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# UV-Patterning of Ion Conducting Negative Tone Photoresists Using Azide-Functionalized Poly(Ionic Liquid)s

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S *Supporting Information*

ABSTRACT: The patterning of solid electrolytes that builds upon traditional fabrication of semiconductors is described. An azide-functionalized poly(1,2,3-triazolium ionic liquid) is used as an ion conducting negative tone photoresist. After UV-irradiation through an optical mask, micron-scaled, patterned, solid polyelectrolyte layers with controlled sizes and shapes are obtained. Furthermore, alkylation of poly(1,2,3-triazole)s can be generalized to the synthesis of poly(ionic liquid)s with a tunable amount of pendant functionalities.
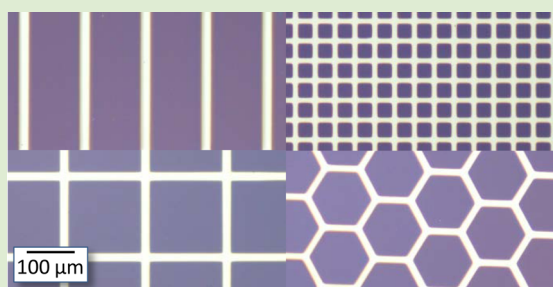
The recent emergence of poly(ionic liquid)s (PILs) has opened attractive alternatives to liquid electrolytes in applications such as batteries, sensors, actuators, solar cells, or catalysis.[1] At the expense of slightly reduced ionic conductivity, the superior mechanical properties of PILs enable enhanced processing and durability, but also the possibility to combine different properties through macromolecular engineering. Recent achievements in the field of PILs have reached the control over size and morphology of nanostructured ion conducting materials,[2−4] as well as the precision synthesis of ion conducting diblock copolymers.[5−9] Self-assembly of the latter into nanoscale morphologies with controlled features have afforded a large area of possibilities for optimizing ionic conductivities as well as mechanical properties.

In addition to self-assembled materials, important efforts are being devoted to the incorporation of (quasi-)solid electrolytes in the fabrication of organic devices, such as dye-sensitized solar cells,[10,11] electrochromic devices,[12,13] supercapacitors,[14] batteries,[15] electrolyte-gated transistors,[16−19] or flexible displays,[20] directly on a chip or on flexible substrates. Although, in the above-mentioned devices, thin layers of semiconductors or metals are classically patterned at the micron scale with various techniques, patterned ion gels are generally deposited with less precise techniques such as transfer printing,[21] spray-coating,[22] or aerosol jet printing.[23] In these examples, the combination of ionic liquids with polymers provides ion gels with mechanical performances suitable for device processing.

To precisely pattern solid electrolytes using traditional methods of the semiconductor industry, we have designed an UV-cross-linkable PIL that can be used as a negative tone photoresist. Only a few approaches for the postpolymerization cross-linking of PILs bearing functional groups have been previously reported for the formation of ionic gels[24] or thermal cross-linking in the bulk.[25] Besides, Long et al. have studied the UV-cross-linking in thin films of ammonium ionenes having styrenic chain ends,[26] whereas Noble et al. reported the UV-cross-linking of polystyrenes having vinyl-imidazolium pendant groups.[27] However, the patterning of solid electrolytes using UV-lithography and optical masks, which is the topic of the present letter, has not been demonstrated so far.

Poly(1,2,3-triazole) **1** (Scheme 1, M_n = 12 kDa and Đ = 2.5) the neutral precursor of azide-functionalized PIL **5**, was obtained by copper(I)-catalyzed polyaddition of the corresponding α-azide-ω-alkyne monomer.[28] Alkylation of the 1,2,3-triazole units with 0.2 equiv of α-azido-α′-bromo-p-xylene **2** (Figures S1 and S2 in the Supporting Information) yielded copolymer **3** having 15 mol % of 1,2,3-triazolium bromide units with pendant azide groups (as determined by integration of the 1,2,3-triazole and 1,2,3-triazolium protons ^{1}H NMR signals). Subsequent alkylation of the remaining 1,2,3-triazole groups with methyl iodide afforded azide-functionalized PIL **4**. The content of pendant azide groups could be tuned by the initial amount of **2** or by the reaction time. Alkylation of poly(1,2,3-triazole)s is thus a general and versatile method to prepare functionalized PILs.[29,30] Besides, it is fully compatible with other quaternizing groups, pendant functionalities, and monomer chemical structures, as well as polymerization methods.[31−34] Anion metathesis was carried out to replace Br⁻ and I⁻ counter-anions of PIL **4** by bis(trifluoromethane)-sulfonimide anions, thus, yielding azide-functionalized PIL **5**.

