SUPPLEMENTAL INFORMATION

Chemical Orthogonality in Surface-Patterned Poly(ethylene glycol) Microgels

Feiyue Teng, Xinpei Wu, and Matthew Libera*
Department of Chemical Engineering and Materials Science
Stevens Institute of Technology
Hoboken, New Jersey 07030, USA
E-Beam Patterned Dose Arrays from PEG-COOH Thin Films

Thin films of PEG with carboxyl terminal groups at each end (PEG-COOH; $M_w = 5$ kDa; Creative PEGWorks) were spin cast onto silicon substrates from 1 wt% solutions in THF. These were then patterned using 2 keV incident electrons in a manner identical to PEG-B and PEG-OH films (see main text).

Fig. S1 shows fluorescence images of a PEG-COOH dose array after exposure to SA-Alexa 488 and NH$_2$-Cy3. The SA-Alexa-488 probes for biotin functionality, and, as one would expect from the absence of biotin in the PEG precursor, Fig. S1A shows that there is no such functionality across the entire dose range. The NH$_2$-Cy3 probes for acid functionality, and Fig. S1B shows that this functionality is clearly present in patterned PEG-COOH. In contrast to the biotin functionality associated with patterned PEG-B films which appears strongly within the lower dose range and then disappears as dose increases (see main text), the reactivity with NH$_2$-Cy3 in PEG-COOH shows an onset at doses of about 8 $\mu$C/cm$^2$ and this reactivity increases with increasing dose.

![Figure S1](image1.png)

**Figure S1:** Thin films of PEG end-functionalized with carboxyl groups was patterned to create a dose array (left) and then exposed to SA-Alexa488 to test for biotin functionality (Fig. S1A) or NH$_2$-Cy3 to test for acid functionality (Fig. S1B).

Fig. S2 compares the amine reactivity as a function of dose for thin films comprised of PEG-B, PEG-OH, and PEG-COOH. These data indicate that amine reactivity appears in the PEG-COOH at lower doses than in PEG-B or PEG-OH, as one can expect since acid groups are present in the initial unirradiated PEG-COOH thin film. The fact that the Cy3 intensity monotonically increases with dose in PEG-COOH system indicates that, in addition to the acid groups introduced with the polymer precursor itself, the radiation chemistry induced by the incident energetic electrons creates an additional population of acid groups. A similar dose-dependent increase in
Cy3 reactivity is observed in both the PEG-B and PEG-OH systems, and reaches a maximum for all three PEG systems at a dose of about 500 µC/cm², indicating the mechanism of radiation-induced amine reactivity is the same in all three systems.

**Figure S2:** The amine reactivity (NH₂-Cy3) of three different end-functionalized PEG thin films as a function of electron dose used for e-beam patterning. (A) Raw Cy3 intensity; and (B) Cy3 intensity normalized to the maximum within each profile. Each data point corresponds to the average and standard deviation of at least three measurements.