

Total Synthesis of an Adhesive Copolymer Containing Catechol Moiety for the Formation of Coacervates

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Abstract

A new, hierarchical strategy for the formation of coacervates and adhesive materials based on design principles originating from marine organisms is described. So our work used epoxide containing catechol precursor moiety in conjunction with allylglycidyl ether to form copolymers.

The copolymers will then be elaborated to cationic or anionic polyelectrolytes via thio-ene reaction. These modular polyelectrolytes would then be subjected to the formation of coacervates.

Coacervation is widely used by marine organisms due to their unique ability to employ water soluble, highly charged anionic and cationic polymeric materials which on mixing, phase separate from aqueous solution and form a distinct, water-insoluble fluid phase (termed a coacervate)

Introduction

The most of known adhesive material e.g. epoxy, the adhesiveness occurs in open air. In marine organisms such as mussels (figure 1) are able to adhesive onto a large variety of substrates even in wet environments. So it is good to learn how a marine organism - like mussels does - generate wet marine bioadhesives and a non-fouling surface. It requires a fundamental understanding of some features e.g. coacervation and the presence of polymer functionalities (e.g. DOPA) that provide energetic wet surface bonding (figure 2). By developing bio-inspired novel advanced materials, new nanostructured films, Self-healing material and coatings can be obtained which have direct relevance to water purification, marine and biomedical applications

The power of this new approach to exploiting biological inspiration in the design of advanced material systems is the opening up of new research fields and directions, which will significantly increase both industrial exploitation of these findings as well as the impact of this research worldwide. We are going to transition the adhesive concepts present in marine organisms such as mussels into bio-inspired practical wet adhesive, coating systems and non-biofouling surfaces.

