

## Hybrid polymeric material bearing ferrocene based pendant organometallic functionality: synthesis and applications in nano-patterning using EUV lithography

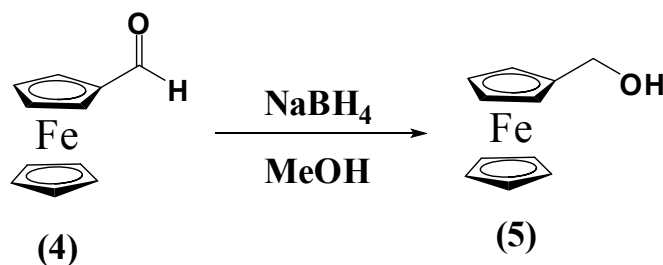
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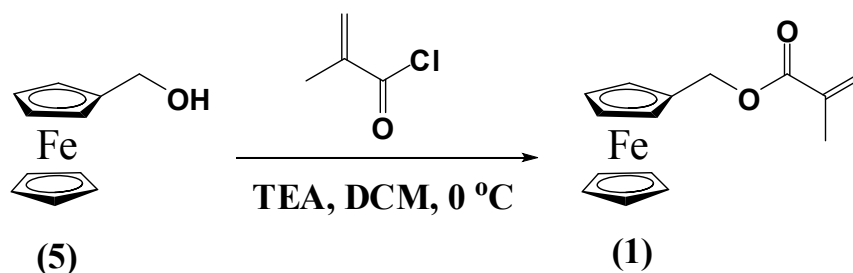
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### Supporting Information

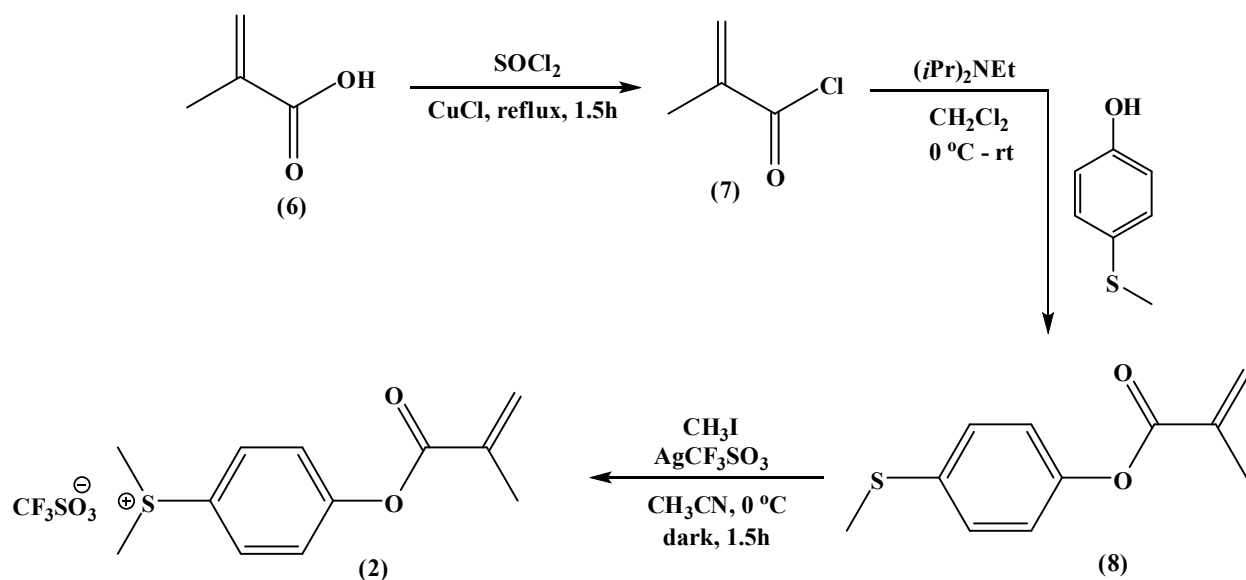
Step 1:



Step 2:



Scheme S1. Synthetic protocol for the FMMA monomer (1).



