Surface X-ray Scattering Study of Segregation of PEG in Polymers

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Abstract

Poly(ethylene glycol) (PEG) is a widely used hydrophilic component in anti-fouling polymer coatings. Here we show that the presence of PEG in a polymer is not a sufficient condition for protein repellence, and that the bulk-dispersed PEG has to bloom to the water-polymer interface to repel the proteins. This is demonstrated by studying the adsorption of the blood clotting protein, fibrinogen (Fg) onto copolymers of PEG and desaminotyrosyl-tyrosine ethyl ester (DTE). While poly(DTE carbonate), a hydrophobic polymer, readily adsorbs Fg, very little is adsorbed when it is copolymerized with more than 8 mol% PEG. However, protein adsorption is reinstated when the polymer chain is made more rigid by iodinating the DTE group (I_2DTE). Small-angle X-ray scattering (SAXS) shows that hydration causes PEG-rich segments to phase separate when the polymer chains are flexible polymers but not when they are rigid. X-ray reflectivity (XRR) data from Langmuir films show differences in the distribution of PEG domains at the polymer-aqueous interface in the non-iodinated and iodinated polymers. Grazing incidence wide-angle scattering (GIWAXS) data confirms the migration of PEG from the air-polymer interface to the polymer-aqueous interface in poly(DTEC-*co*-8% PEG carbonate) but not in poly(I_2DTEC-*co*-8% PEG carbonate). These results show that the inhibitory effect of PEG in these polymers is due to hydration-induced phase separation, and that PEG needs to be present at the surface in sufficient quantity to be protein repellant.