

## Patterned Polyfluorene Surfaces by Functionalization of Nanoimprinted Polymeric Features

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A new procedure is described for surface grafting polymer brushes by step-growth polymerization from initiator-embedded polymeric thin films and micron- and nanometer-scale patterns. An imprint lithographic process, nanocontact molding, was used to prepare thin patterned cross-linked polyacrylate network films on silicon wafers that incorporated 4-bromostyrene in the networks. These networks present reactive 4-bromophenyl functionality at the surface that act as attachment sites for the subsequent Ni(0)-mediated step-growth condensation polymerization of 2,7-dibromo-9,9-dihexylfluorene. The step-growth polymerization medium consisted of 2,7-dibromo-9,9-dihexylfluorene, Ni(0)-catalyst, and bipyridine in a toluene/dimethylformamide solvent mixture. The resulting growth of polydihexylfluorene brushes from the patterned surface was monitored by contact angle, optical spectrometry, surface profilometry and AFM. Brush growth was conducted from patterned features ranging from 100  $\mu\text{m}$  to 100 nm in width and 50 nm in height. The optical and fluorescence behavior of the polyfluorene brushes was similar to that of thin polyfluorene films made by spin coating.

To enable the use of advanced polymeric materials in applications such as polymeric light emitting diodes (PLEDs), photovoltaics, and photovoltaic devices, new methods for applying the polymeric materials in precisely defined patterns are needed. Polyfluorenes, containing two planarized benzene rings per monomer unit, are being considered by many research and industrial groups as a very promising blue light-emitting material due to the chemical and thermal stability, high photoluminescence quantum efficiency, and ease of property tunability through structural modification of the 9-position of the fluorene ring.<sup>1</sup> Conventional manufacturing processes apply the active polyfluorene layer by solvent deposition or evaporation and achieve patterning via a number of complex low resolution (>20  $\mu\text{m}$ ) methods, including shadow masking,<sup>2</sup> ink-jetting,<sup>3–5</sup> photolithography,<sup>6</sup> silk-screening,<sup>7</sup> patterned sublimation source,<sup>8,9</sup> microfluidics,<sup>10</sup> and contact stamping techniques.<sup>11</sup> We now report the direct surface growth of polyfluorene (PF) brushes from patterned polymer features made by contact-molding. This advance should facilitate future developments in high performance polymeric devices.

The preparation of complex patterns in polymer films has been widely explored by classic photolithographic techniques<sup>12</sup> as well as newer methods such as microcontact printing ( $\mu\text{CP}$ ) of self-assembled monolayers,<sup>13</sup> polymer brushes,<sup>14</sup> and block copolymer self-assembly.<sup>15,16</sup> Other nonoptical contact patterning techniques including nanoimprint lithography<sup>17</sup> and “step & flash” imprint lithography<sup>18</sup> have recently been seriously examined. Additionally, a number of surface-bound “living” polymerization techniques including cationic,<sup>19</sup> anionic,<sup>20</sup> ring-opening,<sup>21</sup> ATRP,<sup>22–26</sup> TEMPO,<sup>27</sup> and RAFT<sup>28,29</sup> have been successfully

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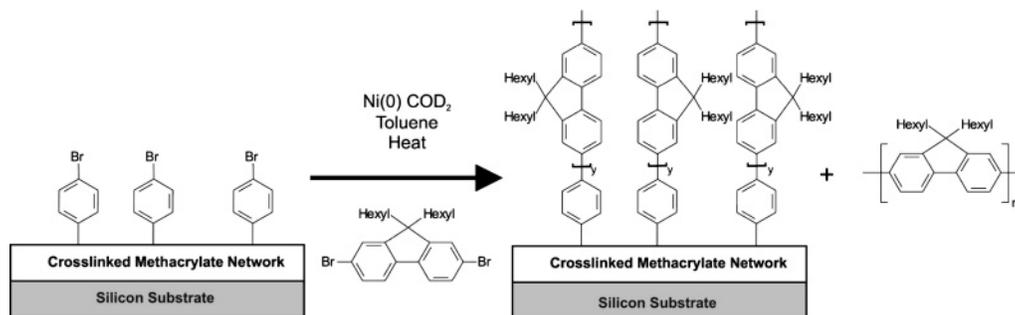
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## Scheme 1. Schematic of Polyfluorene Brushes Grown from Inimer Embedded Polymer Network on a Silicon Substrate



employed to give surface-grafted polymers under controlled growth conditions.<sup>30</sup>

Previously, we have reported novel nanocontact molding techniques for the replication of nanometer-scale features on surfaces using functional cross-linked polymeric materials.<sup>31,32</sup> An advantage of this technique compared with other available methods is precise control of the chemistry through surface modification and incorporation of reactive functionality into the cross-linked polymers. We have shown that complex functionality can be obtained by the covalent incorporation of functional inimers (having both an *initiator* and *monomer* fragment) for “living” free radical polymerization into the photopolymer matrix. Controlled “living” radical secondary brush polymerizations of styrene, acrylates, and other vinyl monomers from embedded inimer sites yield a polymer brush surface that offers the ability to adjust imprinted feature size and chemical functionality in the nanometer-size regime.<sup>32</sup> As a result the surface properties of the patterned substrate can be radically altered.