**Scheme S2:** Synthetic route for the MAPDST monomer (2).

## Experimental Section

### General:

Ferrocene carboxaldehyde and Triethylamine (TEA) were purchased from Sigma-Aldrich and used as received. (4-Methyl mercapto)phenol, methacrylic acid (MAA) and tetramethylammonium hydroxide (TMAH) were purchased from Acros Organics. Methyl iodide and thionyl chloride ( $\text{SOCl}_2$ ) were purchased from Loba Chemie. Tetrahydrofuran (THF) was dried using Na wire/benzophenone and acetonitrile ( $\text{CH}_3\text{CN}$ ) was dried using calcium hydride ( $\text{CaH}_2$ ). AIBN (Azobisisobutyronitrile) was purchased from Paras Polymers, India and recrystallized two times before using for polymerizations. Ferrocenemethanol, Ferrocenemethyl methacrylate, Methacryloyl chloride (7), 4-(methylthio)phenyl methacrylate (8) and MAPDST [(4-(methacryloyloxy)phenyl)dimethylsulfonium triflate] monomer (2) were prepared by following literature reported procedures.<sup>1,2,4</sup>

### *Procedure for the synthesis of Ferrocenemethanol (5):*

Ferrocenemethanol (5) was prepared by following the literature method reported by Christopher et al., 2011.<sup>1</sup> Ferrocenecarboxaldehyde (4.0 g, 18.7 mmol) was added to methanol (120 mL) under nitrogen atmosphere and cooled to 0 °C. Sodium borohydride (1.8 g, 47.6 mmol) was added portion wise over 2 h to the solution and stirred at room temperature overnight. The reaction mixture was quenched with aqueous ammonium chloride solution (0.5 M, 120 mL) and stirred for 30 min. Then, saturated sodium chloride solution (10 mL) was added and stirred for 5 min. The reaction mixture was extracted with dichloromethane (3 × 100 mL). The organic

fractions were combined, dried over magnesium sulfate, filtered, and vacuum dried to afford hydroxymethylferrocene as a yellow solid (3.7 g, 91.6%). M.p.: 76-78 °C.

*Procedure for the synthesis of Ferrocenemethyl methacrylate (1):*

Ferrocenemethyl methacrylate (**1**) was prepared by following the literature method reported by Christopher et al., 2011.<sup>1</sup> Hydroxymethylferrocene (1.0 g, 4.63 mmol) and triethylamine (6.1 g, 60.19 mmol) were dissolved in dry dichloromethane (60 mL) and cooled to 0 °C. Methacryloyl chloride (1.21 g, 11.57 mmol) was added to the solution dropwise over 20 min and allowed to stir at 0 °C for 2 h. The solution was then allowed to stir at room temperature overnight before washing with saturated potassium carbonate solution (2 × 200 mL). The organic layers were combined, dried over magnesium sulfate, filtered, and concentrated. The product was passed through a basic alumina column using dichloromethane as a solvent. The solution was collected, concentrated, and vacuum dried to afford a yellow solid (0.47 g, 35.9%). M.p.: 52-54 °C.<sup>2</sup>

*Procedure for the synthesis of Methacryloyl chloride (7):*

Methacryloyl chloride (**7**) was prepared by following the literature method reported by Lal and Green, 1995.<sup>3</sup> To a solution of glacial methacrylic acid 68.88 g. (800 mmol) and thionyl chloride 95.2 g. (800 mmol) 0.8 g. of cuprous chloride was added at room temperature. The reaction mixture was kept under stirring until the evolution of gases had ceased. The light brown liquid was gently refluxed for 1.5 h and then the water-white fraction boiling at 95-98 °C was collected as the product through distillation. Yield 60-70%.

