Effect of molecular weight on the feature size in organic ice resists

Supporting Information

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Patterning OIR in ETEM: experimental procedure and guidelines

ETEM gas system. The environmental transmission electron microscope (ETEM) used in our experiments is equipped with a gas chamber where a pumping system introduces gases into the column at pressures of up to 10 mbar. Two pressure-limiting apertures separate the gas chamber from the rest of the column. A detailed description of the environmental system design can be found in reference[1]. Figure S1 shows the simplified schematics of the connections between the column and the pumping system. The glass vial with the organic precursor is attached to one of the gas lines and connected to the column through a valve $V_{Gl\text{-}S}$. Gas is introduced into the column through the gas inlet line, and is pumped out through two exhaust lines positioned below and above the specimen. A third exhaust line is connected through the valve $V_{By\text{-}S}$. During our experiments, we keep $V_{By\text{-}S}$ closed to provide better pressure stabilization. The precursor source is also connected to the exhaust system through the valve $V_{Exh\text{-}Gl}$, which is used to pump down the glass vial before the experiment.

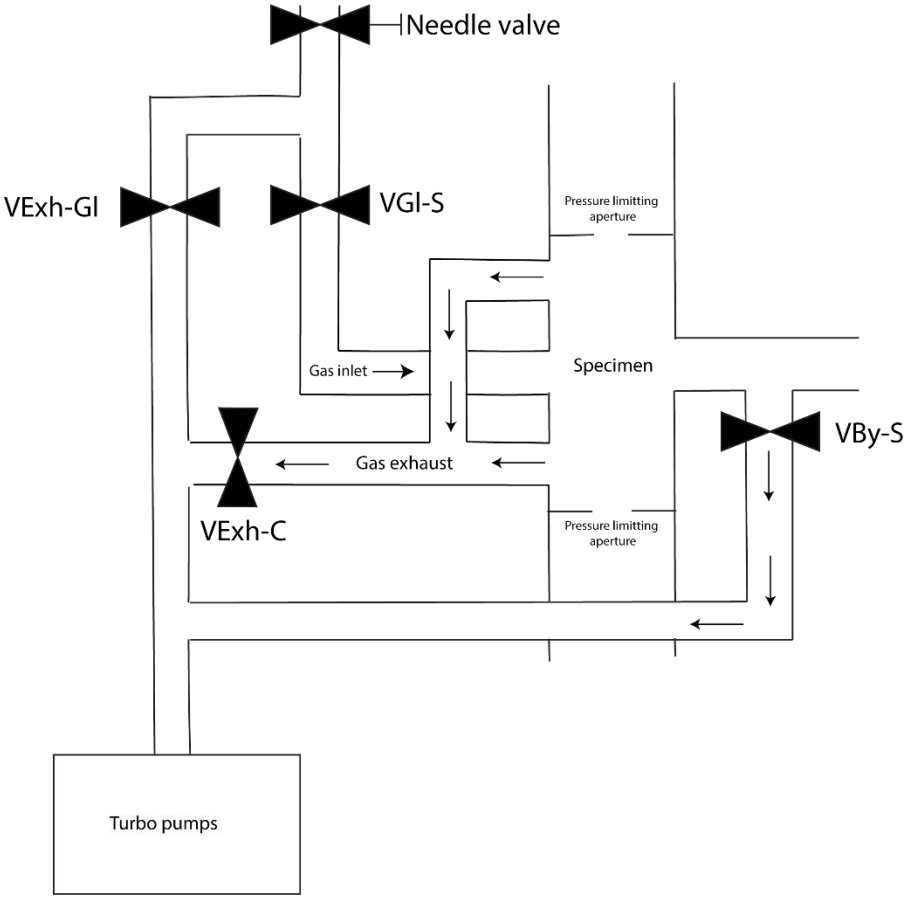

Figure S1. Simplified ETEM schematics.