The present paper examines the surface growth of fluorescent polyfluorene (PF) brushes from contact-molded features. As far as we know, this represents the first application of metal-catalyzed step-growth condensation polymerization from solid surfaces. In fact, we have found no other reports concerning the polymerization of condensation graft polymers from functional surfaces save the well-known and technologically important unit-by-unit sequencing synthesis of biomacromolecules from solid supports.<sup>33</sup> Ni(0)-mediated step-growth polymerization of 2,7-dibromo-9,9-di-*n*-hexylfluorene was conducted from matrix-embedded 4-bromophenyl moieties that served as the initiating sites for brush growth. These condensation polymerizations were performed primarily on patterned surfaces with feature sizes in the 100 nm range. A range of surface analytic techniques, including UV and fluorescence spectroscopy, fluorescence microscopy, contact angle, surface profilometry, and AFM, confirmed surface growth of brushes that are at least oligomeric in nature.

Initial experiments were performed on nonpatterned, flat surfaces to ensure completeness of individual reaction steps and to optimize reaction conditions. A 10 wt-% solution of a methacrylate photopolymer mixture containing a small amount of 4-bromostyrene (4:1 by weight) in propylene glycol methyl

ether acetate (PGMEA) solvent was spun cast onto adhesion promoter coated silicon wafers.<sup>34</sup> Photoinitiated polymerization of the monomer mixture yielded a highly cross-linked network film (50–150 nm thick) with matrix-embedded bromophenyl moieties that subsequently served as reactive sites for Ni(0)-mediated step-growth brush polymerization (Scheme 1). Polyfluorene was then grown from the imbedded bromophenyl moieties using 2,7-dibromo-9,9-di-*n*-hexylfluorene in a toluene/DMF solution of bis(1,5-cyclooctadiene)nickel(0), 2,2'-bipyridyl and free 1,5-cyclooctadiene (COD).<sup>35</sup>

Due to the intrinsic nature of the Ni(0)-mediated condensation polymerization, the polymer formed both in solution as well as tethered in the form of polymer brushes on the surface. Development of brush growth from the surface likely takes place by both the condensation of monomeric units to the growing covalently surface-attached chains as well as grafting of macromolecular units from the polymerization solution. The solution polymer was precipitated into methanol and found to be of high molecular weight:  $M_n = 30\,000\text{--}70\,000$  au and polydispersity index  $\sim 2.0$  (averaged over several runs). Following all polymerizations, wafer surfaces were exhaustively extracted with hot solvent to remove any adsorbed, noncovalently attached polymer. In terms of absolute yield, the majority of polymer formation occurred in solution, as would be expected, though sufficient reaction also takes place from the surface-bound initiating sites. Therefore, the molecular weight (chain length) of the polymer from solution cannot be directly correlated to the polymer brushes grown from the surface though such correlations are made for controlled chain growth brush polymerizations.<sup>22</sup>

To ascertain that surface growth was only taking place from the imbedded functionality, control samples of polymerized photopolymer with no imbedded inimer were exposed to identical polycondensation reaction conditions. In all cases, we saw no presence of polyfluorene on the control samples after solvent rinse, and we were able to confirm that no brush growth or adsorbed polymer from solution occurs on the surface in the absence of inimer. We do not believe that the polymerization is occurring deep inside of the cross-linked photopolymer film forming a swollen IPN-type structure. The cured photopolymer resin is highly cross-linked, and previous studies have shown only a minimal amount of swelling in a variety of solvents.<sup>32</sup> In any case, no evidence of polyfluorene is observed in the control polymerization reaction, which one would expect if functionalization and size change was due to polymerization of polyfluorene within a swollen network.

