ADVANCES IN NANOCONTACT MOLDING FOR THE PATTERNING OF POLYTHIOPHENE

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Introduction

Nanocontact molding and other related techniques of imprint lithography have received much attention as simple and inexpensive tools for the accurate replication of sub-100 nm features.[1,2] We have recently reported on the use of this method for the replication of features as a small as 60 nm.[3] In this technique, an inexpensive mold is made by curing a photopolymer resin against a patterned silicon master written by e-beam lithography. This mold is then used to press into a photopolymer resin. The resin is then cured in contact with the mold, resulting in a highly reproducible positive copy of the original master pattern.

The incorporation of embedded functionality into the photopolymer resin has allowed the utility of this technique to be advanced beyond that of simple pattern transfer. The inclusion of inimers (molecules containing both a dormant initiating site and a monomer functionality) allowed precise control of feature size and surface chemistry through modification of the surface after molding. One such inimer, a methacrylate monomer containing a dormant atom transfer radical polymerization (ATRP) initiator, allowed for the application of controlled free radical polymerization to grow polymer brushes from the surface of the molded features.[3] The molecular weight of the brushes was controlled by the ratio of monomer to initiator and the resulting surface chemistry was decided by the choice of the monomer.

Currently, we are interested in the adaptation of these techniques to functionalize patterned surfaces with conducting and semiconducting polymers for the direct fabrication of organic electronics. In earlier work, bromostyrene was embedded in the resin, and subsequently was used to initiate the Ni(0) mediated polymerization of 2,7-dibromo-9,9-dinonylfluorene resulting in a surface functionalized with short polyfluorene brushes.[4] The current work focuses on the use of functional photopolymer resins for the attachment and growth of polythiophene brushes. Herein, we describe methods for the fabrication conductive nanoscopic patterning of polythiophene. The materials and substrates were characterized by atomic force microscopy (AFM), ellipsometry, UV-vis spectroscopy, fluorescence microscopy, and 2 point conductivity measurements.

Experimental

Thiopheneacetyl-2-oxyethyl methacrylate. Oxalyl chloride (1.1 eq.) was added dropwise to a stirring solution of 3-thiopheneacetic acid (1 eq.) in dichloroethane (10 eq.) and refluxed for 2 h. The solvent was removed under vacuum and the resulting acid chloride was added dropwise to a stirring solution of hydroxyethyl methacrylate (1.1 eq.) and triethylamine (1.2 eq.) in dry tetrahydrofuran (12 eq.) and allowed to stir overnight at room temperature. The solvent was then removed under vacuum and the resulting oil purified on a silica gel column with methylene chloride as the mobile phase.

Contact Molding. For a detailed description of the contact molding process, materials, and instrumentation, see reference 3.

Oxidative Polymerization. $FeCl_3$ (2.18 mmol) was added to a stirring solution of 3-hexylthiophene (0.36 mmol) in 10 mL of methylene chloride in a Schlenk flask containing the patterned substrate. The reaction was stirred for 24 h and the polymer was then precipitated from solution by pouring the mixture into stirring methanol. The resulting brown solid was extracted with methanol and hexane. The patterned substrate which was immersed in the polymerization mixture was extracted with methanol, hexane, and methylene chloride.

GRIM Polymerization. Hexylmagnesium bromide (8.66 mmol) in 10 mL tetrahydrofuran was added to a flask containing the patterned substrate and a stirring solution of 2,5-dibromo-3-hexylthiophene (8.66 mmol) in 50 mL tetrahydrofuran and refluxed for 1h. $Ni(dppp)Cl_2$ (12 mg) was added and the reaction was refluxed for another 12 h. The resulting polymer was precipitated into stirring methanol and filtered through a Soxhlet extraction thimble, which was then extracted with methanol and methylene chloride. The polymer was recovered from the methylene chloride by removal of the solvent under vacuum. The substrate was washed with methanol and methylene chloride.

Results and Discussion

In order to attach polythiophene brushes to the patterned surfaces, appropriate functionality must be incorporated into the acrylate network. The monomers to be incorporated must meet two requirements. First, they must contain a monomer unit reactive under the free radical photopolymerization conditions, and second, a functionality reactive under the chosen brush growth conditions must be present. In this work it was chosen to grow polythiophene brushes by two methods, oxidative polymerization and Grignard metathesis (GRIM) polymerization.[5,6] Incorporation of thiopheneacetyl-2-oxyethyl methacrylate (M1, Figure 1) into the acrylate network provides thiophene functionalities available at the surface to participate in the oxidative polymerization of thiophene. The addition of bromostyrene (M2) to the resin gives bromophenyl sites at the surface which are reactive under Grignard conditions.

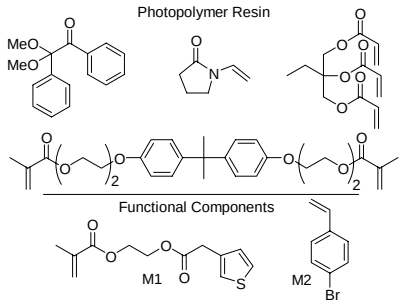

Figure 1. Photopolymer resin and functional components thiopheneacetyl-2-oxyethyl methacrylate (M1) and bromostyrene (M2).