Cryo-transfer holder. We used a single-tilt cryo transfer holder equipped with a temperature controller from Gatan. The holder is equipped with a protective sample shutter, which is used to control the ice thickness (see below).

Organic precursors. We have used commercially available anhydrous n-octane, n-undecane and n-tetradecane with nominal purity ≥ 99 % purchased from Sigma Aldrich.

Preparations for the experiment. Before the experiment, the vial is attached to the exhaust line and pumped down to remove air and water vapor. The gas lines need a baking cycle if other gases were used previously. The cryo holder dewar is pumped down and the holder is inserted into the microscope 1-2 hours before starting the patterning to reduce contamination.

Cooling procedure. After liquid nitrogen is poured in the cryo holder dewar, it takes around 30 min for the sample to cool down from room temperature to about -180^{o}C, and about 15-20 minutes for

the temperature to stabilize. It is important to keep the protective sample shutter closed during cool down to prevent water vapor condensation on the substrate. The pressure in the gas cell will typically drop from 3×10^{-6} mbar to 1.7×10^{-7} mbar. During cool down the holder drifts up to 200 µm in the direction perpendicular and up 30 µm in the direction parallel to the holder axis.

Substrate assessment and STEM alignment. After the cryo holder is cooled down, the protective sample shutter can be opened to check the substrate for contamination and to identify the regions to be patterned. This is carried out in bright-field TEM mode. After the survey, the microscope is switched in STEM mode, loading pre-recorded alignment settings. However, manual fine tuning of focus and condenser astigmatism are always needed. Since our microscope is not equipped with a probe corrector, we rely on Ronchigrams to estimate the quality of alignment.

Ice deposition: stabilizing pressure. Before deposition the column valve is closed and the sample is covered with a protective sample shutter. Valves $V_{By\text{-}S}$ and $V_{Exh\text{-}Gl}$ are closed, while $V_{Gl\text{-}S}$ is opened. After that, the needle valve connected to the glass vial is opened until the desired pressure in the gas cell is stabilized.

Ice deposition: condensation on substrate. After pressure stabilizes, the protective sample shutter is opened so the precursor vapor can condense on the substrate. The time during which the shutter remains open determines the deposited ice thickness. Typical values of gas pressure and duration of shutter opening for various precursors, which were used to deposit 10-12 nm thick ice layers, are listed in Table S1. Ice thickness was estimated using collapsed features. After deposition, the protective sample shutter is closed, the glass vial needle valve is closed, and valves $V_{By\text{-}S}$ and $V_{Exh\text{-}Gl}$ are opened to pump down the remaining vapor. During ice condensation the sample temperature usually increases by 4-6 ^{o}C. After deposition, it will decrease again producing drift. Patterning cannot commence before the temperature stabilizes (~20-30 min) and drift ceases. The whole procedure together with pumping down the precursor and temperature stabilization takes 40-90 minutes, depending on the precursor.

	Octane	Undecane	Tetradecane
Gas pressure (10^{-3} mbar)	4.0	4.6	4.0-4.4
Shutter opening time (s)	30	20	60

Table S1. Typical gas pressure and protective sample shutter opening times required to obtain a 10-12 nm thick layer of ice.

Patterning. The patterning is carried out in STEM mode using a standard FEI TEM User Interface software. The beam is blanked between exposures using the STEM "Blank" function. At the beginning and at the end of each exposure, just after/before unblanking/blanking, the beam is placed in a 'parking position' by the software, so one of the corners of the pattern will be overexposed (see Figure S2).