*Procedure for the synthesis of 4-(methylthio)phenyl methacrylate (8):*

4-(Methylthio)phenyl methacrylate (**8**) was prepared by following the literature method reported by Brown et al., 2009.<sup>4</sup> To a stirred solution of 4-(methylmercapto) phenol (31.72 g, 226.24 mmol) and *N,N'*-diisopropylethylamine (32.16 g, 248.87 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (120 mL) was added dropwise methacryloyl chloride (23.54 g, 225.18 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0 °C under nitrogen. The solution was stirred for 1.5 h at 0 °C and then overnight at room temperature. The dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was then removed using rotary evaporator. Tetrahydrofuran (THF) (150 mL) was added to dissolve the crude product; and the separated *N,N'*-diisopropylethylamine hydrochloride salt was filtered off. The THF was removed using rotary evaporator, and the product redissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic layer was washed with HCl (0.01 M aqueous; 60 mL) then water (2 x 60 mL), dried over anhydrous MgSO<sub>4</sub>, and filtered. The resulted dried organic phase was concentrated in vacuo and the crude product was purified through column chromatography using hexane as eluent to get the pure product, 4-(methylthio)phenyl methacrylate, as white crystalline substance. Yield: 35.5 g, 75%. Mp. 48-50 °C. IR absorption:  $\nu_{\max}$ /cm<sup>-1</sup> 2980 and 2918 (CH), 1730 (C=O), 1638 and 1489 (C=C), 1297 and 1225 (C-S), 1167 and 1085 (C-O).<sup>4</sup>

*Procedure for the synthesis of MAPDST Monomer (2):*

To a solution of 4-(methylthio)phenyl methacrylate (10.0 g, 48 mmol) and silver trifluoromethanesulfonate (12.34 g, 48 mmol) in acetonitrile (80 mL) was added dropwise iodomethane (3.0 mL, 48 mmol) in acetonitrile (20 mL) at 0 °C under nitrogen in the dark. The solution was stirred for 1.5 h at 0 °C and the precipitated silver iodide was filtered off and washed thoroughly with acetonitrile. Acetonitrile was removed from the collected filtrates using rotary evaporator and the crude product was recrystallized from hot THF, giving the pure product, MAPDST, as white crystals. Yield: 11.7 g (65%). Mp. 144-146 °C. IR absorption:  $\nu_{\max}/\text{cm}^{-1}$  3033 and 2932 (CH), 1735 (C=O), 1638 and 1585 (C=C), 1254 and 1220 (CF<sub>3</sub>), 1172 and 1124 (anti-SO<sub>3</sub>), 1032 (symm-SO<sub>3</sub>). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\text{H}}$  = 8.14 (2H, d, *J* = 8.3 Hz, *m,m'*-ArH), 7.57 (2H, d, *J* = 8.3 Hz, *o,o'*-ArH), 6.32 (1H, s, C=CH), 5.95 (1H, s, C=CH), 3.27 (6H, s, S(CH<sub>3</sub>)<sub>2</sub>), 2.01 (3H, s, CH<sub>3</sub> aliphatic); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>):  $\delta_{\text{C}}$  = 165.30 (C=O), 155.01, 135.35, 132.23, 129.17, 124.59, 124.24 (aromatic), 28.90 (SCH<sub>3</sub>), 18.44 (CH<sub>3</sub>).<sup>2,3</sup> HRMS (EI): *m/z* [M<sup>+</sup>] calcd. for C<sub>12</sub>H<sub>15</sub>O<sub>2</sub>S: 223.0787; found: 223.0794 and *m/z* [M<sup>-</sup>] calcd. for CF<sub>3</sub>O<sub>3</sub>S: 148.9526; found: 148.9524.<sup>4,5,6</sup>

