Functionalization of PEDOT by Click Chemistry and ATRP

Hoffmann, Christian; Daugaard, Anders Egede

Publication date: 2012

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Abstract Poly(3,4-ethylenedioxythiophene) (PEDOT) is a conductive polymer which has received increasing attention and many developments have been investigated. PEDOT has been applied in many different areas such as biosensors or polymer solar cells. This work presents a modification of PEDOT films through Click Chemistry with alkynes followed by activator regenerated by electron transfer (ARGET) atom transfer radical polymerization (ATRP) to develop PEDOT films with anti-fouling properties through application of a model system based on a crosslinked surface of polystyrene PS-N3.

Introduction
Conductive polymers demonstrate a material sector of high interest which has been grown during the last few years. Many investigations have been conducted in order to develop the properties and application fields of conductive polymers. One representative is poly(3,4-ethylenedioxythiophene) (PEDOT) which has become an important polymer in many applications such as in biosensors or polymer solar cells. The recently discovered PEDOT-N3 films can be modified through click chemistry with different alkynes, which leads to an open range of functional groups on the conductive polymer backbone especially applications in sensing control over fouling properties are essential. Polyethylene glycol methacrylate (PEGMA) is an important monomer for ARGET reactions which has shown good antifouling properties. The present study is focused on the application of ARGET ATRP to produce anti-fouling surfaces on PEDOT. Initial results on PEDOT and a model system is presented. “Grafting to” processes have earlier been tested and the presented work is compared to these results. Furthermore a solution to confirm the validity of the method is an ARGET ATRP system with PEGMA, which has been tested. The presented work has been performed as a bachelor work at DTU.

Surface coating

![Image](https://via.placeholder.com/150)

Figure 1. Functionalization of PEDOT-N3 film with initiators, which was subsequently grafted through ATRP.

As already tested and reported the polymerization under normal ATRP conditions in an inert atmosphere has been successfully performed. The advantage of ARGET ATRP is the use of a normal instead of an inert and closed atmosphere. Due to its self fluorescence it is difficult to determine the inhibition of protein adsorption of the PEDOT films using fluorescence measurements. For this reason a P5 film modified with covalent bonded azide groups on the surface (PS-N3) has been used for functionalization and further ARGET ATRP reaction.

ATRP study
A well system has been designed to carry out the surface modification. This implies a non inert atmosphere, which should be suitable for ARGET ATRP. The ARGET ATRP reaction in solution was tested to investigate the stability of the reaction in an open vessel. The polymerization of PEGMA was performed through ARGET ATRP in water/methanol or pure methanol as solvents.

![Image](https://via.placeholder.com/150)

Figure 3. ARGET ATRP of poly(ethylene glycol) methacrylate (PEGMA) with Poly(ethylene glycol) methyl ester either 2-bromoisobutyrate as initiator and CuCl2/Tris(2-pyridyl)dithiosemicarbazone (TPMA) as a catalyst system and sodium ascorbate as a reducing agent.

By varying the molar ratios (monomer: CuCl2: initiator: CuCl2: ascorbic acid : CuCl2) and the reaction time the most promising reaction in terms of a controlled reaction were investigated. The reactions have been carried out in microplate wells under UV-VIS absorption measurements. Molecular weight distribution was determined by size exclusion chromatography (SEC).

![Image](https://via.placeholder.com/150)

Figure 4: FT-IR spectroscopy of the polystyrene films before and after introduction of the ARGET initiator, red: not initialized film, blue: initialized film.

The IR measurements clearly show the reaction of the azide groups with the initiator by disappearing of the band at 2100 cm⁻¹, which belongs to the free azides. After the polymerization procedure the reaction mixtures have been exposed with fluorescent Albumin from bovine serum. The anti-fouling properties have been determined by fluorescence measurements.

![Image](https://via.placeholder.com/150)

Figure 5: Left: ARGET ATRP system in microplate wells

Right: Fluorescence measurements after the samples have been exposed with the protein solution.

To establish the surface changes of the polymerized films FT-IR spectroscopy has been used, which show no change in comparison to the initialized surface.

Conclusions
• Polymer synthesis with ATRP was not controlled
• Polymer precipitation leads to the assumption of cross linking reactions, which guide to a better suppression of protein adsorption as already published
• Film initialization with “Click Chemistry” was successful
• Surface polymerization with ARGET ATRP was not successful
• No advantage in terms of protein adsorption

Perspective
The applied method has not provided surfaces with improved antifouling properties compared to the raw polymer surface. These results lead to a more detailed study with different types of monomers and varying of important reaction parameters such as reaction time, ratios between the reactants or the selection of a different system. Furthermore the change from the PS model system to the PEDOT system is the next step. Investigations for the detection of the protein interaction which has been hindered.

Acknowledgment
The Danish Council for Independent Research Technology and Production Sciences (grant 11-10-58/6) is thanked for financial support.

References