CELLULOSE-BASED POLYMERIC MATERIALS

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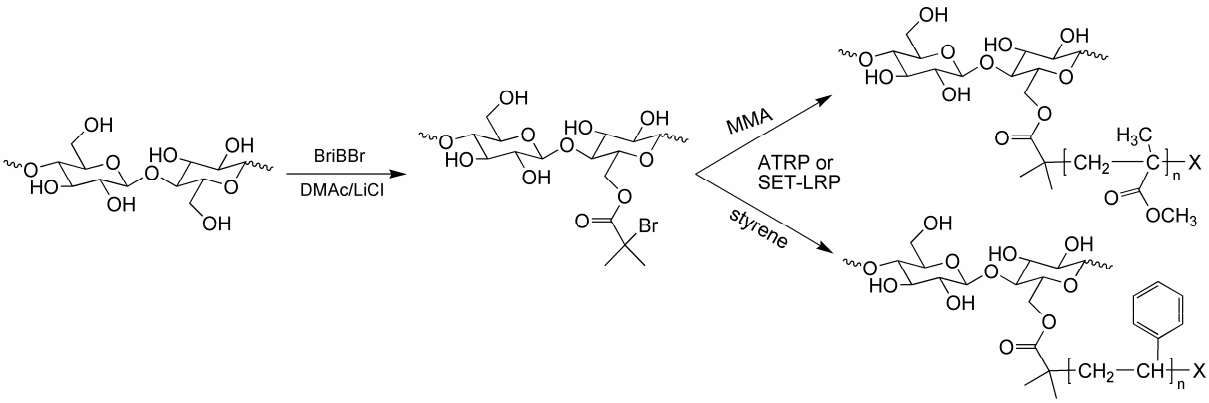
Cellulose is the most abundant organic polymer on Earth. Besides having a unique role in biological systems, cellulose plays an important part in a number of industrial applications. To date, cellulose has been prevalently utilized in its native form or in the form of simple derivatives, such as esters or ethers. However, environmental concerns and economical factors have recently led to the renewal of interest in cellulose-based products. This also provided a strong incentive for development of more sophisticated cellulose-derived materials.

Grafting copolymerization, where cellulose serves as a backbone for attachment of synthetic polymeric grafts, represents a straightforward way to confer new properties to the biopolymer and thus extend its functionality and scope of use. Unlike older heterogeneous approaches, modification of cellulose in solution, employing new methods of controlled radical polymerization (CRP), allows for a precise control of copolymers architecture. This synthetic approach can be divided into three basic steps: i) cellulose dissolution, ii) cellulose acylation to introduce initiation sites, and iii) grafting from the initiation sites *via* controlled radical polymerization.



The first part of this work deals with cellulose dissolution in the *N*,*N*-dimethylacetamide/lithium chloride (DMAc/LiCl) solvent system, which is followed by acylation of cellulose with 2-bromoisobutyryl bromide in order to prepare polyfunctional macroinitiators for grafting polymerization. It was found that cellulose activation, a process facilitating cellulose dissolution in DMAc/LiCl, has a pronounced effect on the efficiency of the following acylation reaction. The current methods of cellulose activation, as well as a newly developed procedure utilizing 1,4-dioxane as an activating agent, were assessed in this regard. Moreover, universality of the dioxane activation scheme was studied in detail using different cellulose samples.

In the central part of the work, atom transfer radical polymerization (ATRP) and single-electron transfer living radical polymerization (SET-LRP) techniques were used for grafting of various monomers from the prepared cellulose-based macroinitators. The research was focused on optimizing polymerization conditions in order to achieve well controlled processes with good initiation efficiency. Copolymers with diverse composition and architecture were synthesized, and their behavior in both the solid state and solution was studied.

Finally, the preparation of (nano)composites based on cellulose graft copolymers will be briefly mentioned to envisage the application potential of the prepared materials.