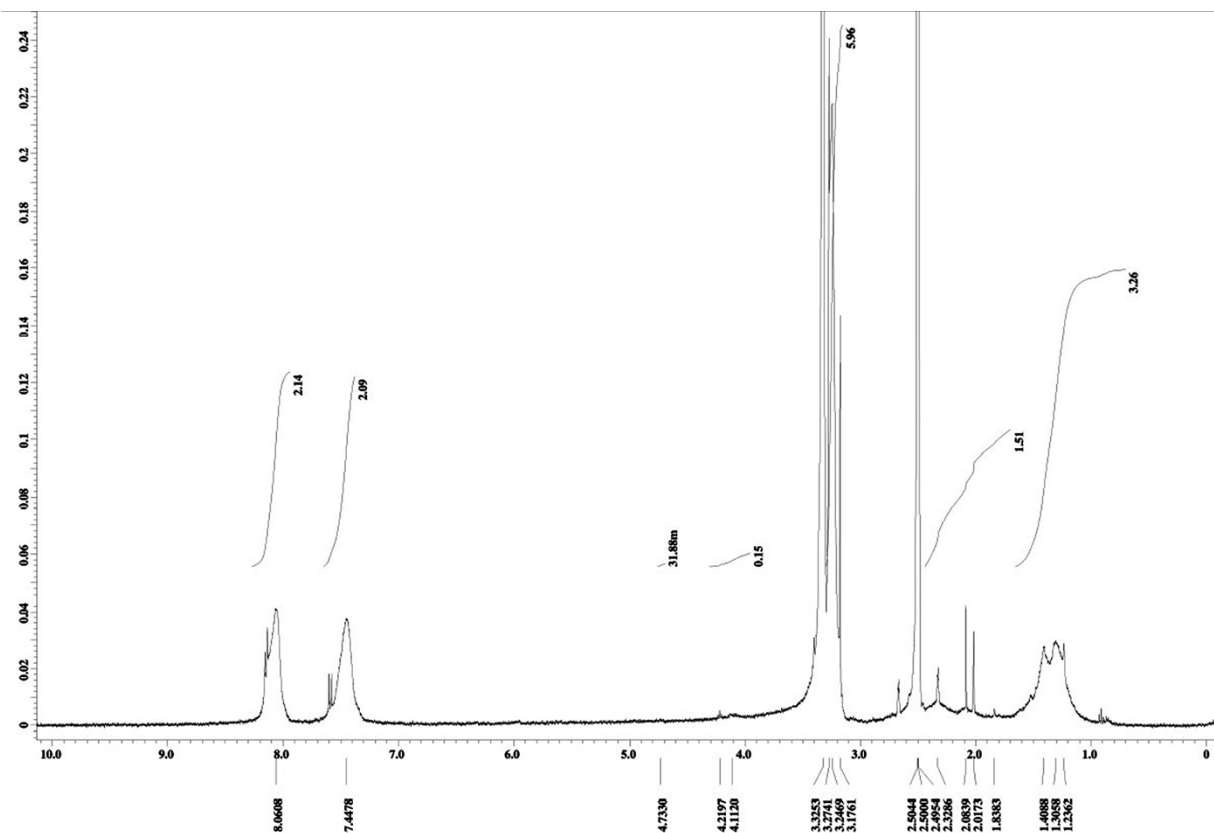
*Procedure for the synthesis of MAPDST-FMMA copolymer (3):*

MAPDST monomer (**2**) (0.9 g, 2.417 mmol), ferrocenemethylmethacrylate (FMMA, **1**) (0.1 g, 0.352 mmol) and AIBN (1% by weight, relative to both the monomers) were dissolved under N<sub>2</sub> in a mixture of THF-CH<sub>3</sub>CN (2:1) in a vial with a side arm and the resulting solution was siphoned to the polymerization flask equipped with a silicone septum and a Teflon stirring bar. The mixture, after five freeze-thaw-cycles, was left under magnetic stirring at 60 °C for 48 hours under N<sub>2</sub> atmosphere. After completion, the reaction mixture was poured slowly into diethyl ether (50 mL) and the separated solid was washed with dichloromethane (DCM). The resulting crude product was dissolved in methanol and then re-precipitated using diethyl ether. The separated white pure product was filtered and dried in a temperature controlled hot air oven at 50 °C for 1 day. Yield: 380 mg (38.0 %). Pale red colour solid. FT-IR:  $\nu_{\max}/\text{cm}^{-1}$  3021 and 2989 (CH), 1753 (C=O), 1587 and 1497 (aromatic C=C), 1261 (CF<sub>3</sub>), 1173, 1031 (substituted and unsubstituted cp ring with Fe). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta_{\text{H}}$  8.06 (2H, br s, *m,m'*-ArH), 7.44 (2H, br s, *o,o'*-ArH), 4.73 (2H, broad peak, OCH<sub>2</sub>), 4.21 & 4.11 (9H, br m, substituted and unsubstituted cp ring hydrogens), 3.24 (6H, s, S(CH<sub>3</sub>)<sub>2</sub>), 2.08 & 2.38 (2H, br peak, CH<sub>2</sub> polymeric), 1.23, 1.30 & 1.40 (3H, br peak, CH<sub>3</sub> aliphatic); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta_{\text{C}}$  174.38 (C=O), 153.59, 132.18, 131.77, 128.73, 124.43, 124.07, 123.15, 121.90, 119.32, 117.18, 113.99 (aromatic, CF<sub>3</sub>), 45.39 (CH<sub>2</sub>), 28.86 & 28.41 (SCH<sub>3</sub>), 17.94 (CH<sub>3</sub>). <sup>19</sup>F NMR (470 MHz; DMSO-*d*<sub>6</sub>)  $\delta_{\text{F}}$  -77.61 (3F, s, CF<sub>3</sub>).