Scheme 1. Synthesis of Azide-Functionalized PIL 5

a) DMF, 72h, 60 °C; b) DMF, 48h, 60 °C; CH₃CN, 18h, 45 °C.
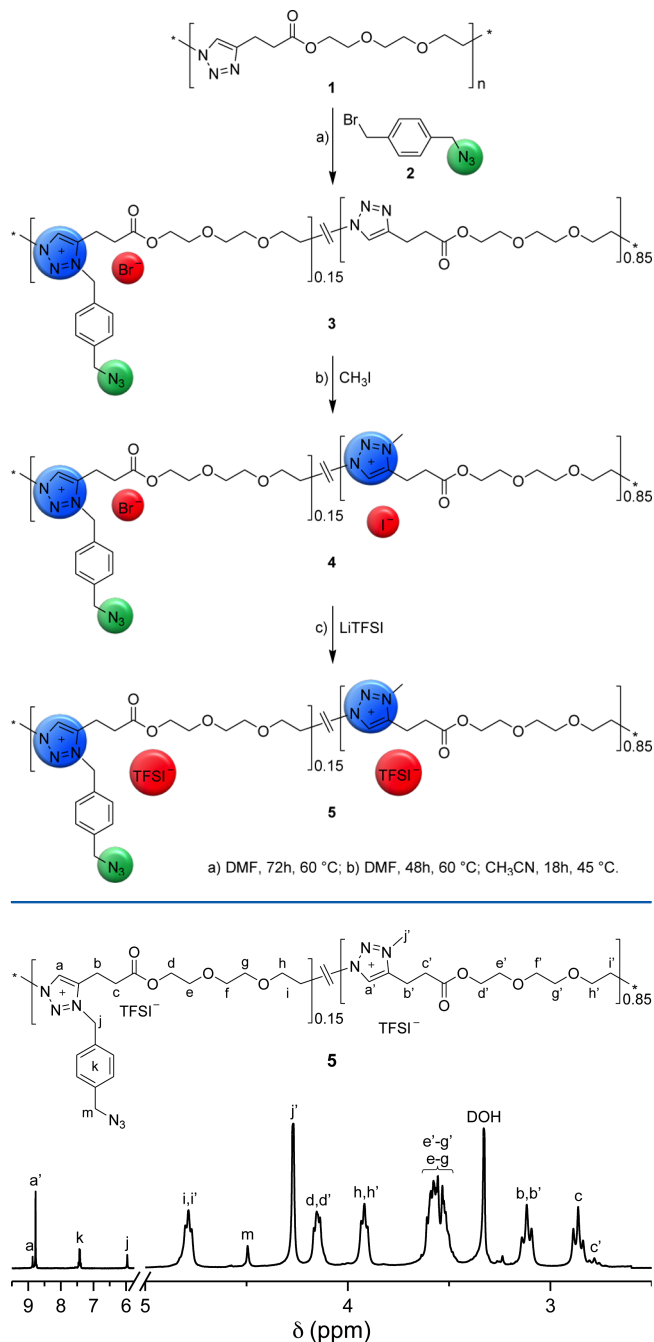
Figure 1. ¹H NMR (DMSO-d_6) of azide-functionalized PIL **5**.

