

RECENT ADVANCES IN CONTACT MOLDING FOR THE NANOSCOPIC PATTERNING OF CONDUCTING POLYMERS

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Introduction

Contact molding and other related techniques of imprint lithography have recently received much attention as inexpensive and versatile methods for the replication of sub-100 nm features.¹⁻³ We have recently reported the use of contact molding for the accurate replication of structures as small as 60 nm. In this technique, an inexpensive, reusable stamp is employed to mold a photopolymer resin.¹ The resin is then cured in contact with the stamp resulting in a highly reproducible positive copy of the stamp.

The incorporation of inimers (consisting of both an initiator functionality and a monomer unit) into the photopolymer resin has allowed the utility of this method to be advanced beyond that of simple pattern transfer. The incorporation of an acrylate monomer containing a dormant atom transfer radical polymerization (ATRP) initiator allows for the modification of the patterned surface after the molding procedure. In the presence of a sacrificial initiator, controlled free radical polymerization conditions can be utilized to grow polymer brushes from the molded features.¹ The molecular weight of the brushes can be varied by the ratio of monomer to initiator and the resulting surface chemistry can be controlled by the choice of the monomer.

The embedding of functionalities to initiate controlled free radical polymerizations is just one of the possible reactions that can be employed to decorate these surfaces with polymer brushes. The incorporation of functional monomers that allow the grafting of step growth polymers to the molded surfaces is also possible. Through such methods, conductive polymers can be attached to the surface.⁴ The ability to functionalize the patterned surfaces with optically and electronically active polymers has many potential applications in the fabrication of inexpensive organic electronics.

Experimental

For a detailed description of the contact molding process, materials, and instrumentation see reference 1.

Results and Discussion

In order to attach the polyfluorene chains to the surface, it was necessary to incorporate a functionality reactive under the requisite polymerization conditions. To accomplish this goal, bromostyrene was added to the photopolymer resin, molded, and cured. The random distribution of the bromostyrene repeat unit in the cured polymer matrix resulted in a portion of the bromostyrene present to be advantageously located at or near the surface of the polymer network and are thus available to react with monomers in solution. The monomer, 2,7-dibromo-9,9-dihexylfluorene, was polymerized under Ni(0) mediated polymerization conditions in the presence of these functionalized substrates (Figure 1).

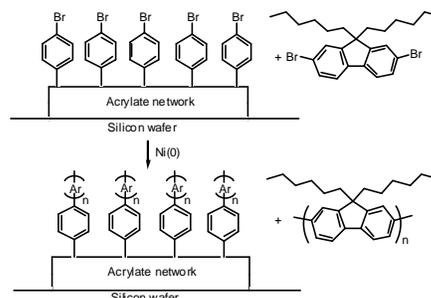


Figure 1. Polyfluorene brush growth under Ni(0) coupling conditions from bromoarene functionalized substrates.

The samples were analyzed before and after the Ni(0) polymerization by atomic force microscopy (AFM). Prior to the reaction, the samples exhibited a feature height of 40 nm. After the attachment of the polyfluorene brushes, the height grew to 43 nm. Furthermore when the substrates were observed under an optical ultraviolet microscope, no emission was observed prior to polymerization, while after the reaction the polymeric features were fluorescent.

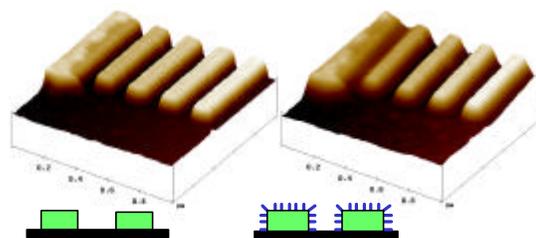


Figure 2. AFM topographs of substrates patterned by contact molding prior to polyfluorene brush growth (left) and after polyfluorene brush growth (right).

These techniques can be adapted to functionalize surfaces with a wide variety of conducting polymers. Polythiophene is one such conducting polymer. This material has generated much interest for potential use in organic electronic devices. In order to attach polythiophene to the surface of the patterned acrylate network polymers, suitable functional monomers need to be synthesized. The proposed structures all possess a methacrylate functionality for incorporation into the acrylate network polymer as well as a thiophene pendant for subsequent brush growth. Incorporation of these monomers into the acrylate matrix allows the surfaces to be functionalized with polythiophene in several manners. First, utilizing monomer **a**, regioregular polythiophene can be grown by iodination of the 5 position on the pendant thiophene ring, followed by a Suzuki cross-coupling polymerization to yield polythiophene brushes.² Alternatively, functional monomers **b** and **c** can be utilized to grow polythiophene utilizing oxidative polymerization techniques.³

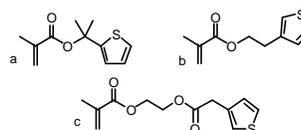


Figure 3 The functional monomers, dimethyl(2-thienyl)methylmethacrylate (a), (3'-(3''-thienyl)propanoyl)-2-oxyethylmethacrylate (b), and 2-(3'-thienyl)ethylmethacrylate (c).

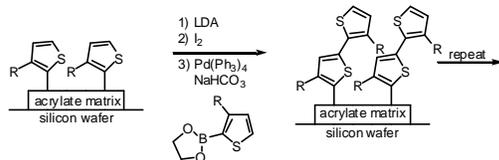


Figure 4. Reaction sequence for the growth of regioregular polythiophene brushes under Suzuki cross-coupling conditions.

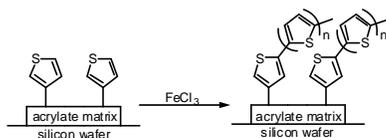


Figure 5. Reaction sequence for the growth of polythiophene brushes under oxidative polymerization conditions.

Summary

Contact molding is a simple method for the replication of nanometer sized features. The utility of the method can be further enhanced by the incorporation of functional monomers in the photopolymer resin. The monomers can be chosen to so that after curing to form a network copolymer, functionalities are presented to the surface that are available to initiate or participate in a second polymerization to modify the surface of the molded features. Through the use of embedded functional monomers, we have shown the ability to tune the size of the molded features utilizing controlled free radical polymerizations as well as modify the surface with optically and electronically interesting materials such as polyfluorene and polythiophene.

Acknowledgements

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