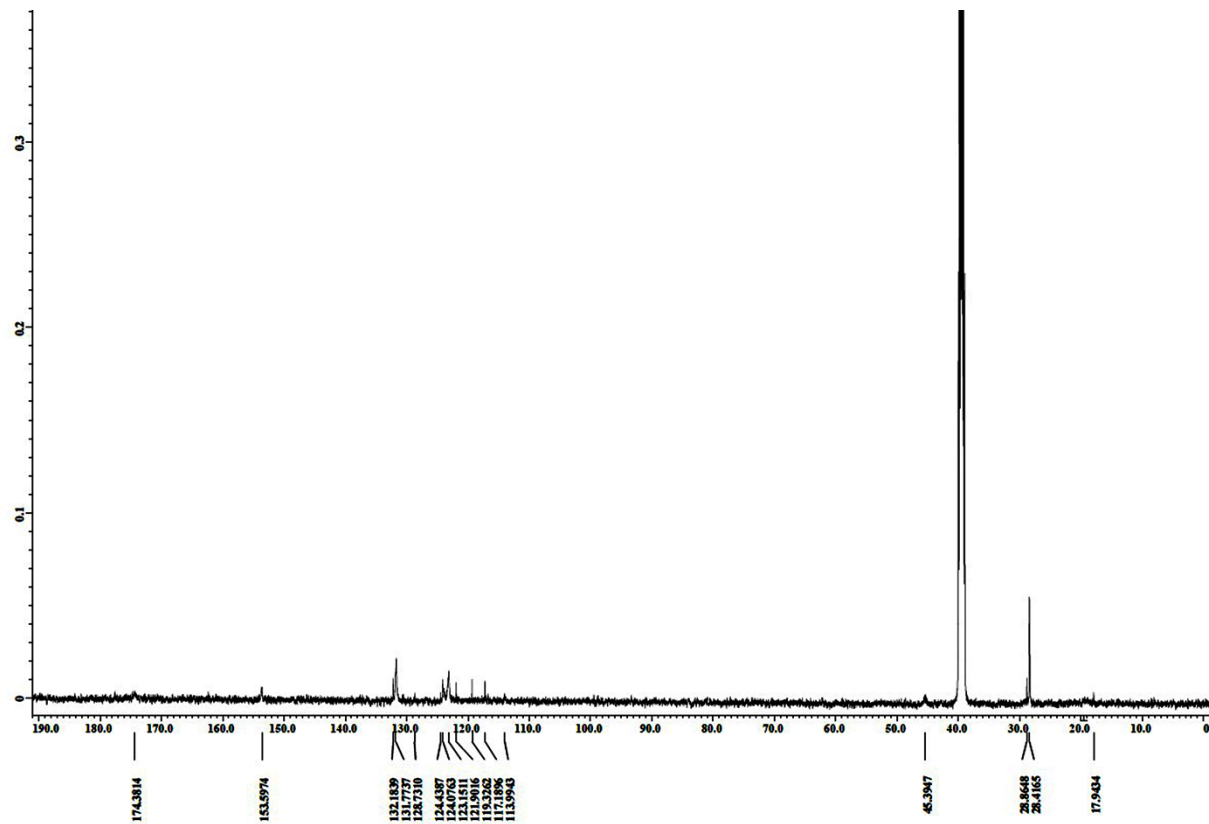
## References:

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6. V. S. V. Satyanarayana, F. Kessler, V. Singh, F. R. Scheffer, D. E. Weibel, S. Ghosh and K. E. Gonsalves, *ACS Appl. Mater. Interfaces*, 2014, **6**, 4223-4232.