¹H NMR of **5** (Figure 1) showed the total disappearance of the 1,2,3-triazole proton at 7.81 ppm and, thus, the quantitative nature of the sequential alkylations. Accordingly, two distinct signals are observed at 8.77 and 8.86 ppm for the protons of the 1,2,3-triazolium groups having N-3 methyl and p-azidomethyl-xylyl substituents, respectively. In addition, the N-3 methyl (at 4.27 ppm) and the N-3 p-azidomethyl-xylyl signals (at 7.42, 5.96, and 4.49 ppm) with matching 15/85 ratios undeniably confirm the structure and composition of **5**.

The broad solubility (Table S1 in the Supporting Information), low glass transition temperature (T_g = −27 °C), low UV absorption in the 365 nm region (Figure S3 in the Supporting Information), and the photoinduced reactivity of

azides are promising features to use **5** as an ion conducting negative tone photoresist. UV irradiation of azides generates nitrene transient radicals prone to rapid and efficient covalent cross-linking in thin films.[35] Major cross-linking pathways involve the formation of aziridines by the addition of nitrenes to sp^2 bonds of the xylyl groups, and the dimerization of nitrenes which yields diazo groups (Scheme S1 in the Supporting Information).

Scheme 2. UV-Patterning of Azide-Functionalized PIL 5
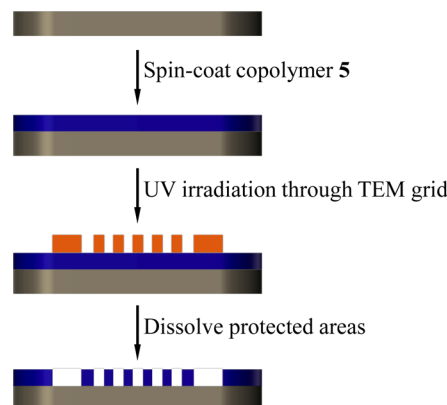
Acetonitrile solutions of **5** (1−2 wt %) were spin coated onto silicon wafers to yield 50−100 nm thick films. TEM grids with linear, squared, or hexagonal features were used as optical masks (Scheme 2). UV irradiation (λ = 365 nm) induced the covalent cross-linking of the uncovered parts of the film. FTIR of the film after 2 h of irradiation (Figure S4 in the Supporting Information) shows total disappearance of the characteristic signals of azide groups at 2100 cm⁻¹, proving that the cross-linking reaction is complete. Anhydrous ionic conductivity of cross-linked PIL **5** was measured by broadband dielectric spectroscopy and compared to **6**, a non-cross-linkable analogue having 100% of 3-methyl-1,2,3-triazolium units (Figure S5 in the Supporting Information), which was also obtained from the same poly(1,2,3-triazole) precursor **1**.[28] The lower ionic conductivity of **5** after cross-linking (σ_{DC} = 7 × 10⁻⁵ S cm⁻¹ at 100 °C) compared to **6** (σ_{DC} = 3 × 10⁻⁴ S cm⁻¹ at 100 °C) is due to the reduced mobility of the polymer chains. Yet, the significant level of ionic conductivity remaining after cross-linking and the temperature evolution of ionic conductivity still following the classical Vogel−Fulcher−Tammann dependence (Table S2 in the Supporting Information) suggest that 1,2,3-triazolium groups are not noticeably affected by UV irradiation or by reaction with azide or nitrene groups.

