

Covalent Grafting of a Patterned, Hyperbranched Polymer onto a Plastic Substrate Using Microcontact Printing

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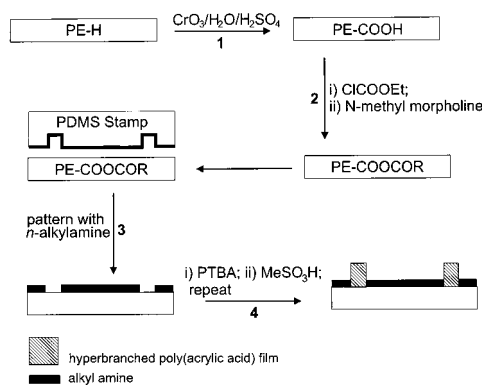
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This paper describes a novel method for micro-contact printing (μ -CP)¹ on plastic substrates. Because plastics have the often-desirable characteristics of being inexpensive, chemically versatile, and sometimes elastic or biodegradable, the results described in this report are a significant advance in stamping-based pattern formation. The physical and chemical properties of plastics are especially important for biomedical applications, which we believe will be most greatly impacted by our new μ -CP strategy. In the proof-of-concept experiments described here, we show that patterned hyperbranched poly(acrylic acid) (PAA) organic thin films^{2,3} can be covalently grafted to oxidized polyethylene surfaces.^{4,5} Scheme 1 outlines the μ -CP-based patterning and polymer grafting steps^{2,3} used to prepare PAA patterns on plastic surfaces.

Recently, Whitesides^{1,6,7} and others^{8–10} described μ -CP, which is a soft lithographic method used to transfer patterned monolayers of alkanethiols,^{11,12} alkanephosphonic acids,¹³ and alkylsilanes¹⁴ onto Au, Ag, Al, glass, and Si/SiO₂ substrates. μ -CP has also been used to pattern polymers on Au surfaces using a two-step process involving μ -CP and subsequent polymer grafting.¹⁵ Polymers have also been printed onto inorganic surfaces using a variant of μ -CP, micromolding in capillaries (MIMIC).¹⁶ Additionally, μ -CP has been used to pattern Au and Ag surfaces

Scheme 1



modified with reactive monolayers¹⁷ and to directly stamp patterns of metal colloids onto polymers.¹⁸ However, to the best of our knowledge, there have been no demonstrations of μ -CP-based patterning of SAMs or polymers onto polymeric surfaces reported in the scientific literature.¹⁹

For some applications, there are advantages to patterning polymers rather than simple monolayers, and therefore we recently showed that it is possible to pattern PAA onto Au surfaces using an approach similar to that illustrated in Scheme 1.^{15a} For example, PAA films can be rendered highly impermeable,²⁰ and thus they hold promise as both wet and dry etch resists.²¹ PAA films are also highly functionalized and therefore amenable to further elaboration.^{2,22} We have also shown that patterned PAA films can be subsequently capped with a thin, conformal layer of poly(ethylene glycol) (PEG) and that such nanocomposites are suitable for precision placement of macrophage and other cell lines on surfaces.²²

Our approach to patterning PAA on polyethylene substrates involves four steps (Scheme 1). First, a purified high-density polyethylene film (Fortiflex J60-110-195, density 0.961 g/mL) is oxidized with a CrO₃/H₂O/H₂SO₄ mixture.^{4,23,24} Second, the acid surface is converted to a carboxylic anhydride using ethyl chloroformate (0.1 mL) and *N*-methylmorpholine (0.1 mL) in anhydrous DMF for 15 min as reported previously.^{2,3} After preparation of a suitable poly(dimethylsiloxane) (PDMS) stamp from an optical test-mask master (USAF resolution test target, Melles Griot), the anhydride-activated polyethylene substrate could be patterned with *n*-hexadecylamine by μ -CP to passivate selected regions of the surface. Finally, unpassivated regions of the plastic substrate react with α,ω -diamino-terminated poly(*tert*-butylacrylate) (PTBA)^{2,3} to yield the amide-grafted polymer layer. Hydrolysis of PTBA with MeSO₃H yields the first layer of PAA, and three additional cycles of activation, grafting, and hydrolysis yield a thick hyperbranched four-layer PAA film (4-PAA). The

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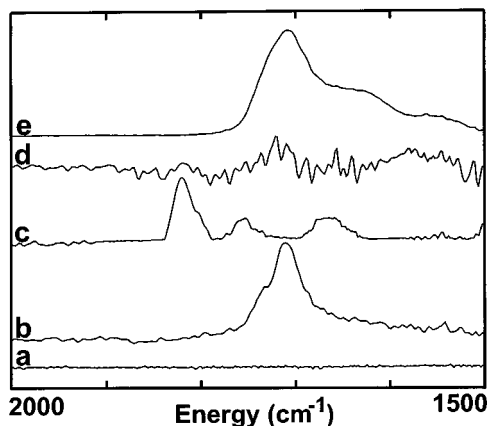


Figure 1. ATR-IR spectra of (a) purified, high-density polyethylene; (b) oxidized polyethylene (PE-COOH) having a strong carbonyl band at 1710 cm^{-1} ; (c) an activated, oxidized polyethylene film revealing mixed-anhydride peaks in the carbonyl region ($1650\text{--}1825\text{ cm}^{-1}$); (d) very weak mixed-anhydride and amide peaks in the region $1550\text{--}1825\text{ cm}^{-1}$ after stamping the activated surface with the *n*-alkylamine-inked PDMS stamp; and (e) a 4-PAA film grafted onto the patterned polyethylene surface. The very strong peak at 1710 cm^{-1} confirms PAA grafting. It is not possible to quantitatively compare the magnitudes of the peaks in ATR-IR spectra such as these.

details of this synthesis and properties of the resulting films on Au^{2,3} and polyethylene⁵ surfaces have been previously reported.