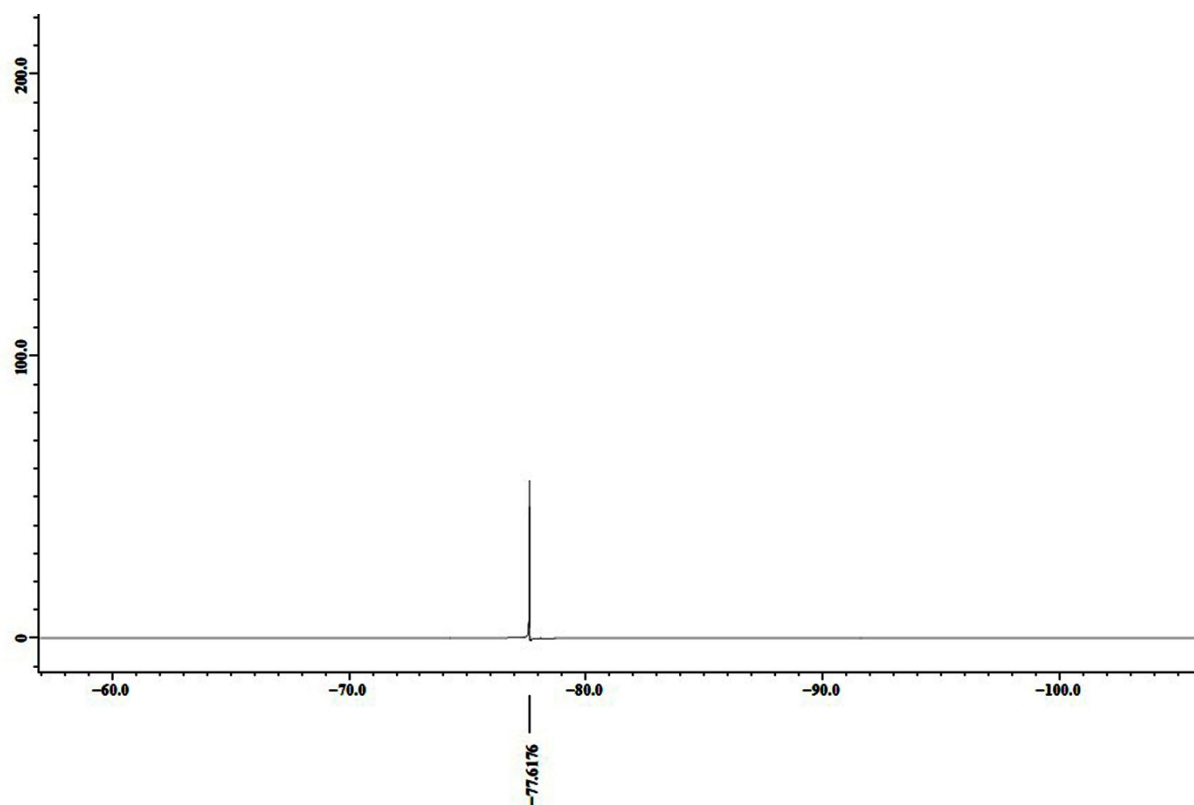
**Figure S1.**  $^1\text{H}$  NMR Spectrum of MAPDST-FMMA Copolymer (**3**):