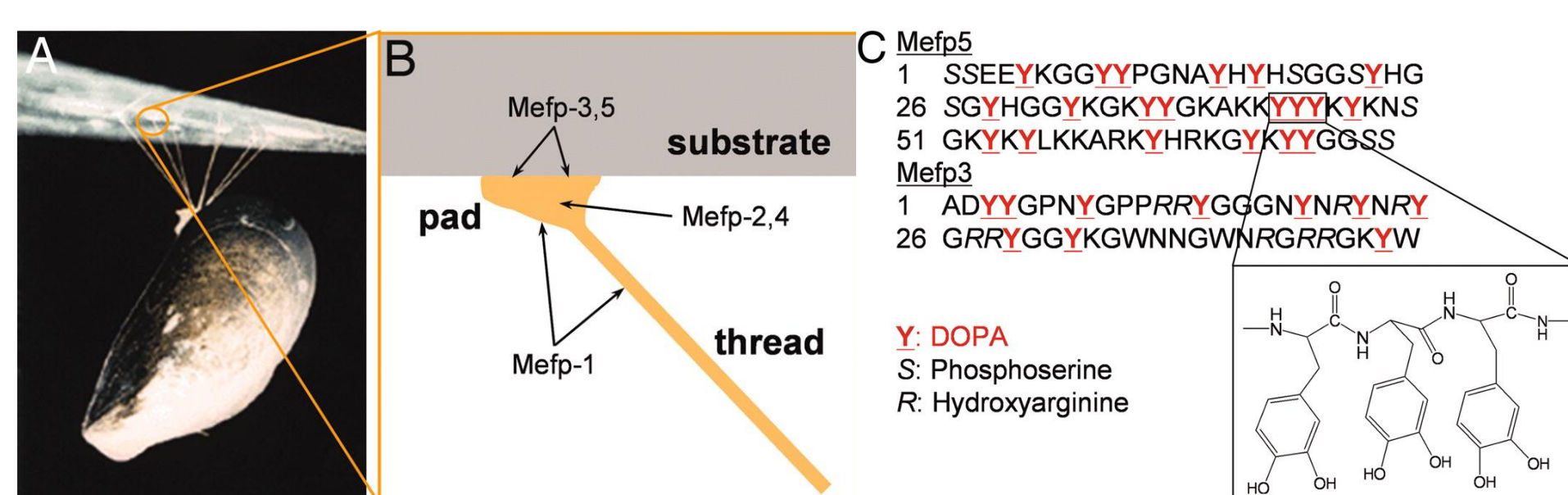


Figure 1. Biodistribution and amino acid composition of mussel adhesive proteins

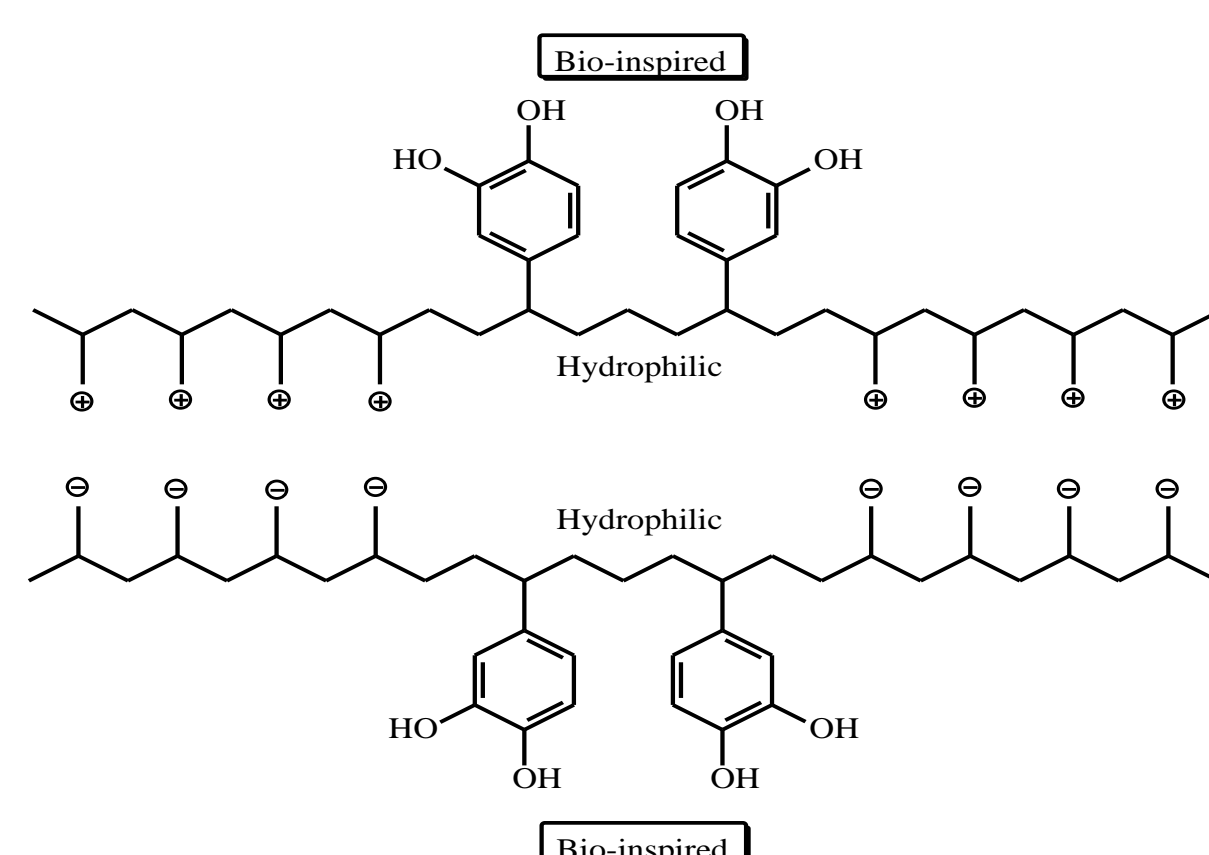


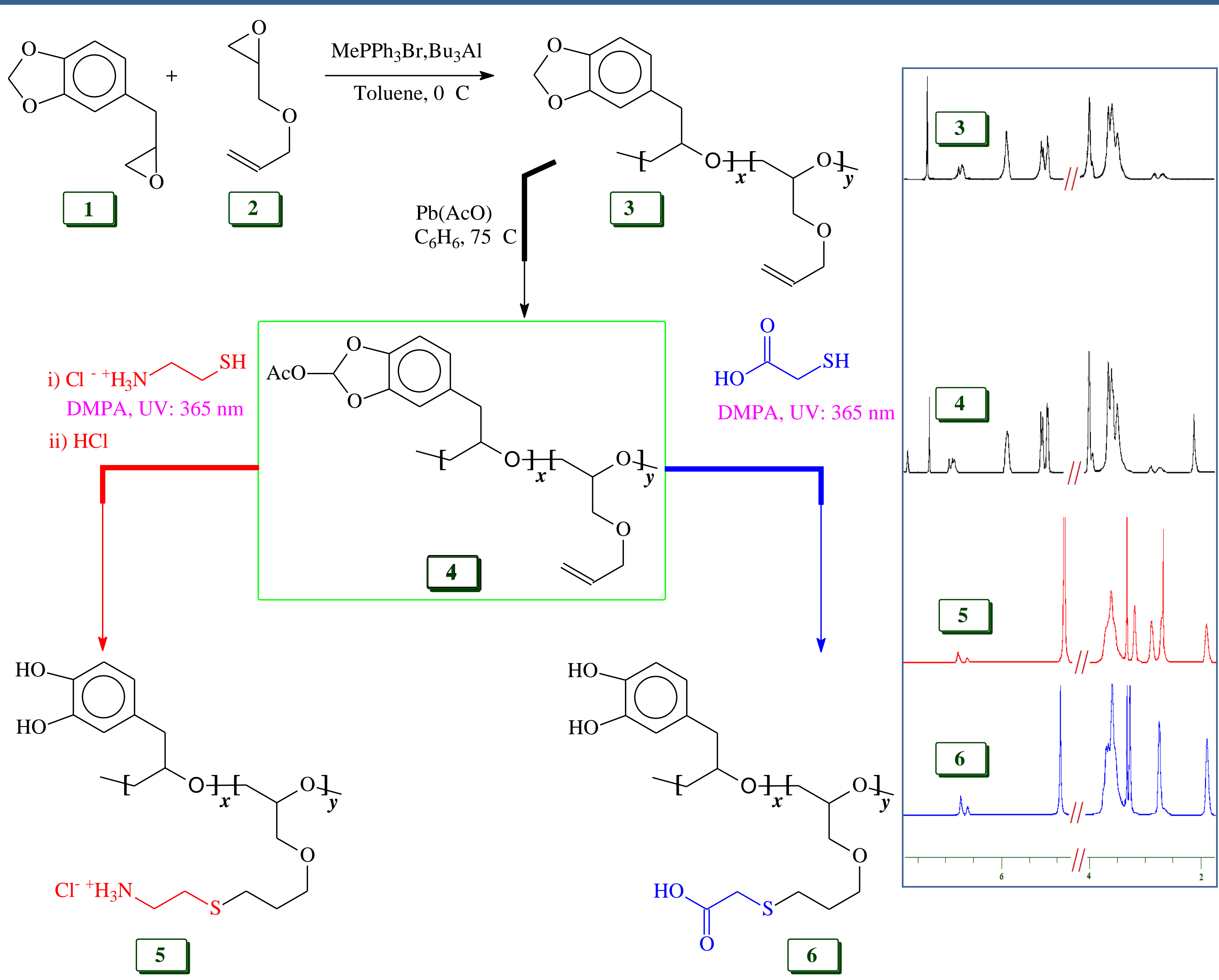
Figure 2. Modeling of final product

Materials and Methods

Materials: m-Chloroperbenzoic acid (MCPBA), tert-butylammonium hydroxide iBu3Al solution (25% in Toluene), 2,2-Dimethoxy-2-phenylacetophenone (DMPA), t-butyldimethylsilyl chloride (TBDMSCl), cysteamine, thioglycolic acid and safrole purchased from Aldrich Chemical, MePPh3Br, and CaH2 purchased from Fluka, and Allylglycidyl ether from Aldrich was dried over CaH2 and distilled. All solvents were of reagent grade. Lead tetra acetate Pb(AcO)4 was freshly prepared as described.

A Perkin Elmer (Series II Model 2400) elemental analyzer and a Fourier transform infrared (FTIR) spectrometer (Perkin Elmer 16F PC) were utilized for elemental analyses and IR spectroscopy, respectively. The nuclear magnetic resonance (NMR) spectra were recorded using a 500-MHz JEOL LA spectrometer. UV light in the dark room and the instrument was developed in our lab

Results



Discussion

A block copolymerization by adding a first monomer and after a while "for complete polymerization" adding a second monomer did not exist. It gave two kind of homopolymers indicated by H-NMR. So, a random copolymerization was done.

The activation of dioxole ring was confirmed by H-NMR and IR.

The thiol-ene addition occurs via radical addition of a thiol across a carbon-carbon double bond. The reaction proceeds with quantitative yield, as evidenced by complete disappearance of alkene peaks in 1H NMR

Conclusions

We have synthesized cationic and anionic water soluble polymer containing catechol moiety. These polymers have a high potential application in adhesive and antifouling; drug delivery. These efforts open the door to synthesize more similar polymers with low cost of starting materials, minimal purification. Finally, this kind of research provides a route to biomimetic of adhesive materials in the marine organism that guide us to understand mechanics of mussel adhesion.

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