linker groups (Scheme 1). We have recently demonstrated the utility of hydrogen-bond acceptor sites, such as carbonates and sulfonates, as the linker component in an efficient dissolution inhibitor.[3] It is thought that by hydrogen bonding with the phenolic functionalities, they strengthen the hydrogen-bonding network between the ortho−ortho linked cresol units, decreasing the solubility of the resin in basic solution (Figure 3).[3] However, once the inhibitor has been exposed, and its aqueous solubility enhanced, the resist material is rendered even more soluble than unadulterated novolac.

The manufacture of ever smaller, faster, and cheaper semiconductor devices requires the ability to print ever smaller features.[4] The minimum feature size resolved by the projection lens systems during microchip fabrication is directly proportional to the wavelength of light used; hence, continual reduction of the exposure wavelength has been a key contributor to improving the

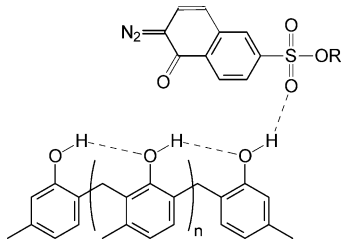


Figure 3. Observed dissolution inhibition is believed to rely upon hydrogen bonding between the ortho−ortho linkages of novolac and a Lewis base (sulfonate group).

resolution of the microlithographic process. The first resists used in production were exposed at 365 nm and the positive tone versions were based on cresol novolak polymer with diazonaphthoquinone (DNQ) **1**-based dissolution inhibitors. While successive generations of chemically amplified resists are being designed and optimized for 248 nm, 193 nm, and very recently 157 nm, dissolution inhibitors for comparable wavelengths have not been developed. The lack of dissolution inhibitor systems for these shorter wavelengths results from a deficiency of candidate inhibitor/resin pairs that meet the performance requirements while being transparent at these wavelengths. Because the diazonaphthoquinone chromophore and its photoproducts absorb strongly below about 300 nm,[5] the photochemical transformation cannot be carried out through the depth of the film, preventing its use in DUV lithography. Hence, any attempt to formulate a dissolution inhibitor-type resist in the DUV demands development of a new photoactive compound (PAC) that bleaches more effectively in the DUV spectral region, but otherwise functions like the diazoquinone-based PAC systems. We have been seeking such a substance for more than 20 years.

Investigations with PACs based on 3-diazocoumarin, **2**, yielded films with promising material properties and a significant reduction in the absorbance of the photoproducts in the DUV.[6] Although the ketene formed from photolysis of the coumarin yielded the expected soluble β-ketoacid, that in turn was thermally labile to decarboxylation which generates an insoluble product. Since baking after exposure is common practice, this side reaction, which reverses the solubility switch and prevents image generation in positive tone, renders this class of products unusable for standard processing.

Diazotized Meldrum's acid, **3**, is known to undergo Wolff rearrangement and its photoproducts have minimal absorbance in the DUV, but unfortunately diazomeldrum's acid is volatile and sublimes from the film during postexposure bake.[7] These unsatisfactory results inspired the design of a new chromophore, 3-diazopiperi-2,4-dione, **4**, which maintains the low absorbance of diazotized Meldrum's acid, but does not exhibit problematic volatility.[8] Unfortunately, simple alkyl and ether derivatives of 3-diazopiperi-2,4-dione are not efficient dissolution inhibitors. On the basis of new

(3) (a) Flanagin, L. W.; McAdams, C. L.; Hinsberg, W. D.; Sanchez, I. C.; Willson, C. G. *Macromolecules* **1999**, *32*, 5337. (b) McAdams, C. L.; Flanagin, L. W.; Henderson, C. L.; Pawloski, A. R.; Tsiartas, P.; Willson, C. G. *Proc. SPIE Int. Soc. Opt. Eng.* **1998**, *3333*, 1171. (c) This subject is addressed in further detail in: McAdams, C. L. Ph.D. Thesis, University of Texas, Austin, 2000.

(4) Moore, G. *Proc. SPIE Int. Soc. Opt. Eng.* **1994**, *2438*, 2.

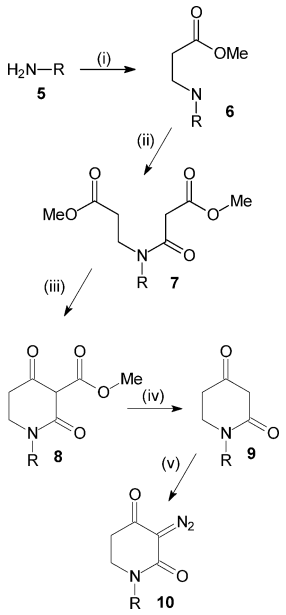
(5) In deep UV, bis-functional tricyclo diazonaphthoquinone (TDQ) shows an absorbance of 1.2 μ^{-1} after exposure.

