Synthesis of novel branched polymers for enhanced oil recovery
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Energy demand is projected to increase by 56% between 2010 and 2040. Even though the relative share of petroleum is anticipated to decline slightly, its consumption is expected to rise by 24% between 2010 and 2030. In order to maintain oil production, additional measures are taken such as the injection of materials that are not normally present into the oil reservoir (enhanced oil recovery: EOR).

An important EOR technique is polymer flooding. Polymer flooding and commercial polymers were introduced in Chapter 1. Such polymers contain acrylamide (AM), which is affordable and offers desirable viscosifying properties. AM can be readily polymerised up to high molecular weights in water as solvent. These commercial polymers, however, are very sensitive to brine salinity, hardness, and high shear forces. In literature, the introduction of branches in the polymer structure is identified to enhance its viscosifying capability as well as shear resistance and resistance to salts. To introduce branching in an industrially-relevant polymerisation procedure, control over the process is required. The latter can be obtained by applying a controlled radical polymerisation (CRP) approach. A promising method in that regard is reversible addition-fragmentation chain-transfer (RAFT), for which the current state of the art was introduced.

Initial polymerisation experiments of AM with RAFT polymerisation were explored in Chapter 2. A RAFT agent from literature and showing promising results, was evaluated and compared with two novel RAFT agents from the same family. These RAFT agents are designed to mediate the polymerisation of AM and influence the molecular weight of the final polymers. Initial polymerisation experiments demonstrated that the RAFT agents offer control over the reaction, which is further evaluated in Chapter 3.

In Chapter 3, one of the RAFT agents from Chapter 2 (3-
SUMMARY

(((benzylthio)carbonothioyl)thio) propanoic acid (BCPA) is applied in the aqueous polymerisation of AM. Control over the reaction was illustrated by linear first order kinetic plots, a linear development of the molecular weight as function of reaction time and a successful chain extension experiment of an AM macro RAFT agent with \(N,N\)-dimethylacrylamide (DMA). The work described in this chapter opens the door to the controlled polymerisation of AM up to high molecular weight, which is shown by the synthesis of linear polyacrylamide (PAM) up to a theoretical molecular weight of 2,600,000 Da.

After the successful synthesis of linear PAM, the focus was shifted towards a branched topology. To that end, hyperbranched PAM was synthesised in Chapter 4 by a facile copolymerisation of AM and \(N,N'\)-methylenebis (acrylamide) (BisAM) in the presence of a RAFT agent. Number average molecular weights up to 481,000 Da were obtained, with polydispersities between 1.62 and 3.25. The role of the RAFT agent was clearly illustrated, as it was found to affected the amount of bifunctional monomer (BisAM) that could be incorporated. The effectiveness of the introduction of branches was displayed by comparison with a linear equivalent (having a larger hydrodynamic volume than the branched counterpart), whereby the branched polymer offered a significantly higher solution viscosity.

Higher molecular weights were targeted in Chapter 5, by application of a two-step synthetic approach. A low molecular weight branched core (macro RAFT agent) was synthesised. Subsequently, this macro RAFT agent was extended with fresh AM. After this second step, star-like branched polyacrylamides (SB-PAMs) with theoretical molecular weights ranging from 12,000 to 2,100,000 Da were obtained. The effect of the degree of branching in the core, as well as the length of the arms after extension (step 2) were clearly illustrated. Rheological behaviour of these polymers was described in Chapter 6. There, elastic behaviour of the SB-PAMs was found to be influenced by the amount of crosslinker in the core of the polymer. The polymers have ultimately been evaluated in a two-dimensional flow-cell, in order to simulate oil recovery from an oil field and more specifically from dead-ends in such fields. A pronounced effect of the polymeric structure on the oil recovery was discovered, whereby some of the branched structures were found to offer advantages compared with linear analogues, with regard to the required polymer concentration and the amount of oil recovered.

In Chapter 7, the properties of SB-PAMs with higher molecular weights were set in direct comparison to linear PAMs and commercial linear hydrolysed polyacrylamides (HPAMs). The SB-PAMs were found to display higher solution viscosities at comparable molecular weight than linear PAMs. Moreover, lower polymer concentrations were required in flow-cell experiments, while higher oil recoveries have been reported for the branched equivalents (17 to 47\% versus 15\% for a linear PAM). The SB-PAMs did display an increase in solution viscosity upon the addition of NaCl and the solutions were found to be stable upon shearing at 1,750 s\(^{-1}\).
Final evaluations of the polymers have been performed in core flood experiments, whereby the oil recovery of the polymer solutions from porous rock was evaluated. The branched equivalents displayed the highest oil recoveries, while offering the lowest pressure drop over the core.

In Chapter 8, the synthesis of novel thermothickening polymers was explored, as an alternative to ultra high molecular weight conventional polymers for EOR. Comb copolymers containing on average 17 arms of N,N-dimethylacrylamide (DMA) and N-isopropylacrylamide (NIPAM) were prepared at 0°C in water with the CRP method atom transfer radical polymerisation (ATRP). Solutions of the copolymers were found to have a lower critical solution temperature (LCST), which is the temperature at which the solubility of the polymer deteriorates. This LCST was found to vary based on the composition of the comb copolymer and for certain polymers the precipitation was preceded by a phase of significant thermothickening, which was predominantly obtained at low shear rates. The latter renders the polymers interesting from an application point of view, as the polymers can be injected into oil fields with low energy consumption (high shear rate and low temperature), whereas they offer high solution viscosity where it is desirable (in the oil field, at a low shear rate and high temperature).
De wereldwijde energievraag is voorspeld met 56% toe te nemen tussen 2010 en 2040. Hoewel verwacht wordt dat het relatieve aandeel licht zal afnemen, neemt de verwachte vraag naar olie met 24% toe tussen 2010 en 2030. Om in de olievraag te kunnen voorzien, worden aanvullende maatregelen getroffen. Een voorbeeld hiervan is de injectie van materialen die van nature niet aanwezig zijn in olievelden, ook wel verbeterde oliewinning (EOR) genaamd.

Een belangrijke EOR techniek is de injectie van waterige polymeeroplossingen in olievelden. Deze techniek en de daarbij gebruikte polymeren zijn beschreven in Hoofdstuk 1. Zulke polymeren bestaan uit acrylamide (AM), een betaalbaar monomeer met goede viscositeit verhogende eigenschappen. AM kan worden geopolymeriseerd tot hoge molecuulgewichten in water als oplosmiddel. Nadelen van dit soort commerciële polymeren zijn de gevoeligheid voor de aanwezigheid van zout, hardheid en hoge afschuifspanningen. In de literatuur is de introductie van vertakkingen in de structuur van polymeren geïdentificeerd als manier om de viscositeit verhogende eigenschappen te verbeteren, samen met de bestendigheid tegen afschuifspanningen en zouten. Om zulke vertakkingen op een industrieel-relevante manier te introduceren, is het nodig om het polymerisatieproces te beheersen. Dit laatste kan worden bereikt door de toepassing van een gecontroleerd radicaal polymerisatie (CRP) systeem. Een veelbelovende methode in deze context is reversibele additie-fragmentatie ketenoverdracht (RAFT) polymerisatie, waarvoor de huidige stand van de techniek is beschreven.

Initiële experimenten van de polymerisatie van AM met RAFT polymerisatie zijn beschreven in Hoofdstuk 2. Een RAFT-agent met veelbelovende prestaties in de literatuur werd geëvalueerd en vergeleken met twee nieuwe RAFT-agenten uit dezelfde familie. Deze RAFT-agenten zijn in het leven geroepen om de poly-