

# Chemically amplified soft lithography of a low band gap polymer

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**A solid state, acid-catalyzed reaction leading to chemically amplified soft lithography is demonstrated with a low band gap conjugated polymer; poly({3-[11-(tetrahydropyran-2-yloxy)undecyl]thiophene-2,5-diyl}-3,4-ethylenedioxythiophene-2,5-diyl).**

$\pi$ -Conjugated polymers are promising materials with which to fabricate organic microelectronic and optoelectronic devices.<sup>1–4</sup> Due to their increasing complexity there is a growing need to deposit multi-layers of conjugated polymers in a spatially controlled fashion. Previous reports describing photolithography of conjugated polymers have been based on photocrosslinking, photoinduced doping/dedoping, photochemical structural transformation,<sup>5</sup> and chemically amplification.<sup>6</sup> Inexpensive soft photolithographic techniques<sup>7</sup> including micro-contact printing, lift-up and micromolding have also been investigated, as have ink-jet<sup>8</sup> and screen printing.<sup>9</sup>

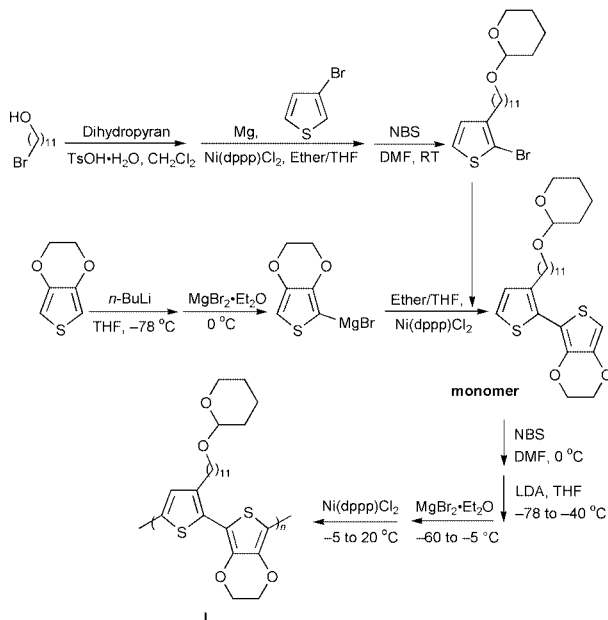
In this communication, a novel method for patterning conjugated polymer films is described. This technique, we term chemically amplified soft lithography, is demonstrated with a novel regioregular conjugated polymer; poly({3-[11-(tetrahydropyran-2-yloxy)undecyl]thiophene-2,5-diyl}-3,4-ethylenedioxythiophene-2,5-diyl) (**I**). 3,4-Ethylenedioxythiophene-based polymers are receiving considerable attention due to their low band-gap, high conductivity, stability and high transmittance contrast ratio between its reduced and oxidized states.<sup>10</sup>

Monomer {3-[11-(tetrahydropyran-2-yloxy)undecyl]thiophenediyl}-3,4-ethylenedioxythiophene and the analogous polymer, **I**, were synthesized according to Scheme 1.† Films of polymer **I** are deep purple in color exhibiting a  $\lambda_{\max}$  of 570 nm and a band-gap of  $\sim 1.67$  eV (740 nm). These values are

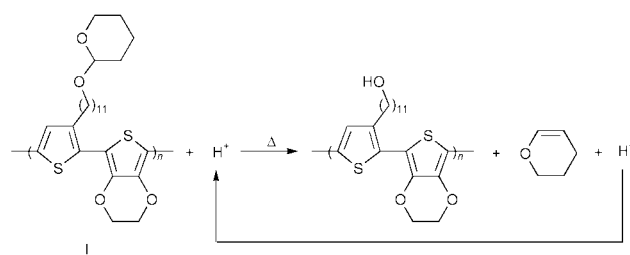
comparable to that of poly(3,4-ethylenedioxythiophenediyl) (PEDOT).<sup>11</sup>

