

SEQUENCE CONTROLLED POLYMERS OF STYRENE AND MALEIC ANHYDRIDE

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ABSTRACT

The polymerization of subunits such as monomers generates a larger molecule which is known as a macromolecule¹. Sequence-controlled copolymers are described as macromolecules with chemically divergent monomer units that are ordered in a distinct yet precise fashion. Controlled monomer sequences are readily found in biology – i.e., in nucleic acids namely DNA and RNA. The ordered sequence has a phenomenal impact on the structure of the macromolecule and in addition fabricate remarkable properties². The fascination with sequence-controlled polymers over the past years can be understood as scientists are striving to impart perfectly controlled sequences in synthetic polymers due to the promising physical and chemical properties that will be established.

Copolymers consisting of styrene (STY) and maleic anhydride (MANh) monomer units have been synthesized for centuries. The result of the copolymerization yields a highly alternating sequence of the monomers. The MANh monomer acts as an electrophile and therefore can only homopolymerize under extreme and harsh conditions. Contrary to MANh, STY consists of an electron-rich double bond and can therefore homopropagate effortlessly³. The use of equimolar quantities of both monomers results in a strictly alternating polymer as the cross-propagation rate is very high for this specific monomer system. The high cross propagation rate ensures swift monomer addition to the polymer chain. As the STY monomer ratio is increased, the alternating polymer microstructure perpetuates following a sheer polystyrene block resulting in a block copolymer⁴.

Whilst SMA copolymers have a great quantity of applications, the focus will be on the utilization of SMA copolymers in phospholipid nanodiscs for the study of membrane proteins.

RAFT polymerization is based on a degenerative chain transfer mechanism, which takes place between a propagating radical, which is provided by the thermal decomposition of an azo-initiator³, in the presence of thiocarbonylthio compounds. These compounds can act as reversible chain transfer agents (CTAs)⁵. One of the main advantages of RAFT polymerization is that by tuning the molar ratio of monomer to RAFT agent allows the production of polymers with a predetermined molecular weight and yield polymers with a well-defined polydispersity index.

The purpose of this study was to synthesize a sequence-controlled polymer via RAFT polymerization with a desired sequence on one MANh unit followed by two STY units. The stabilization effect of these polymers will be investigated and their properties compared to the more common alternating polymer.

References:

1. Hecht, S. Construction with macromolecules. *Mater. Today* **8**, 48–55 (2005).
2. Lutz, J.-F., Ouchi, M., Liu, D. R., Sawamoto, M. & Pinheiro, V. B. Sequence-Controlled Polymers Sequence-Controlled Polymers Synthetic genetic polymers capable of heredity and evolution BACKGROUND READING. *Sci. Sci.* **336**, 341–344 (2013).
3. Klumperman, B. Mechanistic considerations on styrene–maleic anhydride copolymerization reactions. (2010). doi:10.1039/b9py00341j
4. Benoit, D., Hawker, C. J., Huang, E. E., Lin, Z. & Russell, T. P. One-Step Formation of Functionalized Block Copolymers. *Macromol* **2000**, 1505–1507 (1999).
5. Matyjaszewski, K. & Spanswick Radical Polymerization, J. Controlled/living radical polymerization. *Mater. Today* **8**, 26–33 (2005).