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Communications to the Editor

Photopatternable Metallopolymers: Photo-Cross-Linking and Photolithography of Polyferrocenylsilane Methacrylates

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Photolithographic patterning of films of polymeric photoresists has formed the basis of the microelectronics industry for decades.[1] More recently, patterning of functional macromolecules such as π-conjugated materials has attracted attention as a result of the potential uses of electroactive polymers in electronic and optoelectronic devices.[2] While several groups have explored the photocontrol of metallopolymer properties,[3−5] photolithographic patterning of well-characterized metal-containing polymers is virtually unexplored.[6,7] The patterning of polyferrocenes is of potential interest for the creation of micron scale redox-active, semiconductive, or magnetic domains in an easily controllable and reproducible manner. In this Communication we report on the synthesis, photo-cross-linking, and photopatterning of a well-characterized, readily processable metal-containing polymer, a polyferrocenylsilane with methacrylate side groups.

Polyferrocenylsilanes (PFSs) represent a well-developed class of metallopolymers which possess interesting properties due to the presence of the ferrocene unit in the backbone.[8,9] For example, PFS materials undergo reversible oxidation in two steps,[10] and the conductivity of PFS can be controllably increased by several orders of magnitude, to values typical of semiconductors ($\sigma \sim 10^{-8}-10^{-4}$ S cm^{-1}), by oxidative doping.[5,11,12] In addition, thermally cross-linked PFS networks have been successfully used as high yield precursors to shaped, magnetic ceramic materials.[13] A photo-cross-linkable PFS was targeted by attachment of methacrylate substituents, which undergo efficient photoinduced free radical polymerization in the presence of a variety of photoinitiators.[14,15] Substitution of chlorine side groups on preformed polymers bearing Si−Cl units in the main chain has previously been employed to functionalize chlorosilane-containing polymers.[16,17] Utilizing this method, we have prepared PFSs bearing pendant, photopolymerizable methacrylate groups (see Scheme 1).[18]

Transition metal-catalyzed ring-opening polymerization (ROP) of [1]silaferrocenophanes **1** provides a convenient route for preparing PFSs, including copolymers.[19,20] Using this method, a mixture of **1a** (R = R′ = Me) or **1b** (R = Me, R′ = Et) and 20 mol % of **1c** (R″ = Me) were polymerized in the presence of $PtCl_2$ catalyst to give the corresponding random copolymers **2a** and **2b** (Scheme 1). Reaction of 2-hydroxyethyl methacrylate (HEMA) with **2a** or **2b** in the presence of NEt_3 yielded the methacrylate-substituted copolymers **4a** and **4b**, respectively. The NMR data (^{1}H, ^{13}C, and ^{29}Si) were consistent with a copolymer containing 20 mol % of the 2-ethoxy methacrylate (EMA) groups, with estimated molecular weight (M_n) values of ca. 30 000 (see Table 1).[21] Variation of the monomer ratios in the synthesis of these copolymers provides a means to control the amount of methacrylate present. In addition, this method offers the future potential to prepare multifunctional PFS copolymers by selection of the monomer species present during copolymerization with **1c**.

An alternative method for the control of the methacrylate content in photo-cross-linkable PFSs was also explored. This involves selective derivatization of homopolymers **3** with HEMA. Reaction of **3a**, prepared by Pt-catalyzed polymerization of **1c**,[22] with a slight excess of HEMA and NEt_3 yielded PFS homopolymer **5a** as a red gum. The NMR data (^{1}H, ^{13}C, and ^{29}Si) were consistent with a PFS homopolymer with complete substitution of the chlorine groups for EMA.[21] To

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Scheme 1. Synthesis of Methacrylate-Substituted PFSs

