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Physical Properties and Responsive Behavior of Semi-fluorinated Polymer Interfaces[1]

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The macromolecular platform for this research is a polyoxetane, which has a CC-C-O- main chain, specifically P[(-$CH_2CMe(\mathbf{A})CH_2O)(CH_2CMe(\mathbf{B})CH_2O$-)]. If side chain $\mathbf{A} = \mathbf{B}$, the polyoxetane is semicrystalline; If $\mathbf{A} \neq \mathbf{B}$, the copolyoxetane is an amorphous low T_g telechelic used as a soft block. Dynamic interfacial behavior is described for (***1***) $\mathbf{A} = \mathbf{B} =$ $CF_3CH_2OCH_2$-, P(B-3FOx), and (***2***) a soft block where $\mathbf{A}$ = 3FOx and $\mathbf{B}$ = C12, a $CH_3(CH_2)_{11}N^+(CH_3)_2$-$(CH_2)_4O$- side chain used for introducing surface quaternary charge as a *polymer surface modifier* (PSM). For P(B-3FOx) (21kDa), differences in cooling rates from the melt have substantial effects on crystal phase, percent crystallinity, surface topography, and wetting behavior. DSC and WAXD reveal that slow cooling from the melt (≤ 5 $^\circ$C /min) gives α-P(B-3FOx) while quenching from the melt results in β-P(B-3FOx), which forms an ordered mesophase. TM-AFM and SEM for α-P(B-3FOx) shows cold crystallization (25 $^\circ$C) brings about sharp asperities and lath-shaped crystals. A 30° increase in water contact angle is associated with the change from a relatively smooth surface (Wenzel) to an asperity-rich surface yielding a discontinuous three-phase contact line (composite of Wenzel and Cassie-Baxter). Prior research established P[**AB**]-copolyoxetane polyurethanes having soft blocks ***2*** with $\mathbf{A}$ = 3FOx and $\mathbf{B}$ = dodecylammonium-butoxy (C12) are effective *contact* antimicrobial PSMs, but accessible quaternary charge density was unknown. Streaming potential (SP) measurements in microfluidic capillaries have been employed for estimating surface accessible charge. Inner capillary walls were coated with a base polyurethane modified by 1 wt% ***2*-PU**, that is, [HMDIBD(30)P[(3FOx)(C12)87:13-(5100)]. The neat PSM has a constant SP, but SPs for 1 wt% PSM coatings decreased with time. TM-AFM showed that the dynamic behavior of modified surfaces was correlated with PSM phase separation. The results are important in providing a facile method for screening candidate coatings prior to time consuming antimicrobial testing.

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