Responsive polymeric thin films with controlled surface energies, dielectric constants and structure are critical for a variety of emerging nano and micro-scale technologies including fluidics, electro-optical devices and biotechnology. Introducing nanometer sized fluorinated segments offers a means to tune the polymer properties while significantly enhancing chemical and thermal stability. The interfacial structure and dynamics of multiblock semi fluorinated copolymers at their liquid/vapor interface and at interfaces with water and protonated alkanes has been studied using explicit atom molecular dynamic simulations. For semifluorinated diblocks H$_3$C(CH$_2$)$_{n-1}$(CF$_2$)$_{m-1}$CF$_3$ of varying fluorine content, fluorinated groups proliferate and reside longer at the liquid/vapor interface as expected for the lower surface tension components. Aqueous interfaces of these diblocks are sharp and well defined with an enhanced density of protonated groups owing to their reduced hydrophobicity in comparison to fluorinated groups. The enhancement increases with temperature. Protonated alkanes are found to be mutually miscible with the semifluorinated diblock copolymers. Similar surface behavior is observed in semifluorinated multiblock copolymers of the form H-[(CH$_2$)$_n$(CF$_2$)$_n$]$_m$-F where m varies from 3 to 48 with nxm=48. The fluorine enhancement at the liquid-vapor interface depends on both the temperature and block length, with the longest blocks showing the greatest enhancement. Due to mutual phobicity of protonated and fluorinated groups, nm-scale fluorine and hydrogen rich regions occur at the surfaces of these materials, with sizes that also depend on block length and temperature.

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