Harnessing entropic and enthalpic contributions in a negative tone chemically amplified molecular resist

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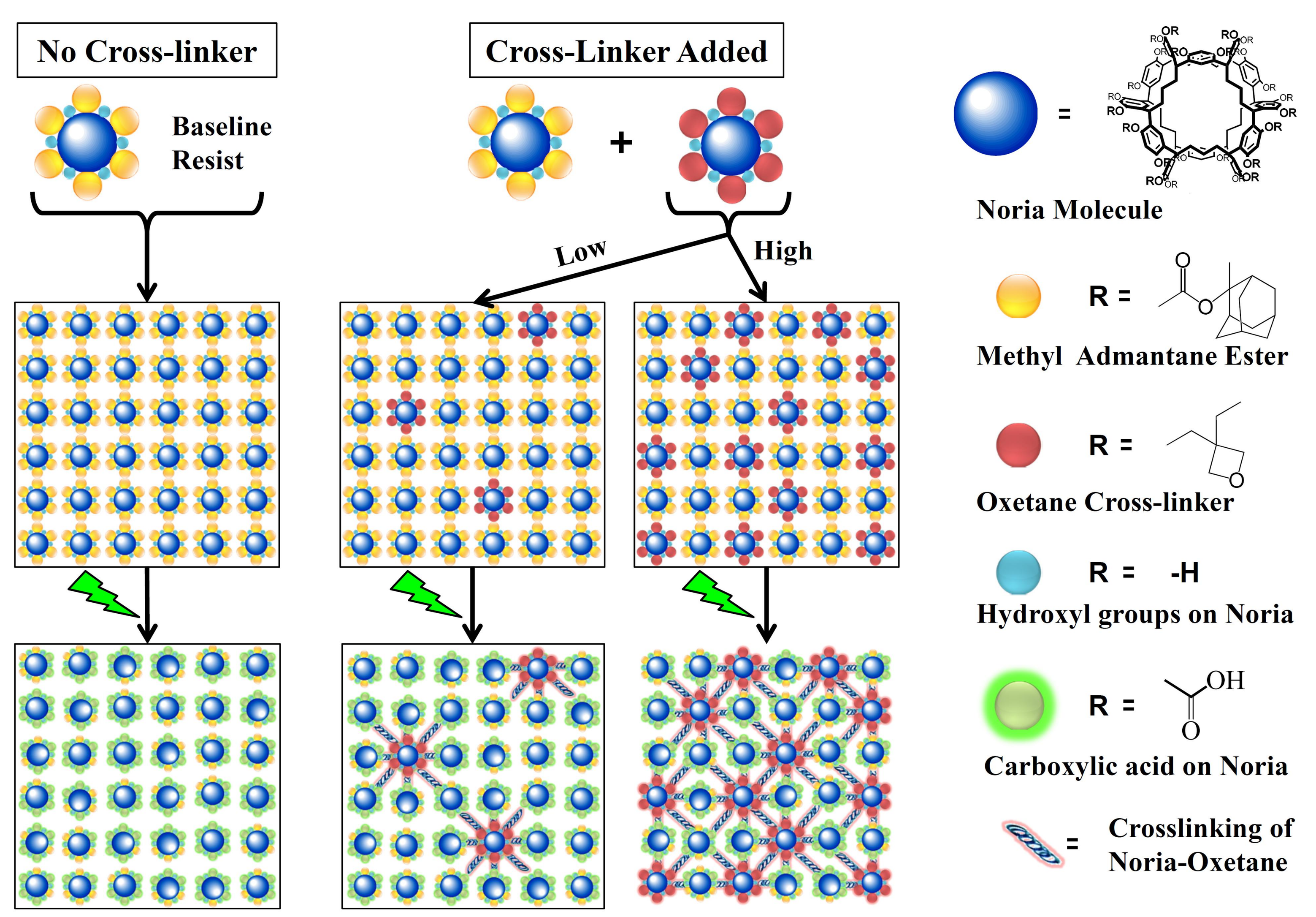
1. Introduction