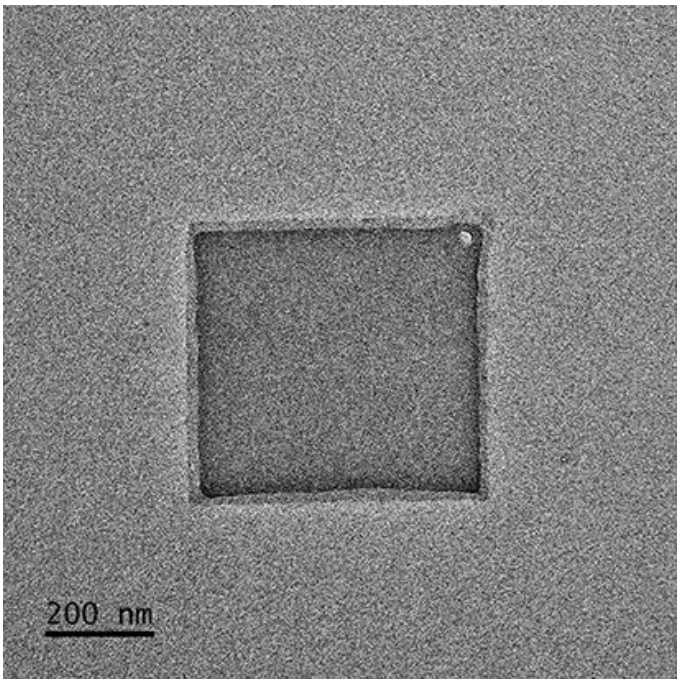

Figure S2. "Parking position" effect on the deposit: the top right corner is overexposed by the electron beam.

Patterning square areas. Area patterns are obtained by the STEM imaging option. The size of the area is defined by STEM magnification. The dose is set by choosing magnification (pixel size), number

of pixels, dwell time per pixel and beam current. Typical parameters are listed in Table S2, except for the beam current, which is discussed below. The minimum dwell time available is 0.1 µs.

Patterning lines. Lines are patterned using "Experiments → Spectrum Profile" menu. The relevant parameters here are STEM magnification, line length, number of dots per line, dwell time per dot and beam current (see Table S2). The minimum dwell time per pixel available is 10 ms.

Patterning tips. Maintaining focus is essential to achieve good resolution. The Si_3N_4 substrate is not ideally flat, so after moving from one sample position to another (if the distance is larger than 1-3 µm), the focus has to be checked and readjusted if needed using the Ronchigram. It is also important to define and check patterning areas in advance to make sure that there are no dust particles or defects.

Areas			Lines			
STEM magnification (x1000)	Number of pixels	Dwell time per pixel, (µs)	STEM magnification (x1000)	Line length (nm)	Line profile size (dots per line)	Dwell time per dot (ms)
80-320	1024x1024	0.1-400	115	360	100	10

Table S2. Typical STEM parameters for area and line patterning.

Setting the beam current. The beam current is set by adjusting the monochromator "focus" value, which actually changes the strength of the gun lens. When the monochromator is operated in unfiltered mode, changing "focus" simply disperses and condenses the beam illuminating the C2 aperture, thereby changing the number of electrons passing through it. The beam current can also be adjusted by changing excitations of the condenser lenses. However, to keep the alignment stable we fixed the condenser system and used the smallest C2 aperture (50 µm) to create the smallest possible beam spot size in absence of a probe corrector. The beam current was measured using pre-calibrated CCD camera. Figure S3 shows a set of Ronchigrams taken at different values of the monochromator focus. The exposure time was t_e=0.04 s. The number of electrons N_e was extracted

from the region marked with red circle. The current as a function of monochromator focus is plotted in Figure S4.

