

Interfacial Shear Rheology of the Perfluorosulfonic Acid Ionomers Monolayers at the Air/Water Interface

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We report that rheology of perfluorosulfonic acid ionomers (PFSI) monolayers are attributed to repulsive interaction of SO_3^- rather than percolation of backbones; electrostatic length of SO_3^- (Debye length, κ^{-1}) is much longer than physical length of backbone (radius, r). To support our statement, we add salts to reduce κ^{-1} by screening the charge of SO_3^- . Until κ^{-1} is reduced to be similar to r , shear moduli does not change, probably because backbone does not contribute to rheology. Additionally, PFSI monolayers do not follow the Cox-Merz rule empirical for polymer solution/melt; when rheology arise from polymeric backbone, they are supposed to follow the rule. Despite rheology are attributed to SO_3^- , it is revealed that equivalent weight (EW) and side chains affect rheology indirectly: (1) As surface activity increases with EW, confirmed by the increase of surface pressure (Π), greater amounts of PFSI adsorb to the interface so that rheology increase; (2) PFSI of longer side chain exhibits larger rheology than PFSI of shorter side chain at the same Π , because the former packs better due to larger translational entropy.