(6) Leeson, M. J.; Yueh, W.; Tattersall, P. I.; Pawloski, A.; Grayson, S. M.; Willson, C. G. **2004**, *16*, 1763−1769.

(7) Grant, B. D.; Clecak, N. J.; Twieg, R. J.; Willson, C. G. *IEEE Trans. Electron Devices* **1981**, *28* (11), 1300.

(8) Willson, C. G.; Miller, R. D.; McKean, D. R.; Pederson, L. A. *Proc. SPIE Int. Soc. Opt. Eng.* **1987**, *771*, 2.

Scheme 2. (a) R = $CH'_2CH_2CH_2CH_3$, (b) R = $CH_2CH_2OCH_3$, (c) R = $CH_2CH_2SCH_3$, and (d) R = Adamantyl; (i) Methylacrylate, (ii) Dimethyl Malonate, (iii) NaOMe or K_2CO_3/18-crown-6, (iv) $HCl_{(aq)}/CH_3CN$ or CH_3CN/H_2O, and (v) Tosyl Azide, NMM



understanding of the mechanism of dissolution inhibition, we have now adapted this chemistry to the design of a functional dissolution inhibitor. The synthesis and photocharacterization of this new family of PACs will be described, as well as the results of initial dissolution inhibition studies.

Results and Discussion

Synthesis of Model Compound. To evaluate the properties and optimize the synthesis of the diazopiperidione-based photoactive solubility switches, the synthesis of a model compound (Scheme 2) was attempted from butylamine, **5a.** The first step, involving the Michael addition of the methyl acrylate, was performed by slow addition of the olefin to a solution of the primary amine in methylene chloride. The reaction was carried out at 0 °C for only a few hours to prevent a second Michael addition to the amine and the product, **6a**, was purified by distillation under reduced pressure.[9] Addition of the malonate group by reaction of **6a** with methyl malonyl chloride or by 1,3-dicyclohexylcarbodiimide coupling with the corresponding free acid failed to produce the amide, **7a**, in satisfactory yield. However, condensation with dimethyl malonate at 160 °C for 2−3 h afforded the amide in a 95% yield after the excess malonate was removed by distillation.

The Dieckman cyclization of **7a** to yield the six-membered heterocycle was achieved by base catalysis. Treatment with sodium methoxide in refluxing methanol afforded **8a**[10] but better yields were obtained by slow addition of the acylic amide in toluene to a refluxing solution of 18-crown-6 and potassium carbonate in toluene. The reaction took place over a 6−8-h period with yields of 90%. The best route for removal of the methyl ester involved heating the material in aqueous acetonitrile for 1 h, which after hydrolysis of the ester, and decarboxylation of the corresponding acid, yielded **9a**.[11] These neutral conditions afforded the piperidione without the aldol byproducts that were observed during the acid-catalyzed reaction.

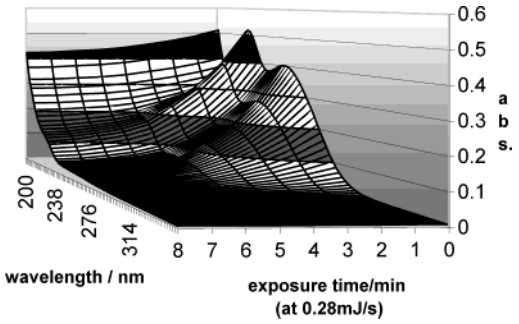


Figure 4. Deep UV bleaching curve of the 3-diazo piper-2,4-dione chromophore.

Diazotization of the piperidione unit using tosyl azide[12] afforded the model PAC, **10a**. The diazopiperidione could be obtained in high yields after purification by column chromatography. UV spectroscopy verified exceptionally low absorbances (<0.05) at 257 nm after DUV exposure (Figure 4). The quantum efficiency of the diazopiperidione at this wavelength is 0.3. The synthesis of related model compounds **10b**−**d** was also achieved starting from 2-methoxy ethylamine, 2-methylthioether-ethylamine, and adamantylamine, but none of these derivatives are efficient dissolution inhibitors.