The presence of the tetrahydropyran-2-yloxy alkyl side chain imparts solubility and reactivity.<sup>12</sup> Similarly to that reported for poly{3-[2-(tetrahydropyran-2-yloxy)ethyl]thiophenediyl} (PTHPET),<sup>13</sup> **I** undergoes a solid state acid-catalyzed reaction depicted Scheme 2. In the absence of acid, thermogravimetric analysis (TGA) (Fig. 1) shows that **I** is stable up to  $\sim 230$  °C but undergoes an 18% loss in mass between 230 and 270 °C. The observed weight loss is consistent with theoretical value of 17.6% corresponding to cleavage and volatilization of the tetrahydropyran moiety as dihydropyran. In the presence of 5% camphorsulfonic acid (mol% based on the thienyl unit) TGA (Fig. 1) indicates that elimination of THP occurs at a much lower temperature. 5 mol% acid is responsible for complete deprotection and thus provides evidence that the reaction is acid catalyzed, *i.e.*, chemically amplified. DSC indicated that the onset of the reaction decreased from  $\sim 230$  to 85 °C in the presence of acid. Reaction of the polymer was confirmed by FTIR, which showed the emergence of a broad peak at  $\sim 3400$   $\text{cm}^{-1}$  attributed to the formation of  $\omega$ -hydroxy groups, and a decrease in signals at  $\sim 2900$   $\text{cm}^{-1}$  corresponding to loss of THP-methylene.

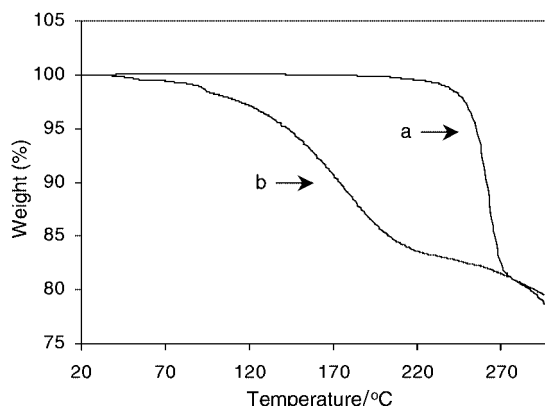
In a novel variation of chemically amplified photolithography and soft lithographic techniques, **I** was patterned by spatial deposition of acid onto the surface of a neat film (90 nm thick), followed by heating and development. In this process, shown schematically in Fig. 2, an ‘acidic ink’ comprising 0.01 M camphorsulfonic acid in THF–hexane was transferred to the



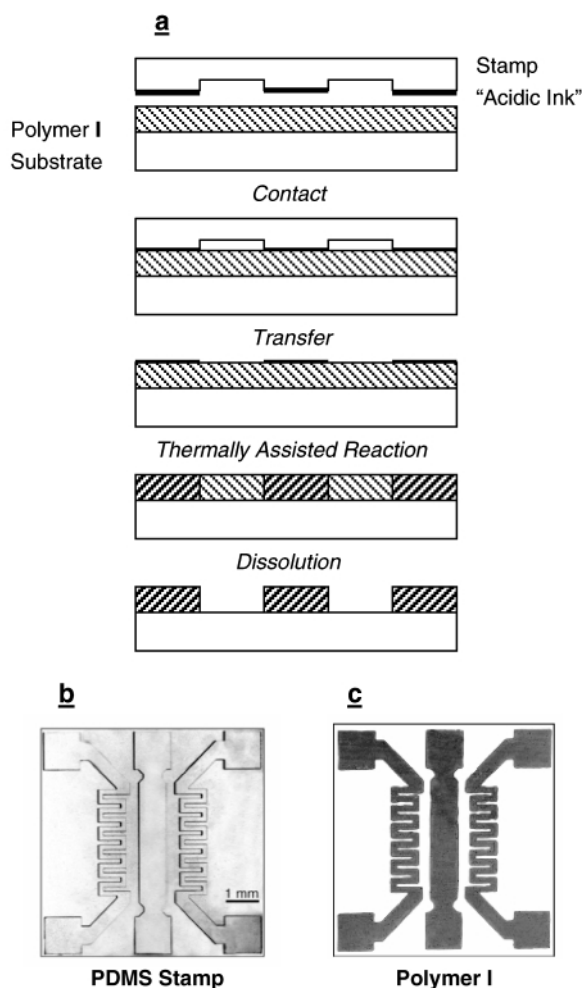
**Scheme 1** Synthetic scheme for monomer and polymer.



**Scheme 2** Acid-catalyzed elimination of dihydropyran from **I**.



**Fig. 1** TGA thermograms of **I**: (a) in the absence of acid and (b) in the presence of 5 mol% camphorsulfonic acid.



**Fig. 2** (a) Scheme depicting chemically amplified soft lithographic process. Micrographs of (b) PDMS stamp and (c) conjugated polymer patterns of **I**.

top of the film by way of a custom-made polydimethylsiloxane (PDMS) rubber stamp. Heating to 130 °C for just 10 s caused elimination of THP in the regions where acid was deposited. No reaction was observed to occur prior to heating as judged by FTIR analysis. The regions reacted were rendered insoluble by virtue of the residual hydroxy group and the overall change in polarity.<sup>6</sup> A positive image of the stamp was obtained by developing the film in solvent (Fig. 2).