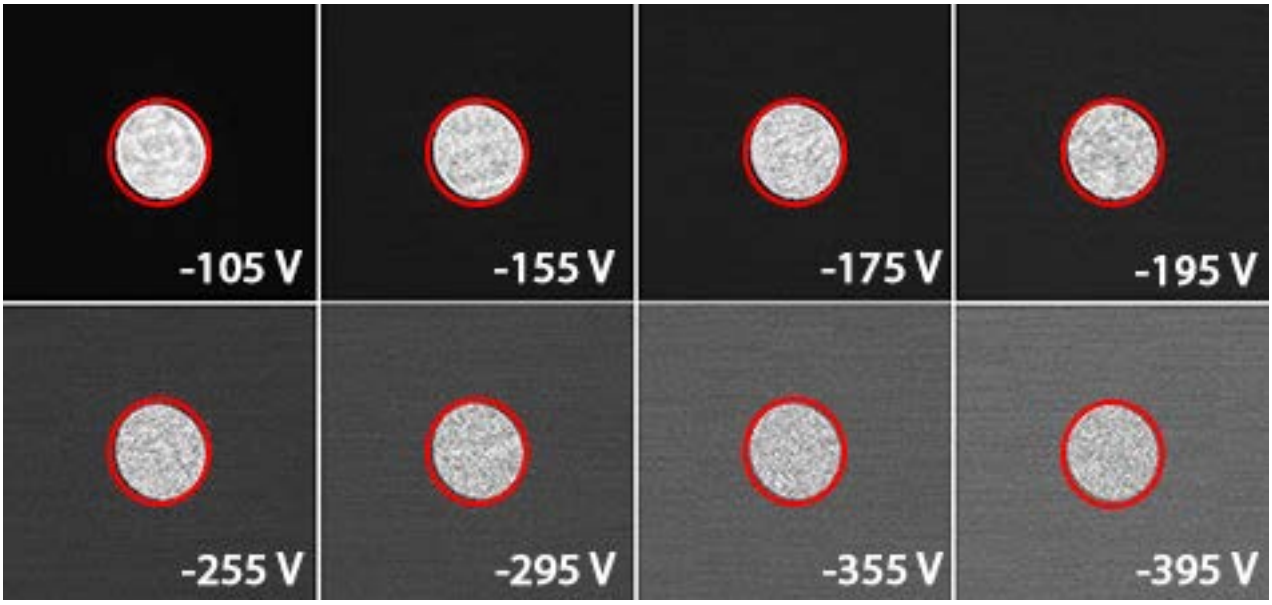

Figure S3. Beam images for different values of the monochromator "focus" (strength of the gun lens). Red circles mark the image areas from which the number of electrons was measured.

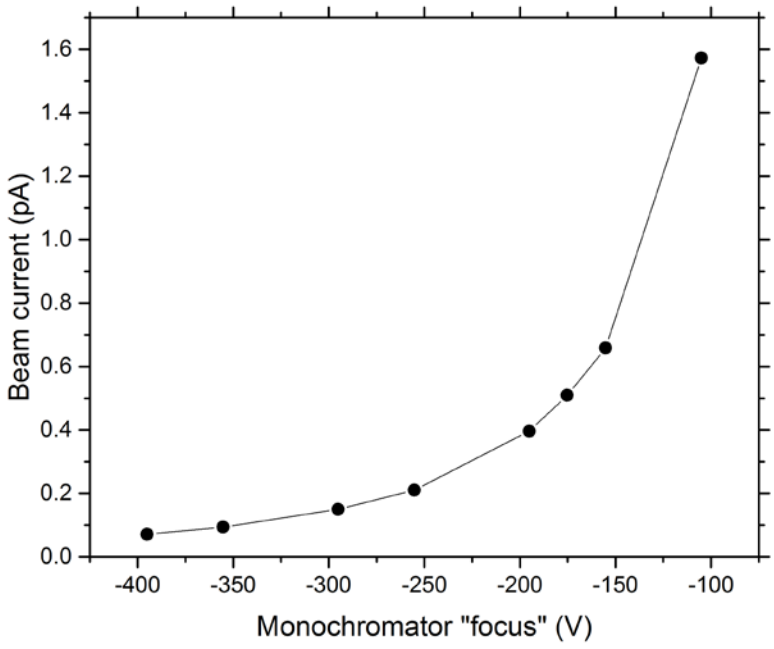

Figure S4. Beam current for different values of the monochromator focus

Warming up. As the holder heats up, the ice sublimates away from the substrate and holder tip, and the pressure in the gas chamber increases. At -100 °C an increase in pressure from 1.7×10^{-7} mbar to $1.2\text{-}1.5\times10^{-6}$ mbar is observed due to water vapor sublimation from the holder tip. Ice sublimation takes place in the temperature range -65-55 °C and the pressure usually raises to $10^{-5}\text{-}10^{-3}$ mbar, depending on the ice and its thickness. It is important to wait until the holder reaches and stabilizes at room temperature, and that the pressure in the gas chamber is pumped down to its initial value (somewhere $1\text{-}2\times10^{-6}$ mbar). Depending on the precursor, the warm-up phase may take from 40 to 80 min. After that, the sample is ready for imaging and characterization.