The oxidative polymerization of 3-hexylthiophene with $FeCl_3$ was carried out in the presence of patterned substrates containing M1 (Figure 2). Polymer with a number average molecular weight of 4.1×10^3 g/mol (PDI = 4.49) was obtained. Elliposometry and AFM measurements showed a 3.1 nm increase in film thickness and a 7 nm increase in feature size after brush growth. A control sample containing no M1 showed no significant change in film thickness or feature size under identical reaction conditions. Initial studies of the optical properties the polythiophene brushes were also conducted. The UV-vis spectrum of the substrate prior to brush growth showed no absorption in the visible region of the spectrum. After brush growth, a large shoulder extending into the visible region indicating brush growth was observed. The molded surfaces were also analyzed by fluorescence microscopy. The cured photopolymer resin with the embedded functionality was nonfluorescent, however after brush growth, these surfaces became fluorescent. Unfortunately, a control sample containing no embedded M1 subjected to the same reaction conditions also exhibited fluorescence.

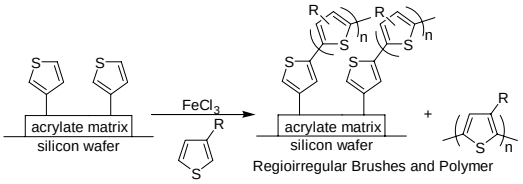

Figure 2. Polythiophene brush growth utilizing the oxidative polymerization of thiophene.

The GRIM method, developed McCullough and coworkers,[6] was shown to be a highly efficient and effective route to polythiophene synthesis. This reaction was observed to proceed cleanly and result in a highly regioregular polythiophene in good yields, and thus was an excellent potential route to polythiophene functionalized surfaces. Substrates with M2 embedded resins were subjected to GRIM polymerization conditions and analyzed as the oxidatively polymerized samples presented above (Figure 3). The polymer obtained from solution exhibited a number average molecular weight of 6.7×10^3 g/mol (PDI = 2.90). Ellipsometry of the wafer surfaces showed an increase of 6.8 nm after brush growth and AFM showed an increase in feature size of 3.2 nm. No change in film thickness or feature size was observed for control samples containing no embedded M2. Analysis of the surfaces before and after brush growth by UV-vis showed little change in the spectra. No absorbance in the visible region of the spectra was observed for these substrates after brush growth indicating a low degree of functionaliztion.

The electrical conductivity of the brushes grown by the various techniques was studied. The samples were doped with iodine and their current/voltage behavior was measured by a two point probing technique. A bulk film of regioregular poly(3-hexylthiophene) was also doped and subjected to the same measurements. For the bulk polythiophene, a conductivity of approximately 100 S/cm was calculated. All of the brush functionalized samples exhibited lower values, but did exhibit conductivity. Brushes grown on resin containing M1 exhibited a conductivity of 6 S/cm which falls within the typical range for polythiophene conductivities. Brushes

grown by the GRIM method gave conductivities of 2.4 S/cm. The lower conductivity of the samples from the GRIM method and the large difference in the conductivities of the bulk polymer and the brushes prepared by GRIM was unexpected. The highly regioregular backbone resulting from the GRIM polymerization should exhibit a much larger conductivity than the more regioirregular brushes prepared by the oxidative method. This may be partly explained by brush density. The failure to observe any change in the surface by UV-vis spectroscopy was likely due to a low degree of functionalization of the surface with polythiophene brushes. A low brush density would be expected to yield a low conductivity. Further work is in progress in increase the brush density at the surface.

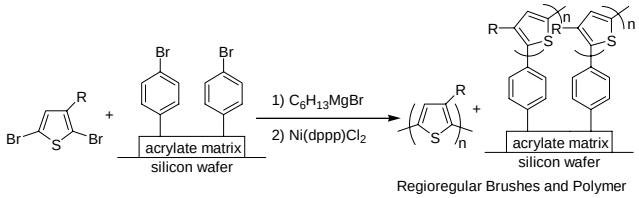

Figure 3. Polythiophene brush growth utilizing the Grignard metathesis (GRIM) polymerization of 2,5-dibromo-3-hexylthiophene.

Conclusions

Nanocontact molding was used to pattern functional resins with feature sizes as small as 100 nm. The functionality incorporated in to the resin was chosen as to allow growth of poly(3-hexyl-2,5-thiophene) brushes from the patterned substrate. Two methods were employed for the attachment of the polythiophene brushes. The first method, oxidative polymerization, was shown to be a simple route for the attachment of polythiophene brushes. The film thickness and feature size was observed to increase by 3-7 nm. Also, conductivities of up to 6 S/cm were measured for polythiophene brushes grown by this method. However, the selectivity of this method proved to be limited with uncontrolled brush growth from surfaces with no added reactive functionality. The GRIM method proved to be much more selective and polythiophene brushes were attached to the patterned polymer surface using this technique. Once again film thickness and feature size increases of 3-7 nm were observed. Optical characterization indicated a lower degree of functionalization than the materials from the oxidative route. Electrical characterization supported this observation yielding a lower measured conductivity of 2.4 S/cm. Presently, further work is in progress to increase the degree functionalization as well to more fully characterize the electrical properties of these materials.

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