Films were characterized by water contact angle measurements in order to track changes in surface energy as a manifestation

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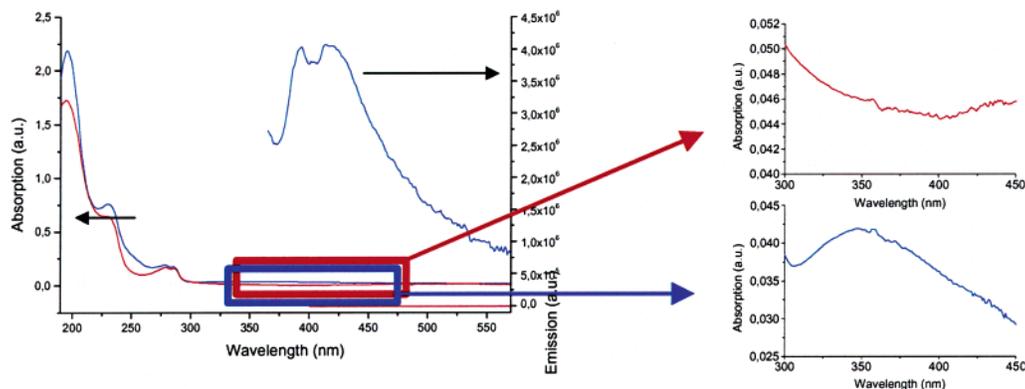
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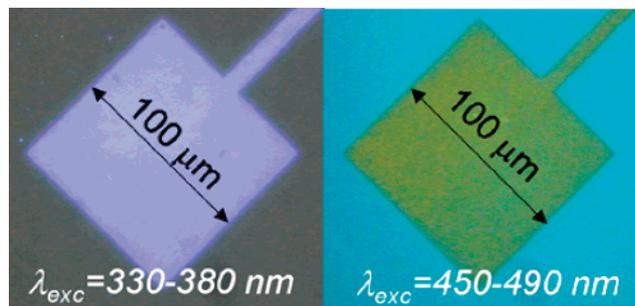


**Figure 1.** UV absorption and emission spectra of flat photopolymer film surfaces before (red) and after (blue) growth of polyfluorene brushes.

of surface modification. The contact angles for films containing imbedded bromophenyl inimer and a control sample containing no bromophenyl inimer were measured before and after brush growth reactions. The incorporation of 20 wt-% of the inimer into the cross-linked photopolymer network had an appreciable effect on the surface energy of the thin film as the measured  $74^\circ$  contact angle was higher than the  $67^\circ$ – $69^\circ$  observed for the undoped film. The contact angle increased to  $91^\circ$  on introducing PF brushes to the surface, whereas the undoped control sample did not change after exposure to polymerization conditions. In comparison, the contact angle of thin films of pure linear PF spun cast onto quartz or silicon substrates was between  $100^\circ$  and  $103^\circ$ .

To monitor changes in feature dimensions due to brush growth, we relied upon profilometry and AFM measurements as performed with earlier polystyrene brush work.<sup>32</sup> We observed an average increase in film thickness of 6 nm in thickness due to PF brush growth. If one makes the assumption that the polyfluorene brushes are fully extended and orthogonal to the substrate, this 6 nm length would correspond to approximately 6 fluorene units, based on a calculated length of a fluorene repeat unit of 10.3 Å. However, the thickness measurements do not take into account the likelihood that the brushes may be longer as they may not stand perpendicular to the film surface as a densely packed surface; therefore, the actual brush length is likely much higher. Unfortunately, making a precise direct determination of the size of the covalently attached brushes is quite challenging, as they cannot be detached and analyzed separately. Both surface profilometry measurements and AFM profiles clearly show that polyfluorene has been attached to the surface with both smoothing of the original feature roughness and increasing peak-to-valley feature height. Optical data (see Figure 1) support the conclusion that brushes are longer than 6 repeat units.

UV–vis absorption and photoluminescence spectra of these films provide a clearer picture of the surface bound polyfluorene brushes (Figure 1). The absorption spectra are dominated by the underlying polymerized acrylate network with broad absorption bands at 230 and 278 nm. The change in the absorption due to the attachment of polyfluorene brushes is slight but measurable. The polyfluorene brush sample exhibits a broad absorption at around 350 nm. To document fluorine inclusion from photoluminescence, samples were exposed to 350 nm, and the resulting emission was recorded at 350–575 nm. As expected, neither the unreacted inimer-embedded sample nor the control sample showed any fluorescence. In contrast, the oligofluorene sample clearly displayed the spectrum typical of polyfluorene emission with  $\lambda_{\text{max}}$  at 392 and 418 nm. The position of the bands is slightly blue shifted as anticipated for shorter conjugation lengths as