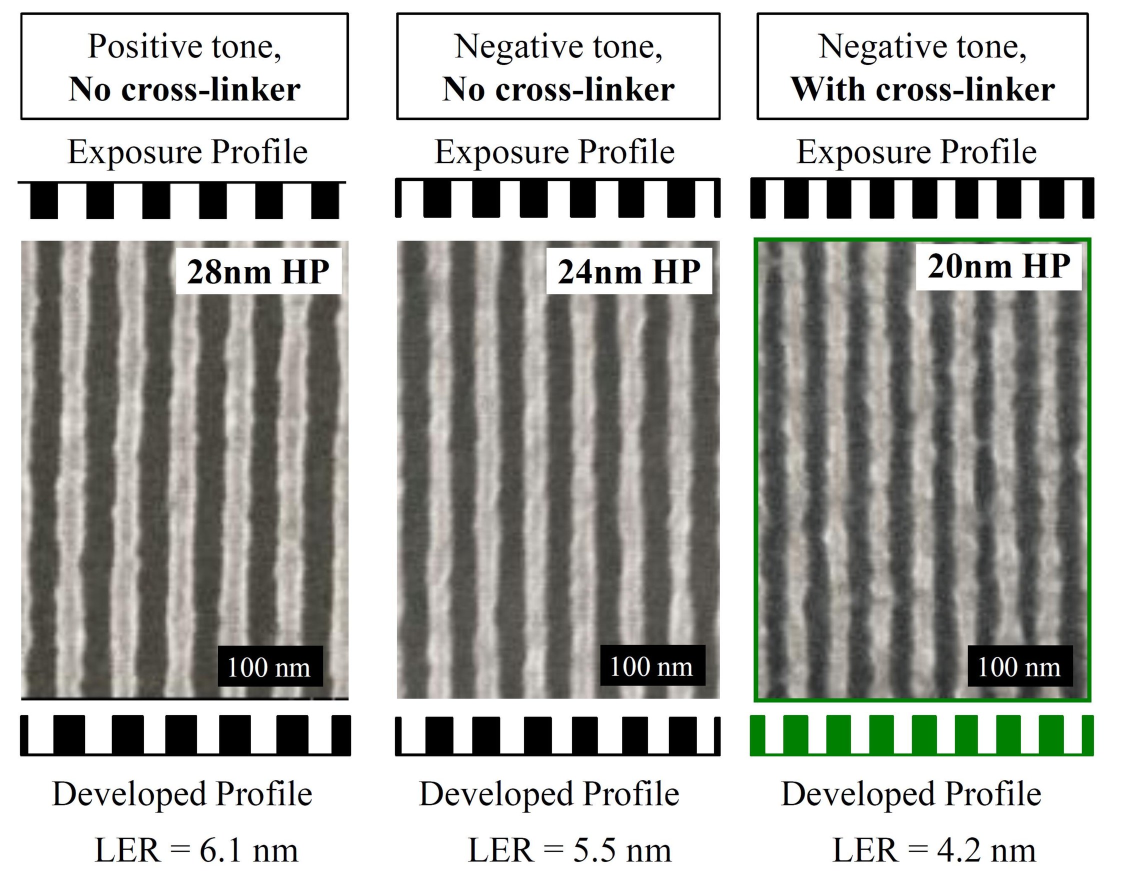
Historically, resists are designed so that chemical changes induced by the radiation emphasize either an enthalpic or an entropic contribution to dissolution. These two types of chemistries are accompanied with a trade-off between sensitivity and resolution. For instance, in the ubiquitous "chemically amplified resists", enthalpic interactions dominate --incident radiation generates acid that catalyzes ester deprotection to change the resist solubility. One acid can catalyze many deprotections to "amplify" the reaction and improve the sensitivity. Unfortunately, acid diffusion beyond the radiation front can degrade resolution and line edge roughness (LER). In non-chemically amplified resists, entropic interactions dominate. Incident radiation modifies the resist molecular weight, either via beam induced decomposition or cross-linking. Molecular weight reductions increase the entropy of dissolution while cross-linking has the opposite effect. Lacking diffusion of a catalyst, as in chemically amplified resists, these systems have higher resolution and lower LER. The cross-linking systems can increase mechanical stability by increasing the modulus if this increase is not accompanied by excessive swelling during development. Generally, non-amplified systems have poor sensitivity.