The negative tone patterns of the cross-linked films were revealed by dissolution of the protected areas in acetonitrile. Optical microscopy (Figure 2) shows excellent replication for pattern sizes ranging from 48 to 285 μm, and interpattern spacings ranging from 25 to 65 μm. The height steps of the patterns measured by profilometry are in the 60−90 nm range and correspond to full removal of the PIL layer. This was corroborated by AFM, which shows very smooth surfaces typical of the silicon substrate where the PIL was removed. Due to the noncollimated UV light source, the step edges of the patterns in the AFM height profiles are asymmetric and range from 3 to 6 μm. Significantly improved resolution should be attained by using state-of-the-art lithographic facilities.
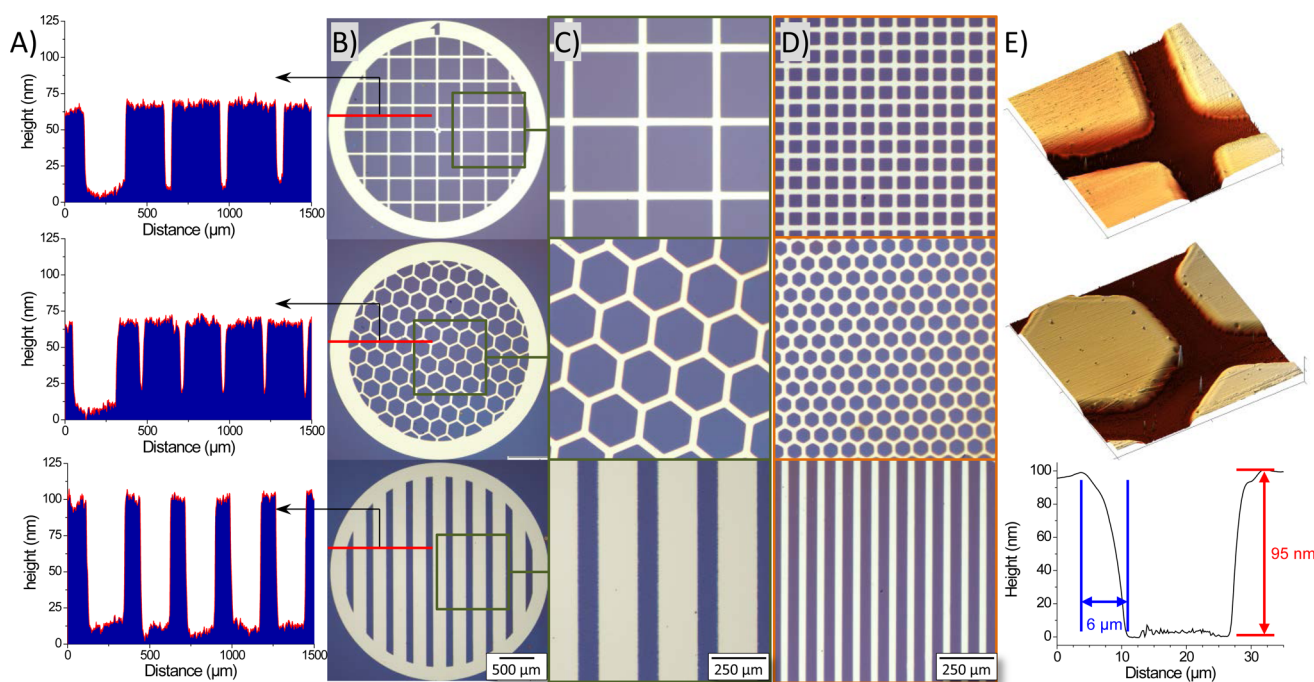
Figure 2. Characterization of photo-cross-linked patterns of PIL 5 on silicon substrates. Columns: (A) profilometry, (B−D) optical microscopy by reflection, and (E) reconstructed 3D-surface from AFM height measurements (size 90 × 90 μm) of G300 (top) and G300Hex (middle) patterns, and height profile taken across the PIL pattern from G300Hex (bottom). TEM masks employed are top row G75 (A−C) and G300 (D), middle row G100Hex (A−C) and G300Hex (D, E), bottom row G100P (A−C), G300PB (D), and G300Hex (E).

To conclude, alkylation of poly(1,2,3-triazole)s with a functionalized quaternizing agent is a general method to provide PILs with pendant functionalities. Light-triggered azide cross-linking through an optical mask enables precise patterning of solid electrolytes and prevents excessive heat during curing, thus, enabling incorporation of sensitive organic molecules such as dyes for OLEDs, solar cells, sensors, or thermoelectrics. Many developments taking inspiration from the semiconductors fabrication by soft lithography can be envisaged, such as chemical amplification that enables reduced curing times and enhanced resolution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures. ^{1}H and ^{13}C NMR of **2**. Solubility, FTIR, and UV spectroscopy of **5**. Ionic conductivity of **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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