Synthesis of Dissolution Inhibitor Candidate, 21. After confirming the appropriate photochemistry with the diazopiperidione model compound, the synthesis of dissolution inhibitor analogues was investigated. The traditional I-line chromophore, DNQ, is not a useful dissolution inhibitor without further modification. However, attaching two such chromophores to a polycyclic linker (Scheme 1) produces a photoactive molecule that was used widely in I-line resists.[13] This PAC is derived from the reaction of bis-hydroxymethyl tricyclodecane and the sulfonyl chloride of DNQ. The tricyclic "linker", or ballast group, consists of a mixture of exo/endo isomers affording the PAC with amorphous characteristics that inhibit crystallization and improve solubility. In addition, the rigid cyclic structure prevents intramolecular interactions between the two photoactive chromophores. Empirically, it has been shown that the proximity of sulfonate and chromophore moieties in the PAC plays a significant role in dissolution inhibition. In light of these previous discoveries, a target structure was envisioned with two of the new chromophores attached via sulfonate linkers to a polycyclic core.

The bis-sulfonate linker was derived from commercially available 4,8-bis(hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]-decane). The most efficient preparation of the bis-

(9) Arbuzov, B. A.; Erastov, O. A.; Remizov, A. B.; Nikanova, L. Z. *Chem. Heterocycl. Compd*. (Engl. Transl.) **1969**, *5*, 730.

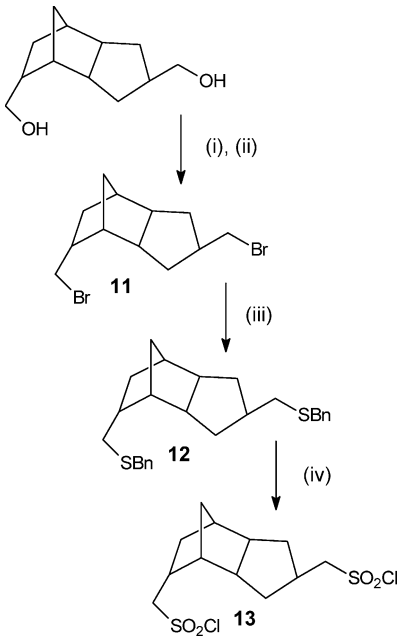
(10) The methyl analogue was prepared by an analogous route by Schultz, A. G.; Lucci, R. D.; Napier, J. J.; Kinoshita, H.; Ravichandran, R.; Shannon, P.; Ying, Y. K, *J. Org. Chem*. **1985**, *50* (2), 217.

(11) The *tert*-butyl analogue has been prepared via an alternative route: Oda, R.; Miyanoki, M.; Okano, M. *Bull. Chem. Soc. Jpn*. **1962**, *35*, 1843.

(12) Tosyl azide was freshly prepared from sodium azide and tosyl chloride and in all cases the materials could be handled safely at room temperature.

(13) Clecak, N. J.; McKean, D. R.; Miller, R. D.; Tompkins, T. C.; Twieg, R. J.; Willson, C. G. U.S. Patent 4397937, 1983.

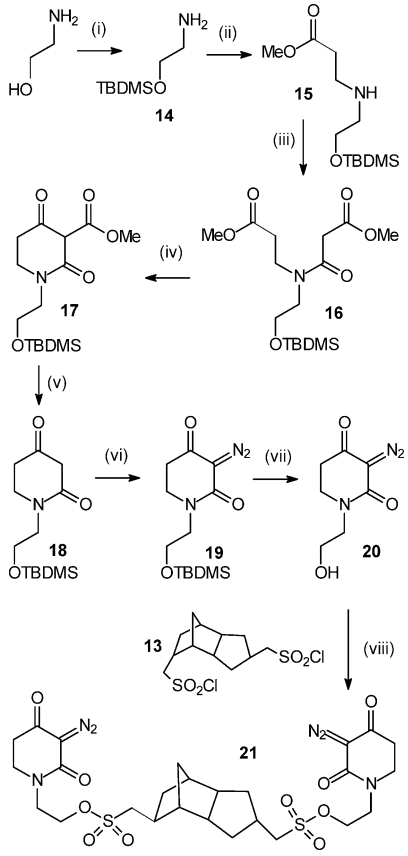
Scheme 3. (i) $TsCl/Et_3N$, (ii) $LiBr/Me_2CO$, (iii) $NaOEt/BnSH$, and (iv) $AcOH_{(aq)}/Cl_2$



sulfonyl chloride (Scheme 3) involved first tosylation of the diol with tosyl chloride and then conversion to the bis-bromide, **11**, using lithium bromide.[14] Addition of the bis-bromide to benzylthiolate led to nearly quantitative formation of the bis-thioether, **12**. Oxidation by bubbling chlorine gas through a solution of the thioether in aqueous acetic acid produced the bis-sulfonyl chloride. Following workup, the benzyl chloride byproduct was removed by distillation under reduced pressure and the crude product was purified by column chromatography to afford the bis-sulfonyl chloride, **13**, in a 73% yield.