In this work, we design a new material which synergizes enthalpic and entropic contributions to improve dissolution and mechanical properties for higher resolution and better LER while retaining high sensitivity. Our approach is to start with a small molecule resist matrix which uses chemically amplified deprotection and add a dilute cross-linker.



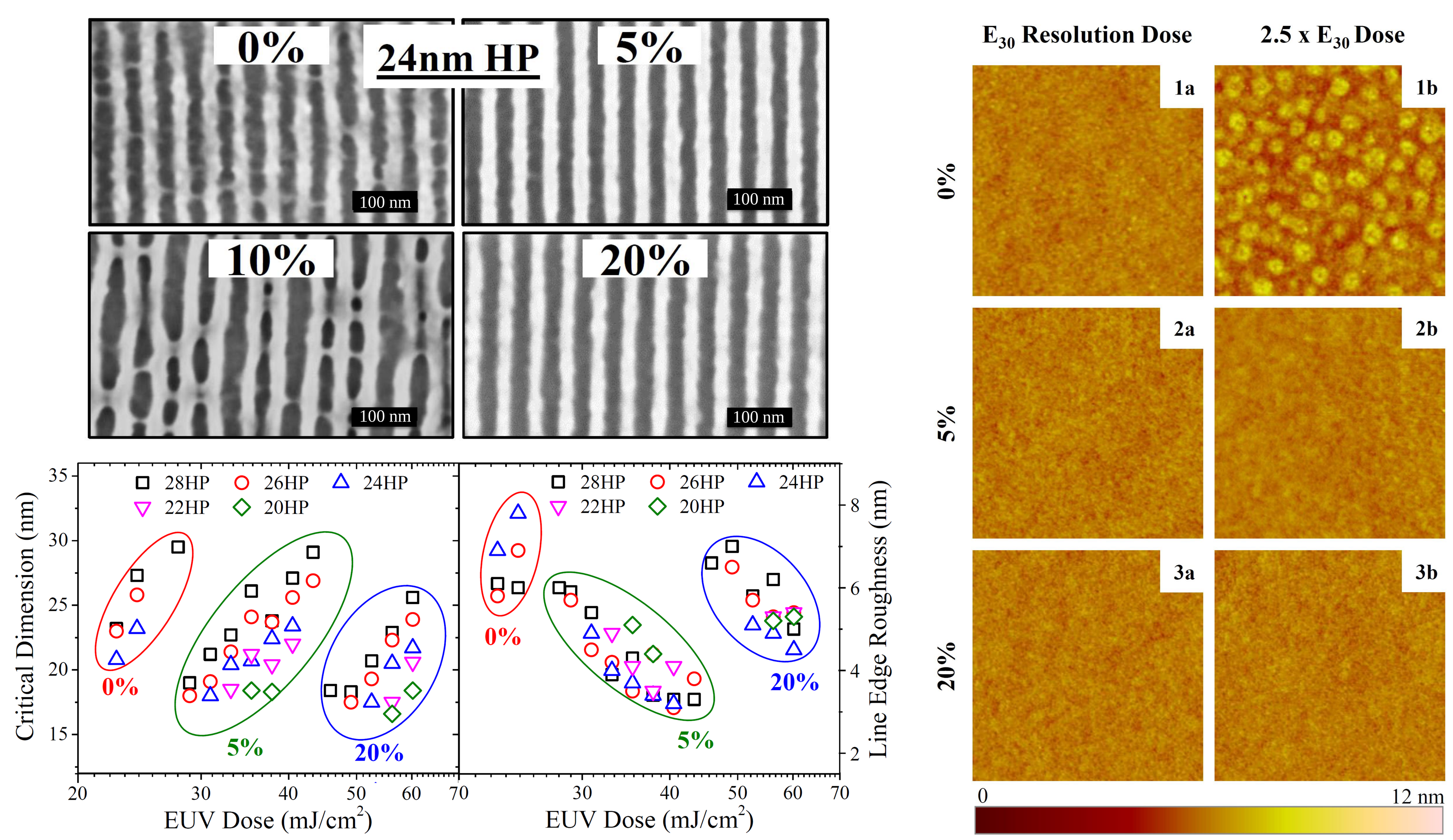
Schematic of the extent of photo-catalyzed cross-linking in our new material. we started with the small molecule, Noria, a ladder-like cyclic resist from the Nishikubo group and used methyl adamantane esters for chemical amplification and oxetane as a cross linking agent.