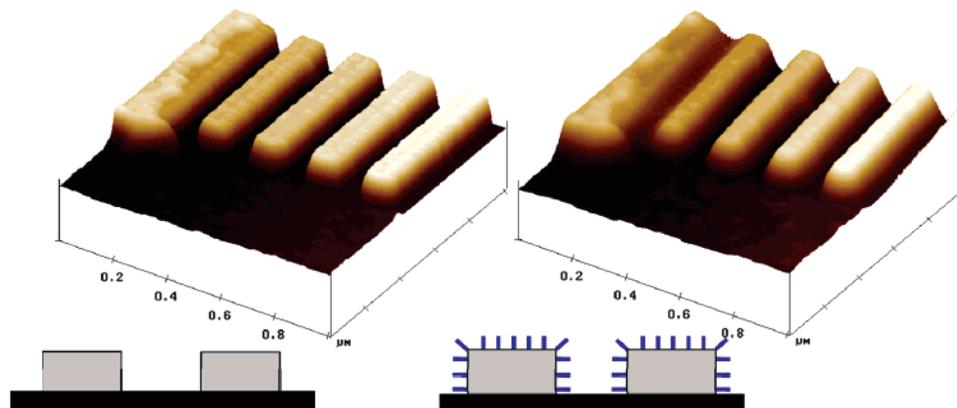


**Figure 2.** Epifluorescent micrographs show square patterned region of grafted polyfluorene after irradiation at noted wavelengths. Left: polyfluorene square fluoresces brightly on irradiation at the shorter wavelength. Right: on irradiation at the longer wavelength where oligofluorene does not absorb, weak fluorescence from the substrate creates dimly lit background behind the dark polyfluorene square.

compared to high molecular weight polyfluorene. Other than the slight blue shift, the intensity of the absorbance and fluorescence observed was found to be consistent with those seen for ultrathin ( $\sim 10$  nm) films of high molecular weight polyfluorene films prepared by spin coating sample on top of cured acrylate films.

On the basis of their absorption and strong fluorescence behavior, we are hopeful that the properties expressed by the grafted polyfluorenes will enable them to be used in PLED applications. The fact that these thin films have good luminescent properties despite their short length may mean that the unique brush morphology we believe is presented by these grafts may lead to interesting electroluminescent behavior. This is currently being studied.

The same functionalization process was then extended to contact-molded polymer features. Polymeric features were contact molded onto as described in our earlier work.<sup>31,32</sup> The inimer-containing photopolymer solution was spun cast and subsequently UV-polymerized while in contact with a transparent patterned mold. This resulted in high fidelity pattern replication into the thin cured photopolymer layer. The test pattern contained line features spanning from 100 nm to 100  $\mu\text{m}$  in width and were 50 nm in height. One of the artifacts of the molding process is a thin residual (scum) layer of cured material that remains in the flat areas between the molded features. This scum layer was removed using an short duration anisotropic oxygen plasma etch process. The etch descumming process reduced the height of the molded polymer features to  $\sim 40$  nm. Previous studies have shown that, since the active inimers are imbedded throughout the film, the functionality is continually refreshed at the surface during etching.<sup>32</sup> The patterned substrates were then subjected to Ni(0)-mediated cross-coupling conditions as described above to yield polyfluorene brushes grafted from the molded polymeric features.



**Figure 3.** AFM images of molded polymeric features before (left) and after (right) growth of polyfluorene brushes. The average feature height increased from 40 to 44 nm.

Epifluorescent micrographs indicate oligofluorene brush growth from micro-patterned features (Figure 2). When the sample was excited at the absorbance wavelength of polyfluorene, 330–380 nm, the polymeric features showed strong blue polyfluorene emission. The background SiO<sub>2</sub> substrate did not emit light when excited at this wavelength. When exposed above the polyfluorene absorption, 450–490 nm, the same sample did not noticeably fluoresce, though the silicon substrate itself weakly emitted background light as can be seen in Figure 2. When samples were exposed at high intensity for several seconds, photobleaching of the PF areas was observed and resulted in dark areas where exposed. The control sample did not show any emission regardless of excitation wavelength. Due to the inherent limited resolution of our epifluorescence microscope only features in the micrometer range were resolved, 100 nm lines were not individually resolved optically.

The imprinted lines of ~100 nm width were measured by atomic force microscopy (Figure 3) before and after grafting of oligofluorene brushes to document changes in dimensions. The average feature height increased between 4 and 6 nm after brush growth. This extent of brush growth from the patterned features is in agreement with the brush growth observed from flat film surfaces as detected by profilometry discussed earlier. It is important to note that the relatively rough texture/structure on top of the imprinted lines originates from the master used in replication and is not a feature of brush growth. We have observed that polyfluorene brush growth has the effect of smoothing out the average surface roughness.

In summary, we present a procedure for surface grafting polyfluorene brushes by step-growth polymerization onto inimer-embedded polymeric thin films and micron- and nanometer-scale patterns. Nanocontact molding was used to prepare the patterned functional surfaces. Film growth was monitored by contact angle, optical spectrometry, and AFM. Though the increase in film thickness is small, it is clear that the functionalized surfaces demonstrate useful properties. This new technique opens up avenues for the preparation of nanopatterned functional materials and represents one of the first examples of functional surface brush growth by a step-growth polymerization route. We are now in the process of using this new technique to prepare operational PLED devices and that work will be reported in a subsequent publication. We are excited about the potential to extend the technique to the selective growth of electronic and biochemical materials onto patterned surfaces.

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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