Supporting information

**Metal-Carbonyl Organometallic Polymers, PFpP, for High-Resolution Positive and Negative Electron Beam Lithography Resist**

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**Materials and instrumentation**

All experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques unless otherwise indicated. THF was freshly distilled under nitrogen from Na/benzophenone. Toluene was dried with molecular sieves before use. Sodium (Na), 1-bromo-3-chloropropane, potassium (K) were purchased from Sigma-Aldrich. Cyclopentadienyl iron dicarbonyl dimers (Fp₂) were purchased from Strem Chemicals Inc. Chlorodiphenylphosphine was purchased from Tokyo Chemical Industry (TCI). Benzophenone was purchased from Fisher Scientific. All chemicals were used as received unless otherwise indicated.

\(^1\)H, \(^{31}\)P NMR spectra were obtained on a Bruker Avance 300 (\(^1\)H NMR: 300 MHz, \(^{31}\)P NMR: 120 MHz) spectrometer at ambient temperature using appropriate solvents. NMR samples were prepared under dry nitrogen atmosphere unless otherwise indicated.

Fourier transform infrared spectroscopies (FT-IR) were recorded using a Perkin Elmer Spectrum RX I FT-IR system. The samples were ground with KBr and then pressed into transparent pellet.

Molecular weights and molecular weight distributions, Mₔ/Mₙ, were characterized using GPC analysis at room temperature with THF as eluent at a flow rate of 1.0 mL/min. The Viscotek GPC max unit used was equipped with a VE 2001 GPC, three PolyAnalytik organic mixed bed columns, PAS-103-L, PAS-104-L, and PAS-105-L, with dimension of 8 mm (ID)×300 mm (L) each and a Viscotek triple detector array, including refractive index, viscosity, and dual-angle light scattering detectors.

**Synthesis of and characterization PFpP**

PFpP is prepared via migration insertion polymerization (MIP) of CpFe(CO)₂(CH₂)PPh₂ in bulk at 105 °C. After 20 h, the polymerization was terminated by cooling down the reaction flask to room temperature. Small amount of THF was added to dissolve the crude product; the crude product was purified via
precipitation into a large amount of hexane and this precipitation procedure was repeated for three times. Finally, the product was collected by filtration and dried under vacuum at room temperature for 24 h. $^1$H NMR (CDCl$_3$): 7.6-7.1 ppm (b, 10H, C$_6$H$_5$), 4.4-4.0 ppm (b, 5H, C$_5$H$_5$), 2.8-2.60 ppm (b, 1H, COCH$_2$), 2.4-2.1 ppm (b, 1H, COCH$_2$), 2.1-1.8 ppm (b, 2H, CH2P), and 1.4-0.8 ppm (b, 2H, CH2CH2CH2).$^{31}$P NMR (CDCl$_3$): 73 ppm, 35 ppm. FT-IR: terminal CO stretching frequency is 2000 and 1911 cm$^{-1}$, acyl CO stretching frequency is 1600 cm$^{-1}$.

FT-IR and $^{31}$PNMR of the resultant polymers are shown in Figure S1(a). Upon the polymerization, the two peaks at 2007 cm$^{-1}$ and 1953$^{-1}$ corresponding to terminal CO in FpP monomer shift to lower frequencies. Particularly, one CO signal appears at 1600 cm$^{-1}$, suggesting acyl CO was formed as a result of migration insertion reaction. $^{31}$P NMR shown in Figure S1(b) also illustrates that the coordination of phosphine to Fe occurred, as chemical resonance for the phosphine in FpP shifts from -15 ppm to 73 ppm. The very weak chemical shift at 35 ppm is attributed to the oxidized phosphorus at PFpP chain end. As such, both FT-IR and $^{31}$P NMR results confirmed the occurrence of migration insertion reaction.

Figure S1. (a) FT-IR of FpP and PFpP; (b) $^{31}$P NMR of FpP and PFpP in CDCl$_3$. 
Figure S2. $^1$H NMR of PFpP produced from bulk polymerization at 105 °C in CDCl$_3$.

The chemical structure of the polymers was also characterized by $^1$H NMR in CDCl$_3$. As shown in Figure S2, the chemical shift at 7.6-7.1 ppm corresponds to the phenyl group; and the resonance signal due to the protons in the Cp ring appears at 4.3 ppm. The integration ratio for these two peaks is 2.2, which is closed to the theoretical value of 2.0. The chemical shift for the propyl spacer appeared at 2.8-0.8 ppm, within which the peaks at 2.8 and 2.4 ppm represent diastereotopic protons from CH$_2$ adjacent to acyl group. GPC analysis reveals that the polymer has M$_n$ of 8200 g/mol with PDI of 1.35.

Preparation of PFpP film by spin coating and electron beam lithography.

To prepare a PFpP thin film by spin-coating, the polymer was dissolved in toluene (1 % by weight) and the solution was filtered by PTFR membrane with pore size of 0.22 μm. Then the resist was spin-coated on a cleaned silicon substrate and baked at 100°C for 5 min, which gave a uniform film with thickness of 67 nm. Electron beam lithography was carried out using Raith 150\textsuperscript{TW}O system with 20 kV acceleration voltages and 1.4 nA beam current. To obtain a contrast curve, the resist film was exposed with an area dose from 0.1 mC/cm$^2$ to 10 mC/cm$^2$. To explore its resolution capability, line arrays with period from 20 nm to 500 nm were exposed with a line dose ranging from 15 nC/cm to 150 nC/cm, and from 3 nC/cm to 30 nC/cm, for negative and positive tone, respectively.

Investigation of PFpP as negative and positive resist.

To study its negative tone behavior, the developer should be able to dissolve the unexposed area, but not the exposed and thus cross-linked area. Many solvents satisfy
this criterion, and we developed the resist using THF and anisole, both for 1 min, followed by rinsing with 2-propanol (IPA). As for positive tone, the developer should be strong enough to dissolve the exposed area having drastically reduced molecular weight due to chain scission upon exposure to electron beam, yet weak enough to not severely attack the unexposed area. To start with, we examined the two most popular developers used respectively for positive resist PMMA and ZEP-520 (Zeon Corporation), namely methyl isobutyl ketone (MIBK) : IPA = 1:3 and amyl acetate. The exposed resist was developed for 30 sec for MIBK : IPA and 1 min for amyl acetate, followed by rinsing with IPA before drying. After development, the contrast curve was obtained from measurement using Dektak 8 Stylus Profilometer, and the high resolute structure was imaged using scanning electron microscope (SEM) and atomic force microscope (AFM).

**PFpP’s resistance to dry plasma etching.**

To study PFpP’s resistance to dry plasma etching, O₂ reactive ion etching (RIE, 20 sccm O₂ gas flow, 20 mTorr pressure and 20 W RF power) was carried out using a Phantom II RIE system (Trion Technology Inc.). The etching rate of the synthesized PFpP resist was compared with the most popular EBL resist PMMA and ZEP-520A under the same etching condition.

![Contrast curve of PFpP showing negative tone](image)

**Figure S3.** Contrast curve of PFpP showing negative tone
**Figure S4.** SEM image of exposed line array pattern with 80 nm period developed by MIBK:

IPA = 1:3