2. Developer Optimization



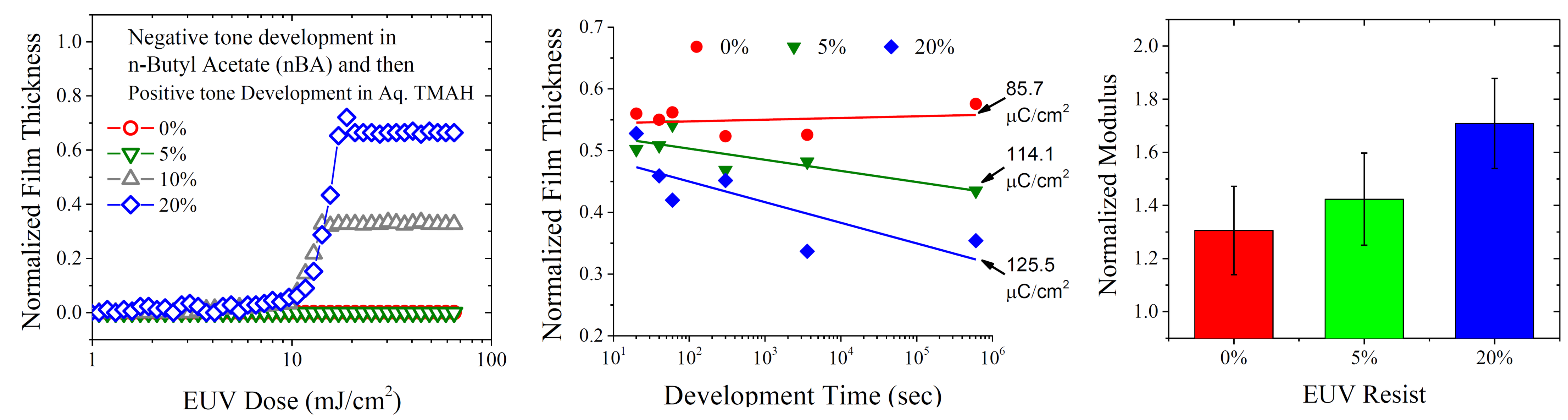
Optimization of developer chemistry increased resolution and lowered LER for negative tone compared to positive tone. Cross-linker significantly improved resolution and LER.