The attenuated total reflectance-IR (ATR-IR) spectrum of a purified and cleaned polyethylene surface indicates the absence of a carbonyl stretching peak in the region between 1500 and 2000 cm^{-1} (Figure 1a). However, after oxidation, a new peak appears at 1710 cm^{-1} (Figure 1b), which is due to acid functionalization of the polyethylene surface. Contact angle measurements confirm this chemical change: prior to oxidation, the plastic surface is hydrophobic ($\theta_a = 105^\circ$), but the oxidized polyethylene film is hydrophilic and has a contact angle of only $\theta_a = 65^\circ$.²⁴ After conversion to the mixed anhydride, the acid carbonyl band disappears, and three new anhydride bands are present at 1820 , 1760 , and 1660 cm^{-1} (Figure 1c).⁵ The anhydride-activated polyethylene surface was patterned by manual application of the PDMS stamp inked with a 5 mM ethanolic solution of *n*-hexadecylamine for 3 min . Anhydride groups in the regions of the surface contacted by the stamp react to yield *n*-alkylamides. Finally, physisorbed material that might be present on the surface was removed by washing with ethanol and then drying in a stream of N_2 . After the surface was stamped with the *n*-alkylamine and washed (Figure 1d), two very weak peaks were still apparent: an anhydride band at 1820 cm^{-1} and an acid band at 1720 cm^{-1} . Since the stamp is designed to passivate most of the polyethylene surface, these bands are consistent with almost complete reaction between the amine and the anhydride. We could just barely detect an amide II peak at 1560 cm^{-1} , which serves to confirm covalent attachment of the *n*-alkylamine to the functionalized polyethylene surface. After four layers of PAA are grafted to the oxidized polyethylene surface, the contact angle is $\theta_a = 50^\circ$, which is characteristic of PAA.⁵ The intense acid carbonyl peak at 1710 cm^{-1} in Figure 1e also confirms PAA grafting.^{2,3,5}

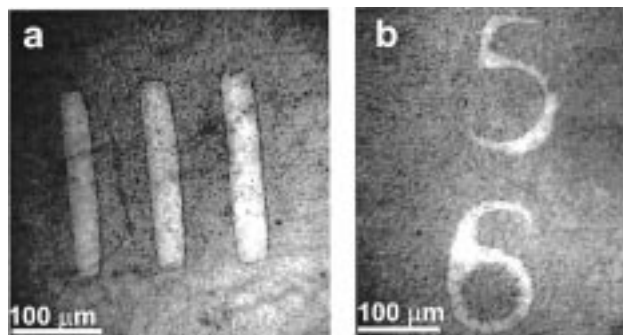


Figure 2. Optical micrographs of a 4-PAA-patterned polyethylene surface: (a) lines having critical lateral dimensions of $35\text{ }\mu\text{m}$; (b) the numbers 5 and 6, having critical lateral dimensions of $20\text{ }\mu\text{m}$. Both images reveal the absence of polymer growth in the *n*-alkylamide-passivated region.

Figure 2a shows an optical micrograph of patterned 4-PAA lines and *n*-alkylamide spaces. The optical contrast of the image was enhanced by mounting the polyethylene substrate on an Au surface and wetting it with a thin layer of water. We speculate that this enhances the relative differences in the refractive indexes of the polyethylene and PAA regions of the surface. The critical lateral dimension of the 4-PAA lines is $35\text{ }\mu\text{m}$. At the resolution of this image, the interface between the polymer and the *n*-alkylamide is well-defined. Figure 2b is an optical micrograph of the numbers 5 and 6 transferred from the stamp to the polyethylene surface. The resolution in this region is $20\text{ }\mu\text{m}$. The smallest features we have thus far been able to pattern on polyethylene have dimensions of $10\text{ }\mu\text{m}$, but these are rather hard to image visually using our current approach.

In summary, we have shown that polymer features having critical lateral dimensions as small as $20\text{ }\mu\text{m}$ can be patterned on plastic surfaces using a combination of reactive $\mu\text{-CP}$ and covalent grafting of multiple PAA layers. Improvements in pattern resolution seem straightforward and await only improved imaging capability. Moreover, because the PAA films are highly functionalized, these polymer-modified polymer surfaces have the potential to be of significant technological importance. Finally, the general patterning approach we have described is simple and inexpensive and should be broadly applicable to a wide range of plastics and other materials.

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