Title

Phosphorylcholine Substituted Polyolefins: New Syntheses, Solution Assemblies, and Polymer Vesicles

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Date of Award

9-2012

Document Type

Campus Access

Degree Name

Doctor of Philosophy (PhD)

Degree Program

Polymer Science and Engineering

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Subject Categories

Materials Chemistry | Polymer Chemistry

Abstract

This thesis describes the synthesis and applications of a new series of amphiphilic homopolymers and copolymers consisting of hydrophobic polyolefin backbone and hydrophilic phosphorylcholine (PC) pendant groups. These polymers are synthesized by ring opening metathesis polymerization (ROMP) of a novel PC- cyclooctene monomer, and copolymerization of various functionalized cyclooctene comonomers. Incorporation of different comonomers into the PC-polyolefin backbone affords copolymers with different functionalities, including crosslinkers, fluorophores, and other reactive groups, that tune the range of applications of these polymers, and their hydrophobic/hydrophilic balance.

The amphiphilic nature of PC-polyolefins was exploited in oil-water interfacial assembly, providing robust polymer capsules to encapsulate and deliver nanoparticles to damaged regions of a substrate in a project termed `repair-and-go.' In repair-and-go, a flexible microcapsule filled with a solution of nanoparticles probes an imperfection-riddled substrate as it rolls over the surface. The thin capsule wall allows the nanoparticles to escape the capsules and enter into the cracks, driven in part by favorable interactions between the nanoparticle ligands and the cracked surface (*i.e.* , hydrophobic-hydrophobic interactions). The capsules then continue their transport along the surface, filling more cracks and depositing particles into them.

The amphiphilic nature of PC-polyolefins was also exploited in aqueous assembly, forming novel polymer vesicles in water. PC-polyolefin vesicles ranged in size from 50 nm to 30 μm. The mechanical properties of PC-polyolefin vesicles were measured by micropipette aspiration techniques, and found to be more robust than conventional liposomes or polymersomes prepared from block copolymers. PC-polyolefin vesicles have potential use in drug delivery; it was found that the cancer drug doxorubicin could be encapsulated efficiently in PC-polyolefin vesicles.

In another application, PC-polyolefins were used as antifouling coatings for ultrafiltration (UF) and reverse osmosis (RO) water purification membranes. These polymers were found to reduce

surface fouling in both UF and RO membranes. Finally, PC-substituted ruthenium benzylidene catalysts were synthesized and evaluated for ROMP in water. PC-substituted catalysts proved effective towards productive metathesis of water soluble cyclic olefins including PEG-substituted oxanorbornene.

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