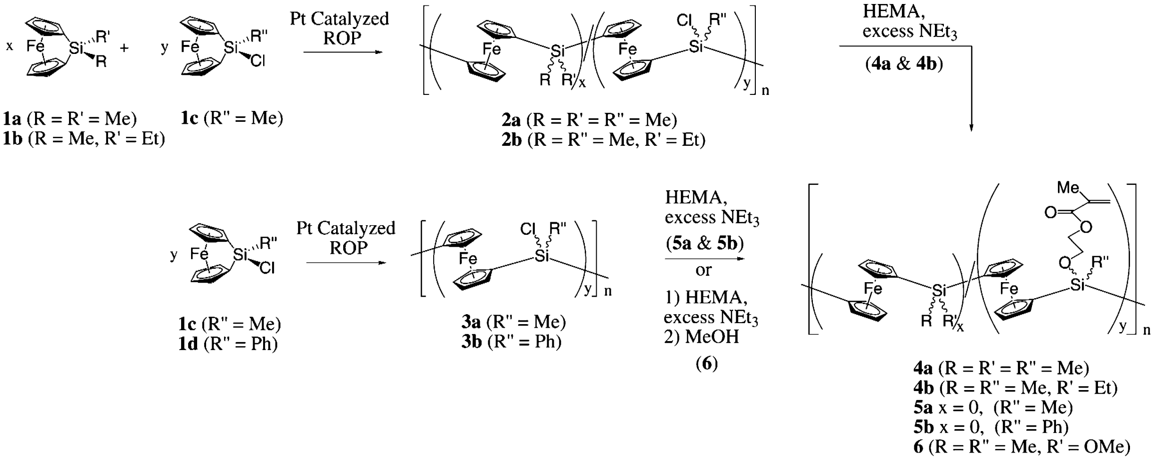

Table 1. Composition and GPC Data for Methacrylate-Containing Polymers 4−6

polymer	*x*:*y*	M_n[a]	PDI
4a	4:1[b]	33 200[d]	1.76
4b	4:1[b]	33 500[d]	1.86
5a	0:1	30 000	2.72
5b	0:1	31 000	1.82
6	1:1[c]	25 200	1.96

[a] Determined by GPC in THF, relative to polystyrene standards. [b] Estimated from ^{1}H NMR analysis in $CDCl_3$. [c] Estimated from ^{1}H NMR analysis in C_6D_6. [d] Estimated based on the corresponding methoxy-substituted derivative of **2**. See Supporting Information.

demonstrate the potential for control of the methacrylate content in the polymer, the random copolymer **6** was prepared by reacting **3a** with 0.5 mol equiv of HEMA, followed by the addition of excess MeOH (Scheme 1). ^{1}H NMR analysis confirmed the 1:1 ratio of the EMA and methoxy substituents in the polymer (Table 1).[21] As the T_g values of **5a** and **6** (both determined by DSC to be 16 °C) are below room temperature, the preparation of an analogous film-forming polymer with a T_g above room temperature was desirable. Variation of the substituents at Si in PFSs is known to allow tuning of the physical properties of the polymer, including the T_g.[8] Thus, the phenyl-substituted PFS **3b** was prepared from the corresponding [1]silaferrocenophane **1d**,[23] and after derivatization with HEMA, the homopolymer **5b**, with a T_g above room temperature, was isolated as a yellow powder.[24]

Photo-cross-linking of the polymers was initially briefly investigated in solution. Exposure of toluene solutions of the methacrylate-substituted PFSs **4**−**6** with ca. 5 mol % of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone to direct sunlight led to precipitation of gel-like particles in nearly quantitative yield over a period of several hours. Subsequent work focused extensively on photo-cross-linking of thin films of the polymers prepared by spin-casting from a solution of the PFS **5** or **6** (typically 2−10 wt % in chlorobenzene) and a photoinitiator onto glass or silicon substrates. The film thickness could be controlled from less than 100 nm to greater than 1 μm.[25] Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BPO) was chosen as the photoinitiator in the films as it has the advantage of absorbing light in the visible range[15] and absorbing strongly at ca. 375 nm, where PFS has a local minimum in its absorption spectrum.[8]

Using a shadow mask, thin films of the methacrylate-bearing PFSs containing codissolved BPO were irradiated with UV light for 30 min. Unexposed regions of the film were found to retain the solubility characteristics of **4**−**6**, and retention of the exposed areas on the substrate resulted upon rinsing with THF. The photo-cross-linked material was insoluble in all solvents for **4**−**6** (e.g., THF, CH_2Cl_2, toluene, chlorobenzene). FTIR monitoring of thin films of **5a** (with BPO) cast on silicon substrates before and after irradiation supports the successful cross-linking by photoinduced polymerization of the EMA side groups. The most notable changes in the IR spectra of the photo-cross-linked films are the complete disappearance of a band at 1679 cm^{-1}, assigned to υ(C═O) for BPO, and significant broadening of a band at 1720 cm^{-1}, assigned to the C═O stretching mode of the EMA group, as has been observed previously for photo-cross-linked EMA substituents on polymers.[26] In the absence of initiator, virtually no photo-cross-linking occurs.