Ice crosslinking vs. contamination writing. We tested whether the patterned structures could be the result of contamination writing as opposed to crosslinking of the molecules. First, we applied the patterning protocol (parameters in Table S2) at cryogenic temperature on the bare substrate without introducing any organic precursor. Second, we applied the same patterning protocol at room temperature with the organic precursor in the column. Neither attempts resulted in patterned structures.

Patterning 3 nm lines on octane

Using a beam current I_{0L}=0.21 pA, we patterned ~3 nm lines on octane (Figure S5), which, however, showed discontinuities. These lines either partially collapsed during development or are disrupted by stochastic effects since at each beam position only a few electrons participate to the dot-exposure at such a low current.

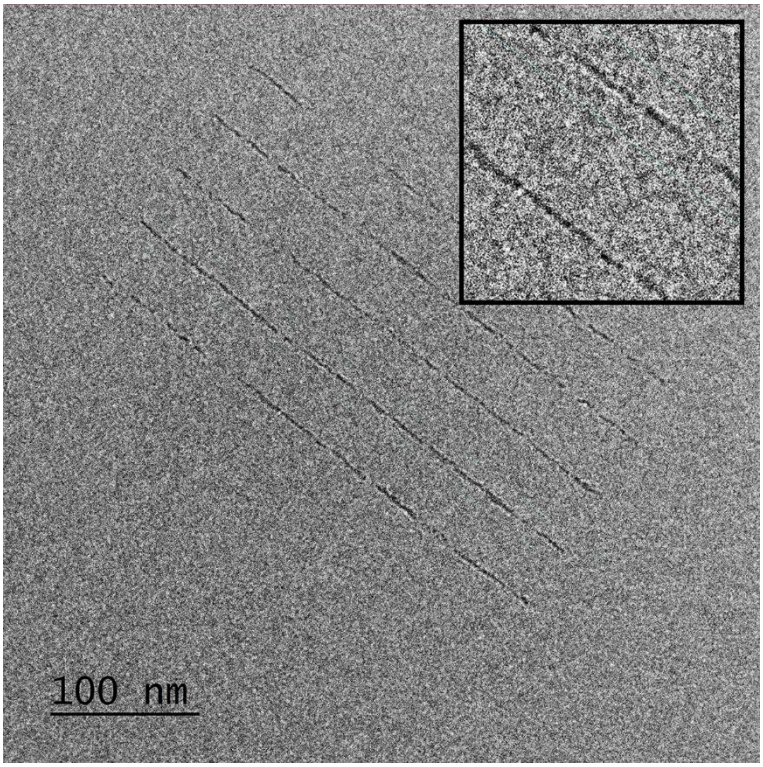

Figure S5. Parallel lines patterned on octane OIR using beam current 0.21 pA. Patterning parameters: line length L=360 nm, dwell time per dot τ_L=10 ms, number of dots N=100. Line dose was defined as $D=I_{0L}\tau_L/\Delta x_L$, where I_{0L} is the beam current, $\Delta x_L=L/N$.

