

## Atom Transfer Radical Polymerization

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### Description

Well-defined amphiphilic copolymers of styrene and poly(ethylene glycol) methyl ether methacrylate (PEGMA) were successfully synthesized using reverse atom transfer radical polymerization (RATRP). The initial feed ratio of the macromonomer, PEGMA has a significant effect on the copolymer yield. Copolymer yield decreased with increasing the monomer feed ratio of PEGMA, but number average molecular weight followed the opposite trend. The resultant copolymers were characterized by nuclear magnetic resonance (NMR) spectroscopy to confirm their structures and comonomer compositions. The macromonomer content in the copolymer has a significant effect on the thermal and mechanical properties.

Atom transfer radical polymerization (ATRP) is one of the most promising approaches for controlled radical polymerization.[1] ATRP can be used in two different initiating systems: (a) an alkyl halide and transition- metal compound in its lower oxidation state of CuBr complexed by two molecules of ligand for example 4,4'-di(alkyl)-2,2'- bipyridine or one molecule of N,N,N',N'',N'''- pentamethyldiethylenetriamine (b) a conventional radical initiator such as azobis(isobutyronitrile) (AIBN) with the transition-metal compound in its higher oxidation state of CuBr<sub>2</sub> complexed by an appropriate ligand.

The latter approach has been named reverse atom transfer radical polymerization (RATRP) and was successfully used for copper- based heterogeneous and homogeneous systems in solution and in emulsion as well as for iron complexes. These systems successfully used to prepare polymers with predetermined molecular weights, low polydispersity (PDI), and precise end functionalities as well as a variety of copolymers with controlled topologies and compositions.

ATRP is a controlled radical polymerization process and is based on the reversible homolytic cleavage of the C–X bond of an alkyl halide or pseudohalide. Once again, the control of the polymerization is achieved by maintaining a low concentration of radicals throughout the polymerization. A transition metal complex is used which helps with the activation and deactivation of the growing polymer chains. Activation and deactivation occur throughout the polymerization and, ideally for good control, deactivation should be fast so that the propagating chain radicals are quickly converted to dormant species after addition of a few monomer units. ATRP is suitable for the polymerization of a variety of monomers, including styrene, (meth)acrylates, (meth)acrylamides, acrylonitrile, and vinyl pyridine, essentially, any compounds that have stabilizing groups such as a phenyl or carbonyl next to the carbon radicals.

However, acidic groups (methacrylic or carboxylic) tend to poison the catalyst or protonate nitrogen-based ligand groups, which leads to interference in polymerization. Although, techniques have been developed to provide moderately successful polymerization of acidic monomers, such as carefully selected conditions (type of initiator, catalyst complex, and solvent pH) and the use of protected monomers, it still requires The equilibrium constant is largely dictated by the monomer structure, which has two direct consequences. First, under ideal conditions, the polymerization rate is essentially fixed dependent on the monomer structure. Second, it is necessary to optimize the reaction conditions: solvent, catalyst complex, initiator, concentration of components, etc. for every unique monomer.further development.

The diverse variety of initiators accessible for ATRP is a compelling advantage for this method. Essentially, any halogenated compound that is activated by alpha-carbonyl, phenyl, vinyl or cyano groups can be utilized. Common ones being, halogenated alkanes, benzylic halides, haloesters, alpha-haloketones, and alkyl and aryl sulfonyl chlorides. The dormant species becomes re-activated with the use of the transition metal catalyst via an electron transfer process. Typically, transition metals in the lower oxidation state are used, since they have the ability to form more reactive complexes. A variety of catalysts have shown to be successful in ATRP, including Ti, Mo, Re, Fe, Ru, Os, Co, Ni, Pd, and Cu, with Cu being the most widely utilized and successful for a wide range of conditions. Without the catalyst, the formation of radicals cannot proceed. There must be a coordinate bond present, for example, in CuBr the bromine must be bonded directly to the Cu.