Controlled synthesis of starch-based branched polymers
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Summary

Starch is one of the most abundant polysaccharides that have been widely utilized by humans in many application areas like food, pharmacy, textile, and oil exploration. The properties of starch depend on the botanical resource mainly due to the change in the amylose to amylopectin ratio as well as their molecular weight. Nevertheless, chemical modification methods are often needed in order to widen the range of available properties and thus meet different requirements for (novel) applications.

In chapter 1, the applications of green solvents like ionic liquids (ILs) and supercritical carbon dioxide (scCO2) for the modification and processing of starch were introduced. ILs has been widely used in many research areas because of their negligible volatility, thermal and chemical stability. In the case of starch modification, not only ILs are recognized as good reaction media, in some cases they can also serve as catalysts for chemical reaction or as better plasticizers than traditional ones like glycerol. Like ILs, one reason for the introduction of scCO2 in the physical (e.g. foaming and impregnation) and chemical (esterification) processing of starch is its low environmental impact. Moreover, the good dissolving capacity, permeability and low viscosity inherent to scCO2 make it more attractive for application. In addition to green solvents, the controlled chemical modification of starch was introduced in this chapter as well. It has been proved that several properties of modified starch can be enhanced or even tailored by regioselective functionalization. Besides this method, the performance of starch derivatives can also be tuned by controlled grafting like atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT).

In the following chapters, controlled grafting of waxy potato starch for potential applications like enhanced oil recovery was exploited. To take the advantage of the inherent high molecular weight and branched structure of waxy potato starch, macroinitiators based on starch backbone were synthesized homogeneously in dimethylacetamide/LiCl solution. Then different (co)polymers were grafted from the obtained macroinitiators by aqueous copper-mediated living radical polymerization (Cu0-mediated LRP). The obtained (branched) structure is expected to endow copolymers with a high steric hindrance which may prevent the “shrinking” of the hydrodynamic volume of macromolecule in high salinity solution and thus obtain better rheological performance than linear (co)polymers.
In chapter 2, the focus was put on the controlled grafting of waxy potato starch with polyacrylamide (PAM) which is widely used in industry. Both kinetic study and GPC characterization evidenced the controllability of Cu\(^0\)-mediated LRP on the grafting of PAM from the macroinitiator. Further characterization by rheology and DLS also proved that PAM chains with a degree of polymerization (DP) from 600 to 200 were grafted on the starch backbone at the molecular level.

As can be seen in chapter 3, both linear and starch-based branched poly ([2-(methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide) (PSBMA) were synthesized by aqueous Cu\(^0\)-mediated LRP in sodium nitrate solution. Linear kinetic curves obtained from \(^1\)H-NMR suggest controlled polymerization even if, due to the electrostatic interaction between the charged (co)polymer and the GPC column, no reliable direct evidence could be obtained. Nevertheless, viscosity curves measured at different salinity and temperature values indicate that this starch-based zwitterionic copolymer is more sensitive to temperature and presence of salts than the analog linear one. This suggests that maybe branched zwitterionic (co)polymers are more suitable for applications that require thermal-responsive rheological behavior for better performance, like EOR for high-temperature reservoirs.

Based on chapter 2, a series of starch-g-poly(acrylamide-co-N-isopropylacrylamide) (St-g-(PAM-co-PNIPAM)) with much longer grafted chains (DP around 5000) were synthesized by aqueous Cu\(^0\)-mediated LRP within 15 min (Chapter 4). NIPAM is known as one building block of thermo-responsive (co)polymers with lower critical solution temperature (LCST). St-g-(PAM-co-PNIPAM) with 25 mol% of NIPAM intake not only displays good thermal-thickening behavior at a low shear rate (\(\leq 10 \text{ s}^{-1}\)) which is favorable for the EOR application, but also maintains stable viscosity in saline solution with NaCl concentration ranges from 0 to 100000 ppm. Besides the branched NIPAM copolymer, strong thermal-thickening behavior was also observed on St-g-PAM solution. This is attributed to the strong intramolecular hydrogen bond which is also sensitive to the change of temperature.

To investigate the influence of intramolecular interaction on the rheological performance of branched copolymer, negatively charged sodium 2-acrylamido-2-methyl-1-propanesulfonate (SAMPS) was introduced into the waxy potato starch-based copolymer (Chapter 5). With 25 mol% of SAMPS intake, both AM/SAMPS and AM/SAMPS/NIPAM copolymers display much higher viscosity than that of AM/NIPAM copolymer in fresh water due to larger hydrodynamic volume resulted from the strong intramolecular electrostatic repulsion. Although AM/SAMPS/NIPAM copolymer also displays thermo-thickening behavior at a low
shear rate (≤ 3 s⁻¹) in high salinity solution, unlike St-g-(PAM-co-PNIPAM), the intake of 25 mol% NIPAM unit plays a negative role on the viscosity when the salinity is higher than 50000 ppm.

In the future, it would be of interest to study the influence of homogeneous grafting on the biodegradability of the starch backbone and consequently the influence on the rheological property. In the case of zwitterionic copolymers, due to the effect of strong intramolecular interactions on the solubility of copolymers, the synthesis of branched copolymers that have block sidechains with short polyzwitterions at the end and the study of their rheology in saline solutions would also be an interesting topic. The controlled synthesis of starch-based copolymers like St-g-Poly((AM-r-SAMPS)-b-NIPAM) is another attractive project to study the influence of sidechain structure on the thermo-thickening property and saline-resistance property of highly branched copolymers.
Summary