Estimation of patterned features linewidths

We estimated the width w of the patterned lines by fitting their bright-field out-of-focus intensity profiles $I(x)$ (Figure S6) with a simple two-parameter model. We treat the lines as Gaussian phase objects described by the function:

$$f(x) = \phi e^{-x^2/2a^2}, \tag{1}$$

where x is the object-plane coordinate along the perpendicular to the line, $a=w/2$, and $\phi=C_E V_0 t_{max}$ is the maximum phase shift value with C_E=10.1 mrad V^{-1} nm^{-1} at 80 kV accelerating voltage, V_0 the mean-inner potential of the material, and t_{max} the thickness of the line at its center. The image intensity profile of this phase object when observed at a small defocus is

$$I(x) = 1 - \frac{Z}{2\pi}\frac{d^2 f(x)}{dx^2} = 1 - \frac{\phi\lambda Z}{2\pi a^4}(x^2 - a^2)e^{-\frac{x^2}{2a^2}}, \tag{2}$$

where λ=4.2 pm is the electron wavelength at 80 kV, and Z is the defocus value. The defocus can be considered small if $\phi\lambda|Z|/(2\pi a^2)<<1$.

We fit the line profiles normalized to the background intensity with eq. (2) and extract a and $b=\phi\lambda Z/(2\pi)$ (Figure S6 b) as fit parameters. The defocus value is then estimated as $Z=2\pi b/(\phi\lambda)$. We consider a mean-inner potential V_0=(10.0±0.5) V, applicable to amorphous carbon with uncertain hydrogen content[2], and t_{max}=(12±3) nm from the collapsed features, which give a phase shift ϕ=(1.2±0.3) rad. Figure S6 b shows the best-fitted normalized profile $I(x)$. The measured linewidth in this case was $w=2a$=2.96±0.04 nm, and defocus Z=-(200±50) nm. Since $\phi\lambda|Z|/(2\pi a^2)$=0.07<<1, the procedure is self-consistent.

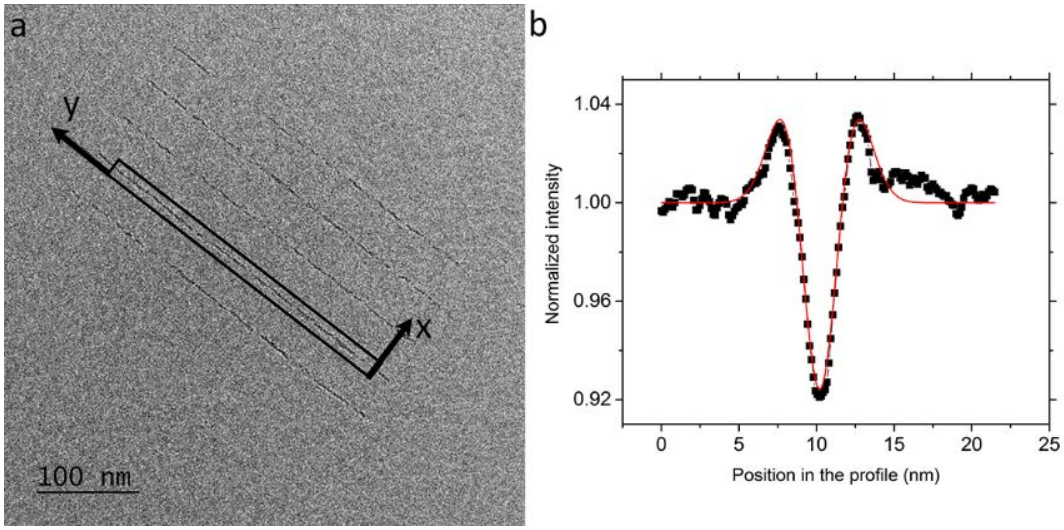

Figure S6. (a) Lines patterned on octane with (b) normalized intensity profile $I(x)$. The data is averaged along the y-direction in the area marked with black rectangle. Intensity profile (black squares) fitted with equation (2) as model (red line). The resulting best-fit parameters are a=(1.48±0.02) nm, b=-(0.166±0.004) nm^2. Uncertainties are assigned as standard errors from the fit.