Using UV-vis and FTIR spectroscopic analysis, it was found that 2.1  $\mu\text{g cm}^{-2}$  acid was typically transferred to the surface of film using the stamping procedure. The molar ratio of acid to thienyl rings is calculated to be 1 : 4 for a 90 nm thick film. The reaction is thus catalytic in acid and chemically amplified. FTIR of the imaged polymer film indicated a loss of THP and formation of  $-\text{OH}$  as described previously. UV-vis spectra of

the polymeric patterns were similar to **I** indicating that the conjugated polymer backbone is left intact. Furthermore, redox doping of the film with oxidants such as  $\text{FeCl}_3$  resulted in a color change from deep purple to transparent pale gray and an increase in transmittance from 46 to 91% at 570 nm (for a 50 nm thick film) indicating its potential suitability for patterned electrochromic devices. The conductivity of the doped form is  $12 \text{ S cm}^{-1}$ , on a par with poly(3-alkylthiophenediyl).

In summary, chemically amplified soft lithography is a non-photolithographic method that circumvents photochemical damage. Films are formed prior to patterning, which may allow for further control of film thickness, morphology, and adhesion over other deposition methods. Furthermore, since the patterned polymer is rendered insoluble, it is possible to deposit multiple layers of similar or dissimilar conjugated polymers. Evaluation of patterned films in field effect transistors, light emitting devices, and electrochromic devices is in progress.

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## Notes and references

† Analytical and spectroscopic data of monomer {3-[11-(tetrahydropyran-2-yloxy)undecyl]thiophenediyl}-3,4-ethylenedioxythiophene and the analogous polymer **I**. Monomer:  $^1\text{H NMR}$ : 7.23 (d,  $J = 5.2 \text{ Hz}$ , 1H), 6.92 (d,  $J = 5.2 \text{ Hz}$ , 1H), 6.36 (s, 1H), 4.57 (m, 1H), 4.24 (m, 4H), 3.92–3.82 (m, 1H), 3.73 (m, 1H), 3.54–3.44 (m, 1H), 3.38 (m, 1H), 2.67 (t,  $J = 7.9 \text{ Hz}$ , 2H), 1.83–1.21 (m, 24H). Elemental analysis: Calcd. for  $\text{C}_{26}\text{H}_{38}\text{S}_2\text{O}_4$ : C 65.21, H 8.00. Found: C 64.97, H 7.92. Polymer **I**:  $^1\text{H NMR}$ : 7.05 (s), 4.56 (s), 4.38–4.32 (m), 3.92–3.35 (m), 2.73 (s), 1.83–1.27 (m).  $M_w = 4000 \text{ g mol}^{-1}$ . Elemental analysis: Calcd. for  $\text{H}(\text{C}_{26}\text{H}_{36}\text{S}_2\text{O}_4)_n\text{Br}$ : C 63.97, H 7.46. Found: C 65.15, H 7.42.

- 1 H. Sirringhaus, N. Tessler and R. H. Friend, *Science*, 1998, **280**, 1741.
- 2 Z. Bao, A. Dodabalapur and A. J. Lovinger, *Appl. Phys. Lett.*, 1996, **69**, 4108.
- 3 A. R. Brown, D. M. Deleeuw, E. E. Havinga and A. Pomp, *Synth. Met.*, 1994, **68**, 65.
- 4 J. H. Burroughes, D. D. C Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539.
- 5 S. Holdcroft, in *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, vol. 4, John Wiley & Sons, Chichester, 1997.
- 6 J. Yu, M. Abley, C. Yang and S. Holdcroft, *Chem. Commun.*, 1998, 1503.
- 7 W. S. Beh, I. T. Kim, D. in, Y. Xia and G. M. Whitesides, *Adv. Mater.*, 1999, **11**, 1038.
- 8 T. R. Hebner and J. C. Sturm, *Appl. Phys. Lett.*, 1998, **73**, 1775.
- 9 Z. Bao, Y. Feng, A. Dodabalapur and A. Lovinger, *Chem. Mater.*, 1997, **9**, 1299.
- 10 L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, 2000, **12**, 481.
- 11 A. Kumar and J. R. Reynolds, *Macromolecules*, 1996, **29**, 7629.
- 12 K. A. Murray, S. C. Moratti, D. R. Baigent, N. C. Greenham, K. Pichler, A. B. Holmes and R. H. Friend, *Synth. Met.*, 1995, **69**, 395.
- 13 J. Yu and S. Holdcroft, *Macromolecules*, 2000, **33**, 5073.