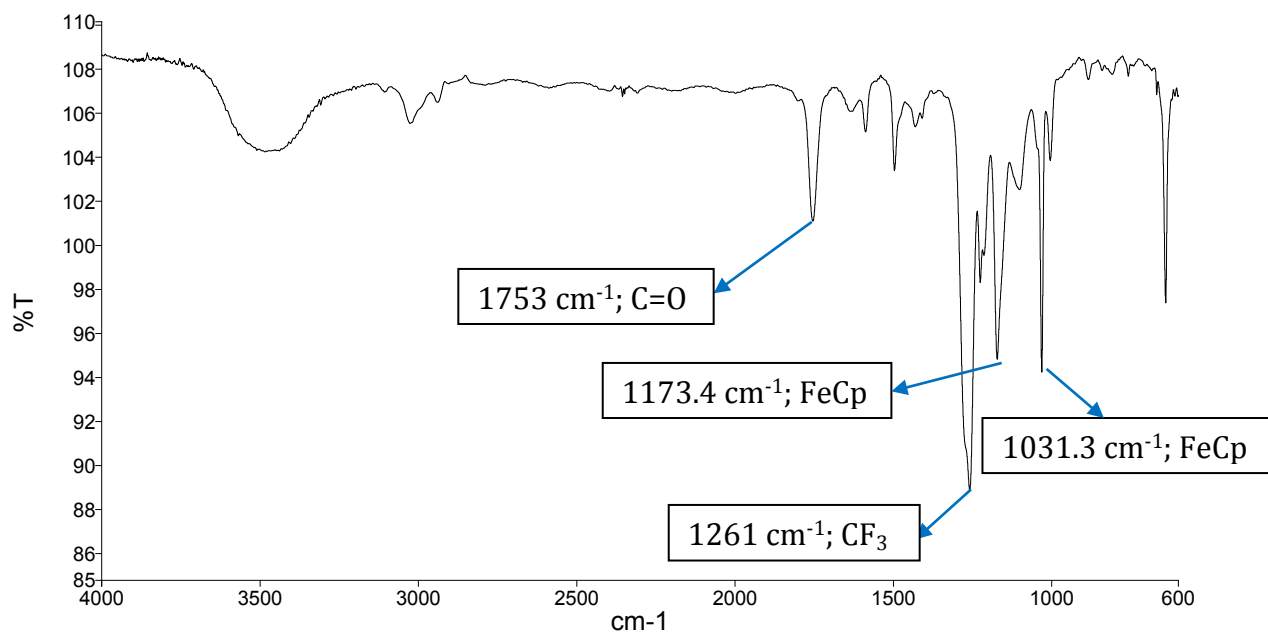
**Figure S2.**  $^{13}\text{C}$  NMR Spectrum of MAPDST-FMMA Copolymer (**3**):



**Figure S3.**  $^{19}\text{F}$  NMR Spectrum of MAPDST-FMMA Copolymer (**3**):



**Figure S4.** FT-IR Spectrum of MAPDST-FMMA Copolymer (**3**):



## **RESIST PROCESSING - LITHOGRAPHY**

### **Substrate Coating:**

Resist solution was prepared using polymer 2% by weight in methanol by subsequent filtration through a 0.2  $\mu\text{m}$  Teflon<sup>®</sup> filter and was used in all experiments. For EUV exposure evaluation, resist solutions were spin-coated on HMDS treated 200 mm Silicon wafer for around 40 nm thin films followed with a soft-bake.

### **Softbake:**

The resist films were subjected to soft-bake at 100 °C on a hotplate and the soft-bake was given for 90 sec. At this temperature the resist did not appear to be sensitive to this soft-bake time. However, in order to dry out the solvent completely we had to apply soft-bake for 90 sec.

### **Exposure Parameters:**

The photoresist coated thin films were flood exposed with the respective  $E_0$  array using SEMATECH Berkeley Microfield Exposure Tool (MET) which is a high resolution EUV (13.5 nm) lithography tool. Samples were exposed using mask IMO228775 with Field of R4C3.

### **Post-exposure bake:**

To obtain good resist mask edges we followed post-exposure bake (PEB) method. The substrate was put on the hot plate set to 115 °C for 90 sec. The decomposition temperature ( $T_d = 238.9$  °C) of MAPDST-FMMA copolymer suggest that post-exposure bake temperature may be increased up to 200 °C without risk of unexposed cross-linking.

### **Development:**

Development was completed for the exposed samples of MAPDST-FMMA copolymer in 0.003 N tetramethyl ammonium hydroxide (TMAH) solution prepared in DI water by maintaining pH = 11.5 at room temperature for 8 sec, rinsed in de-ionized water for about 10 sec and then blow dried with pure nitrogen gas

0.003 N TMAH developer solution was prepared by adding 0.00714 gram of TMAH in 25 mL DI water and the pH of the developer solution was maintained at 11.5.

### **Imaging:**

Resolution and image quality were determined by examining the developed resist profiles with HRSEM images, which were taken using Nova Nano SEM 450 FEI instrument HRSEM at JMI Central University, New Delhi, India.