Onset dose, contrast and saturation dose in hydrocarbon OIRs and polystyrene resists with different molecular weights

Figure S7 shows onset dose, contrast and saturation dose of hydrocarbons OIR and polystyrene resists with different molecular weights[3]. Polystyrene resists were patterned in SEM at 20 keV, so the comparison between data sets is only qualitative. Onset doses (Fig. S7 a) and contrast (Fig. S7

b) in both cases increase with the inverse molecular weight. The saturation doses (Figure S7 c), instead, show a monotonic increase with the inverse molecular weight in polystyrene, which differs from the non-monotonic trend observed in OIR.

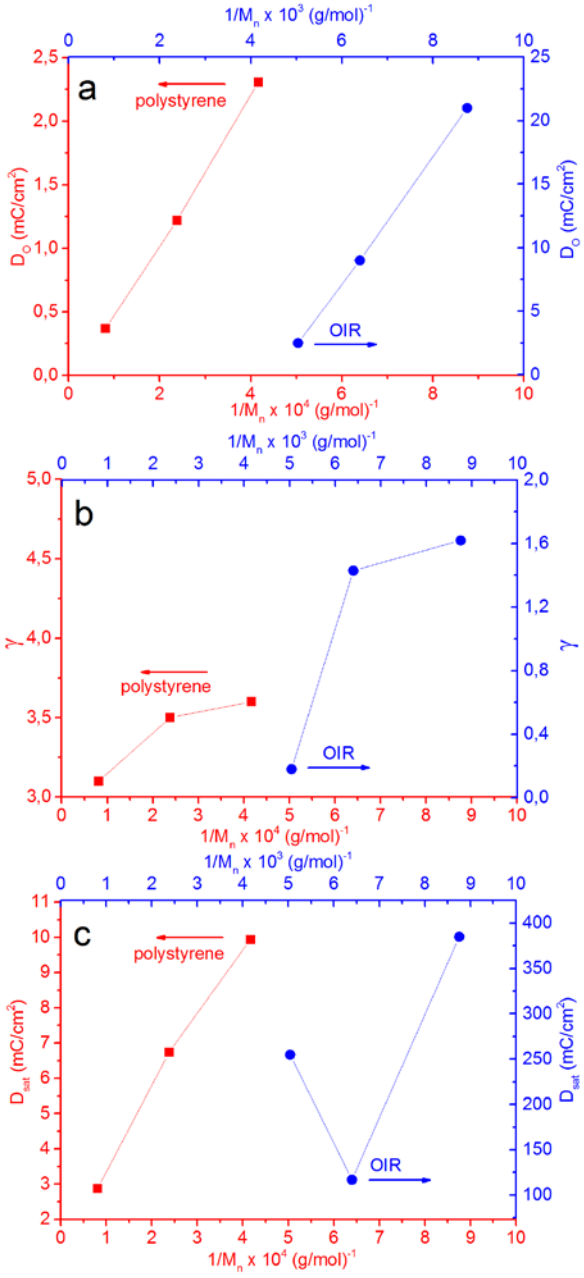

Figure S7 (a) Onset doses, (b) contrast values and (c) saturation doses plotted as a function of inverse molecular weight for polystyrene resists (red data points/axes) and hydrocarbon OIRs (blue data points/axes).

(1) Mølgaard Mortensen, P.; Willum Hansen, T.; Birkedal Wagner, J.; Degn Jensen, A. Modeling of Temperature Profiles in an Environmental Transmission Electron Microscope Using Computational Fluid Dynamics. *Ultramicroscopy* **2015**, *152*, 1–9.

(2) Schowalter, M.; Titantah, J. T.; Lamoen, D.; Kruse, P. *Ab Initio* Computation of the Mean Inner Coulomb Potential of Amorphous Carbon Structures. *Appl. Phys. Lett.* **2005**, *86* (11), 112102.

(3) Dey, R. K.; Cui, B. Effect of Molecular Weight Distribution on E-Beam Exposure Properties of Polystyrene. *Nanotechnology* **2013**, *24* (24), 245302.