

Peptoid Photoresists with Precisely Controllable Length and Composition

CNF Project Number: 2733-18

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Primary CNF Tools Used: ASML 300C DUV stepper, Woollam RC 2 ellipsometer, JEOL 6300 e-beam

Abstract:

Here we present the synthesis of peptoid with precisely controllable length and composition. Peptoids were synthesized using an automated peptide synthesizer. The 10-mers were purified and protecting groups serving as solubility switches were introduced. MALDI-TOF mass spectrometry was applied to characterize the peptoid structure and molar mass. The photolithographic performance was investigated by DUV and e-beam exposures resulting in a line-space pattern of 1 μm and 50 nm, respectively.

Summary of Research:

Introduction. Today's widely used polymeric resists are typically based on random copolymers. These polymers are polydisperse and relatively large, with molar masses ranging from 5,000-15,000 g/mol [1]. Characteristics such as these can affect resist performance, and therefore it is necessary to explore other architectures for new resist platforms. For sequence-controlled polymers, on the other hand, the monomers are arranged in a specific, user-defined order. Monomer sequence regularity strongly influences the molecular, supramolecular, and macroscopic properties of polymer materials, showing promise for the creation of a new type of small molecule photoresist. In this respect, peptoids represent a particularly advantageous group, since they can be specifically varied in their structure, length and sequence of the amines used [2].

Peptoid Synthesis. A solid-phase peptoid synthesis approach using a 2-chlorotrityl based resin was used [3]. The bromoacetylation step was carried out by adding bromoacetic acid (BAA) in DMF and N, N-diisopropylethylamine (DIPEA) to the resin. The resin was then washed repeatedly with DMF. Amination was performed by reacting the acylated resin with the amine in DMF. After cleaving, protecting, and purifying using preparative high-pressure liquid chromatography (HPLC), the peptoids were characterized using MALDI-TOF mass spectrometry, see Figure 1.

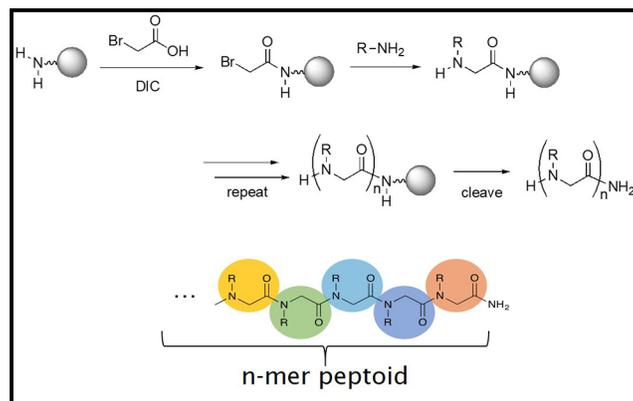


Figure 1: Synthesis and characterization of peptoid photoresists with precisely controllable molecular structure.

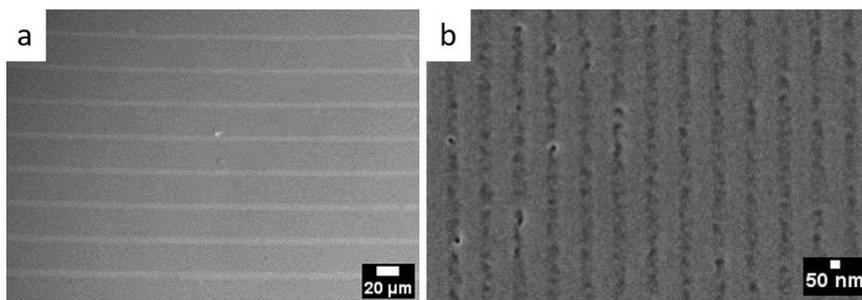


Figure 2: (a) Line pattern measured using scanning electron microscopy; (a) after DUV exposure on an ASML PAS 5500/300C DUV wafer stepper ($\sim 40 \text{ mJ/cm}^2$), feature size $1 \mu\text{m}$, (b) after exposure on a JEOL 6300 to $75 \mu\text{C/cm}^2$ e-beam radiation. The feature size is 50 nm .

Characterization and Results. Herein we design peptoids that incorporated side chains with a variety of chemical moieties serving functions such as adhesion to the underlying substrate, etch resistance, and solubility switching. Precisely sequence control allowed us to probe not only the optimal composition of the aforementioned moieties but also their order in the peptoid. As the peptoids examined were 10-mers, the structure of the side chains was also carefully chosen to avoid crystallization and tune the glass transition temperature. Protecting groups serving as solubility switches were selected with the goal of groups that possessed a high radical cation acidity, a property that is previously shown to correlate closely with the sensitivity of EUV resists. First DUV photolithography and electron beam exposures of the synthesized 10-mers are showing defined line patterns, see Figure 2.

Conclusions and Future Steps:

Sequence-controlled peptoids with different sequences and compositions of the used amines have been successfully synthesized and the performance as a positive tone photoresist was evaluated performing DUV and e-beam exposures.

