Biocatalytic Atom Transfer Radical Polymerizations

Abstract: While peroxidase-initiated free radical polymerizations have long been known and extensively investigated, it only emerged in recent years that peroxidases and other metallo-enzymes can control radical polymerizations following an atom transfer radical polymerization (ATRP) mechanism. This has opened the possibility to enzymatically mediate the synthesis of vinyl, acrylate and acrylamide polymers with well-defined molecular weight and narrow molecular weight distribution. Biocatalytic ATRP can significantly broaden the scope of ATRP. For example, laccase was used to polymerize N-vinylimidazole, a monomer that cannot be polymerized in a controlled way by classical ATRP. The enzyme could be removed quantitatively from the polymer after the polymerization, yielding narrowly dispersed poly(N-vinylimidazole) with no detectable traces of copper ions. Such polymers are ideally suited for drug delivery purposes. Moreover, enzymes can be enclosed into nanoreactors due to their size and their rich surface chemistry. Thus, it was possible to confine biocatalytic ATRP into polymersomes and protein cage nanoreactors, e.g. to fill polymersomes with a polymer. Biocatalytic ATRP also allows to fine-tune surface-initiated “grafting from” polymerizations by adjusting the affinity between the surface and the proteins. Hemoglobin catalyzed the synthesis of poly(N-isopropyl acrylamide) grafts with predetermined thicknesses in 4 nm steps. Protein repellent monomers could also be polymerized, but the increase in brush thickness was considerably lower. A further exciting application of biocatalyzed ATRP is to use the reaction as an assay to detect and quantify ATRP-active biomarkers. We have developed a highly sensitive, yet very simple assay for malaria infections which could become an essential tool in malaria eradication campaigns.