Kinetics of Surface-Initiated Atom Transfer Radical Polymerization

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High degree of controllability in atom transfer radical polymerization (ATRP) allows production of well-defined polymers both in solution as well as at interfaces. The latter case, also known as surface-initiated ATRP (SI-ATRP), results in polymer ensembles tethered by one side to the substrate known as polymer brushes. In this work the initiator layer is attached covalently to the surfaces using aryldiazonium chemistry which is a relatively recent approach for assembling ATRP precursor layers.

The first step consists of electrochemical grafting of 4-(hydroxyethyl)benzenediazonium tetrafluoroborate, followed by acylation of the hydroxyl groups using 2-bromoisobutyryl bromide. The initiator layer structure, thickness, and number of bromine atoms were determined using ellipsometry and X-ray photoelectron spectroscopy (XPS). SI-ATRP of methyl methacrylate was conducted in various solvents (dioxane, N,N-dimethylformamide, acetonitrile, and water/methanol mixture) with different ligands [2,2’-bipyridine (bpy), pentamethyldiethylenetriamine (PMDETA), and tris(2-aminoethyl)amine (Me6TREN)] on gold and glassy carbon substrates. The kinetic curves (i.e. thickness versus time) were analyzed using a kinetic model, in which the ATRP equilibrium was assumed to be established fast. Parameters such as the activation constant, deactivation constant, and surface radical concentration were determined from the experimental data employing computer simulations. The main observation from this study is that an increase in solvent polarity decreases polymer growth rate and hence the overall thickness of the polymer. This is attributed to the enhanced loss of deactivator species in polar solvents.

References
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