While these initial results show the potential of peptoids as photoresist materials, the ongoing research is still at an initial stage. In the future, the length, sequence as well as the effect of different site moieties on the photolithographic performance will be investigated.

References:

- [1] Patterson, K.; Yamachika, M.; Hung, R.; Brodsky, C.; Yamada, S.; Somervell, M.; Osborn, B.; Hall, D.; Dukovic, G.; Byers, J.; Conley, W.; Willson, C. G., Polymers for 157-nm photoresist applications: a progress report. SPIE: 2000; Vol. 3999.
- [2] Gangloff, N.; Ulbricht, J.; Lorson, T.; Schlaad, H.; Luxenhofer, R., Peptoids, and Polypeptoids at the Frontier of Supra- and Macromolecular Engineering. *Chemical Reviews* 2016, 116 (4), 1753-1802.
- [3] Culf, A. S.; Ouellette, R. J., Solid-phase synthesis of N-substituted glycine oligomers (alpha-peptoids) and derivatives. *Molecules* (Basel, Switzerland) 2010, 15 (8), 5282-5335.

Controlling the Crystallite Size Distribution of Metal Organic Frameworks (MOFs) Using Base-Mediated Equilibrium Dynamics

CNF Project Number: 2763-19

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Primary CNF Tools Used: Dynamic Light Scattering: Malvern Nano ZS Zetasizer and Malvern NS300 NanoSight

Abstract:

Metal-organic frameworks (MOFs) are crystalline, porous materials with potential applications ranging from gas separations to catalysis. However, the synthesis of MOFs remains a “black box” — which makes it challenging to prepare frameworks with controlled crystallite size distributions. Generally, MOFs are prepared from the conjugate acid of the organic “linker” combined with a metal precursor and a source of base to deprotonate the acid. This is most commonly achieved using the decomposition of the solvent *N,N*-dimethylformamide (DMF). However, we hypothesized that the slow addition of base could instead be achieved simply by adding base slowly via syringe pump to a reaction mixture.

We have found indeed that the crystallinity of MOFs, specifically the framework Zn-MOF-74, can be improved by adding organic base slowly to the reaction mixture (Figures 1 and 2).

Summary of Research:

The improvement in crystallinity could be observed by powder X-ray diffraction and scanning electron microscopy (not shown). We attempted to further support our findings using the dynamic light scattering (DLS) instruments available at CNF, specifically the Malvern Nano ZS Zetasizer. However, the prepared MOFs were found to form unstable colloids in all tested media (including water and organic solvents), and thus did not yield meaningful data despite numerous attempts (Figure 3).

Unfortunately, the MOFs were also found to rapidly settle from solution, which also negatively impacted the DLS measurements. As such, we have abandoned DLS measurements at CNF for the time being.

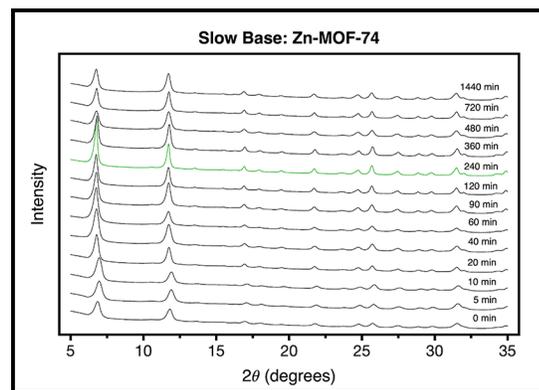


Figure 1: Powder X-ray diffraction patterns of Zn-MOF-74 prepared at a range of base addition times.

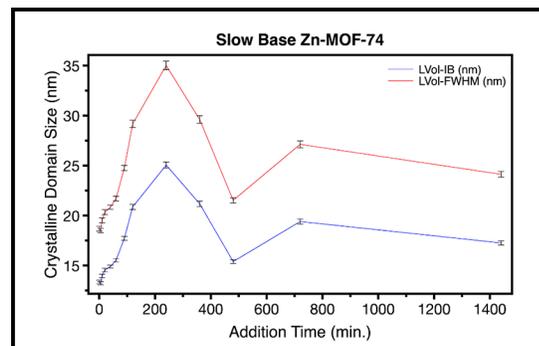


Figure 2: Average crystalline domain sizes of Zn-MOF-74 crystallites prepared by slow addition of base.

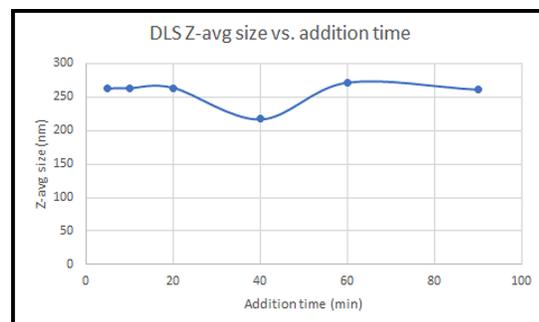


Figure 3: Attempted DLS measurements of MOFs, which yielded unmeaningful results.