The diazopiperidione groups that were attached to the bis-sulfonate ballast group were synthesized from *tert*-butyldimethylsilyl ether (TBDMS) protected[15] 1-amino-2-hydroxy ethane, **14** (Scheme 4). Selective protection of the alcohol group was achieved by reaction with *tert*-butyldimethylsilyl chloride and imidazole in 87% yield. The optimized conditions for the Michael addition involved adding methyl acrylate dropwise over a period of 1 h at 0 °C and then removing the reaction mixture from the ice bath and allowing it to be stirred for an additional 18 h. The crude mixture of **15** contained an appreciable amount of bis-substituted material and was purified by column chromatography in 56% yield. The condensation reaction between the amine and dimethyl malonate provided **16** in almost quantitative yields. Cyclization with the potassium carbonate and 18-crown-6 ether followed by heating in aqueous acetonitrile afforded the protected piperidione, **18**. Reaction of **18** with tosyl azide and *N*-methylmorpholine followed by deprotection with 48% HF (aqueous) afforded the hydroxyl-functionalized photoactive compound, **20**. The inhibitor candidate, **21**, could then be prepared by reaction between the bis-sulfonyl chloride **13** and 2

Scheme 4. (i) $TBDMSCl/Et_3N$, (ii) Methyl Acrylate, (iii) Dimethylmalonate, (iv) K_2CO_3/18-crown-6, (v) CH_3CN/H_2O, (vi) TsN_3/NMM, (vii) $HF_{(aq)}/CH_3CN$, and (viii) NMM



equiv of **20**. *N*-methyl morpholine was used as a base and the reaction was stirred for 18 h at 0 °C. Purification by column chromatography led to decomposition of the material, so it was extracted with dichloromethane, washed with 1 M HCl and brine, dried over $MgSO_4$, and used without further purification.

UV spectrometer studies demonstrated that the new PAC did bleach well, showing little absorbance over the range of the DUV after exposure; however, it demonstrated poor dissolution inhibition of novolac.[16] This surprising and distressing result is believed to result from rapid base decomposition of the unexposed inhibitor via displacement or elimination of the sulfonate. To circumvent this proposed side reaction, a second PAC candidate was designed that incorporated a phenolic sulfonate linkage.[17]

Synthesis of Dissolution Inhibitor Candidate, 30. The new target molecule (PAC 2), **30**, was synthe-

(14) This bis-chloride analogue has been prepared by decomposition of the corresponding bis-chloroformate: Richter, R.; Tucker, B. *J. Org. Chem.* **1983**, *48* (15), 2625.

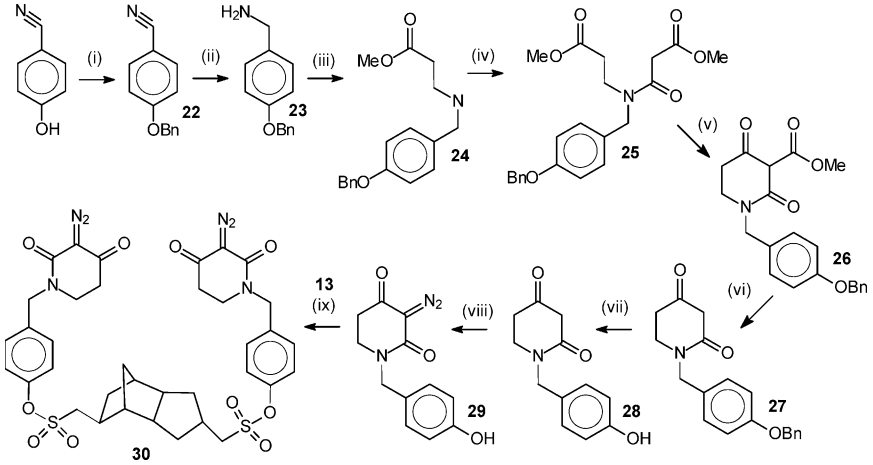
(15) The trimethylsilyl protecting group was used during initial investigations, but exhibited cleavage during later steps in the synthesis.

(16) Novolac resin was used as the polymer for dissolution inhibition studies, even though it is not completely transparent at 248 nm because suitably transparent polymers were not available at the time of this study. Since this study, fluorinated poly(norbornanes) have been demonstrated as a suitable resist material at wavelengths as low as 157 nm: Tran, H. V.; Hung, R. J.; Chiba, T.; Yamada, S.; Mrozek, T.; Hsieh, Y.-T.; Chambers, C. R.; Osborn, B. P.; Trinique, B. C.; Pinnow, M. J.; MacDonald, S. A.; Willson, C. G. *Macromolecules* **2002**, *35* (17), 6539.