3. Islands of Resolution



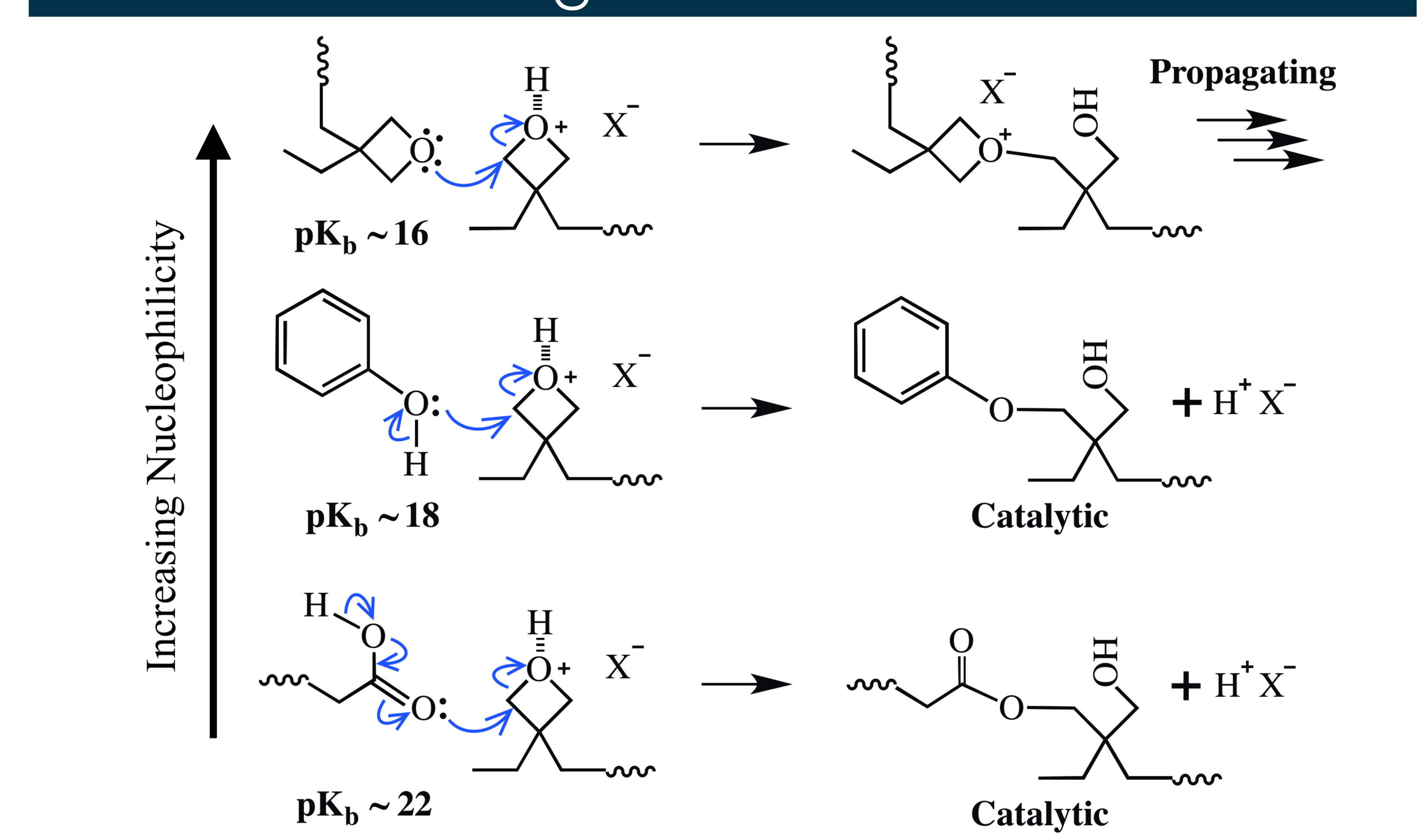
Both 5% and 20% Noria-oxetane concentrations improve performance while 10% swells badly causing webbing and pattern collapse. The process window is also significantly increased for 5% and 20% Noria-oxetane concentrations. The high resolution and low LER improved the Z-factor by 6 and 2 over Noria-MAd respectively. AFM imaging also revealed segregation of material after bake at high dose while the oxetane samples had reduced material diffusion.

4. Oligomerization not highly crosslinked network is preferable



Negative tone development followed by positive tone development removes all but the crosslinked material revealing that the 5% oxetane material only oligomerizes and does not form a crosslinked network. However the oligomerized material still traps unreacted material as shown by the thickness decrease with extended development times. The crosslinking increases the material modulus but the stiffness increase is modest and does not account for the improved patterning performance. Instead the solubility contrast from both enthalpic and entropic components enhances patterning.

5. Crosslinking reactions are favored



The low pK_b of oxetane increases the probability of acids residing on the oxetane moiety. Cross linking reactions regenerate the acid.

6. Conclusion

We demonstrated a blended resist system with higher performance by combining enthalpic and entropic contributions to solubility contrast. The key is to work in a dilute cross-linking regime, not previously studied, to synergize the enthalpic and entropic effects. Light cross-linking allows a high level of deprotection, reducing swelling, but still acts to inhibit phase segregation in the material and improve diffusion and dissolution properties.

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