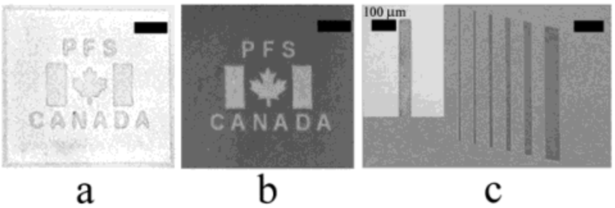

Figure 1. Photographic images of photolithographic relief patterns of polymer **5a** on silicon prepared with shadow masks. Patterns in (a) and (b) were prepared using inkjet printed masks which were the inverse of each other. Line patterns in (c) were prepared using a metal shadow mask (the inset shows the narrowest line at higher magnification). Scale bars (except inset in (c)) are 1 mm. Darker areas are covered with polymer.

Because of the successful photo-cross-linking of **4**−**6**, photolithographic patterning experiments were performed. Stencil masks printed from a standard inkjet printer onto transparencies were tested for large feature (millimeter scale) patterning on glass and silicon substrates and were found to work very effectively (see Figure 1a,b). Although the use of these masks limits the resolution of feature sizes achievable, this technique offers a simple, low-cost method for the controlled two-dimensional patterning of PFS networks over large areas.

We also investigated photopatterning of smaller feature sizes using PFSs **5** and **6**. Using a shadow mask, well-defined micron-size lines of photo-cross-linked PFS networks were successfully deposited with micron-size separations (Figure 1c). The patterning of micron scale

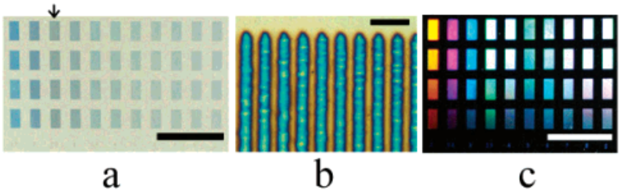

Figure 2. Photographic images of photolithographically printed diffraction grating patterns of **5a** on silicon of (a) large area pattern showing rectangular features, (b) close-up of a portion of a single rectangular feature (indicated in (a)) at 1500 times magnification, and (c) same area as in (a) showing the diffraction from the grating lines. Scale bar in (a) and (c) is 1 cm and in (b) is 10 μm.

features over large areas was also successfully demonstrated. Figure 2a shows a photolithographically patterned array of PFS networks on silicon created using a contact mask possessing diffraction gratings with line widths ranging from 1 to 10 μm. The smallest feature size that was reproducibly achieved was 3 μm, which was prepared from the 2.5 μm line width mask area (Figure 2b). The slightly wider lines of the relief image after etching relative to the mask features may be due to cross-linking of methacrylate side groups by free radicals that propagated beyond the edges of the exposure pattern. However, though not completely separated, features down to 1 μm were patterned, and strong diffraction from the PFS networks could be observed (Figure 2c). Current work is focused on more detailed studies of the photo-cross-linking parameters to optimize the conditions of the method and the resolution.

In summary, polyferrocenylsilanes bearing pendant photo-cross-linkable methacrylate groups have been synthesized. The effective photo-cross-linking and micron-scale photolithographic patterning has been demonstrated. These materials provide a simple method for the controlled photopatterning of organoiron polymer networks over several length scales from microns to centimeters. Efforts are also underway to control the material properties of the resulting photo-cross-linked networks for a variety of applications such as uses as magnetic film precursors and as electroactive gels.

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Supporting Information Available: Experimental details, synthetic procedures, and characterization data for polymers **3b** and **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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