(17) It has also been found that with the sulfonate linkage conjugated with an aryl substituent, the photoproducts absorb strongly in the DUV, but when the linkage is reversed, the aryl sulfonate ester is virtually transparent. McAdams, C. L. Ph.D. Thesis, University of Texas, Austin, 2000.

(18) Kaplan, M.; Meyerhofer, D. *Polym. Eng. Sci.* **1980**, *20*, 1073.

Scheme 5. (i) $BnCl/K_2CO_3/KI$, (ii) $LiAlH_4/AlCl_3$, (iii) Methyl Acrylate, (iv) Dimethylmalonate, (v) K_2CO_3/18-crown-6, (vi) CH_3CN/H_2O, (vii) $H_2/Pd/C$, (viii) TsN_3/NMM, and (ix) NMM



sized in a fashion similar to the previous examples, using 4-benzyloxybenzylamine, **23** (Scheme 5). The primary amine was prepared in an overall 87% yield by benzyl protection of *p*-hydroxybenzonitrile followed by reduction of the nitrile unit with lithium aluminum hydride in the presence of aluminum chloride. Michael addition with methyl acrylate afforded the secondary amine in 66% yield after purification by silica gel column chromatography. Amidation with methyl malonate, followed by the base-catalyzed cyclization, yielded the piperidione, **26**. Hydrolysis and decarboxylation of the pendant ester was achieved as before by heating in aqueous acetonitrile, and the piperidione, **27**, could be purified by recrystallization in a 64% yield. The reductive deprotection of the benzyl group had to be carried out before diazotization. If the reduction was attempted at pressures above 80 psi, reduction of the piperidione ring occurred, but when carried out at 30 psi, the hydroxyl-functionalized product could be isolated by filtration in a 98% yield. Finally, diazotization with tosyl azide using *N*-methylmorpholine gave the PAC, **29**, in 56% yield after chromatographic purification. The bissulfonyl chloride, **13**, was functionalized with this new phenolic chromophore using 2 equiv of **29**, and *N*-methyl morpholine as a base. After 18 h of reaction at 0 °C the second candidate, **30**, was purified by column chromatography in 96% yield and investigated as a dissolution inhibitor.

The photoproductsof **30** demonstrated excellent transparency; and the aryl sulfonate linkages exhibited increased stability over that of **21** both during chromatography and during film development. These materials demonstrate excellent dissolution inhibition properties when incorporated into novolac resists.[16] With incorporation of 0.5 *m* diazopiperidione, **30**, the novolac dissolution rate when unexposed to 257-nm radiation was 0.1 nm/s, while the dissolution rate was increased significantly to 300 nm/s after exposure at 257 nm yielded the expected chemical transformation (Figure 5). This magnitude of discrimination between dissolution rates of resist before and after UV exposure is at least as high as that of traditional novolac-DNQ systems, making this an attractive system for practical application. Studies are presently underway to investigate the use of related chromophores with other acidic polymers for use at lower wavelengths.

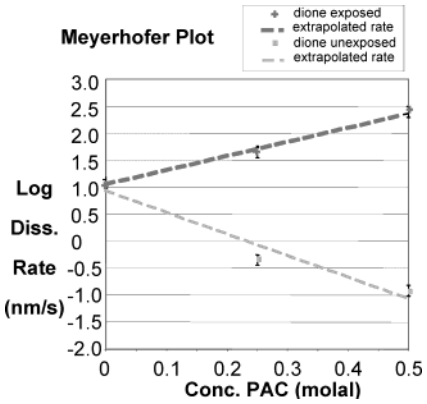


Figure 5. Meyerhofer plot[18] illustrating the difference in solubility between exposed and unexposed resist as a function of PAC dose.

Conclusions

In conclusion, a variety of new N-functionalized diazopiperidiones have been prepared. These compounds readily undergo photolysis to produce soluble acidic products that are transparent at the DUV wavelengths, making them ideal chromophores for 248-nm lithography. Attachment of these chromophores to a tricyclic alkane with sulfonate linkages provided candidate compounds for functional testing. When an appropriately designed phenolic sulfonate linkage was employed, the new PACs performed in a manner exactly analogous to the DNQ-based PACs, but they bleach very effectively in the deep UV. The new DUV PAC, **30**, and analogues thereof, are being formulated with a variety of acidic polymers to produce valuable imaging materials.

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Supporting Information Available: Experimental procedures and full characterization for all compounds discussed (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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