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Copper-mediated homogeneous living radical polymerization of acrylamide with waxy potato starch-based macroinitiator

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ABSTRACT

Cu⁰-mediated living radical polymerization (Cu⁰-mediated LRP) was employed in this research for the synthesis of starch-g-polyacrylamide (St-g-PAM). The use of a controlled radical grafting technique is necessary, as compared to the traditional free-radical polymerization methods, in order to obtain a well-defined structure of the final product. This is in turn essential for studying the relationship between such structure and the end-properties. Waxy potato starch-based water-soluble macroinitiator was first synthesized by esterification with 2-bromopropionyl bromide in the mixture of dimethylacetamide and lithium chloride. With the obtained macroinitiator, St-g-PAM was homogeneously synthesized by aqueous Cu⁰-mediated LRP using CuBr/hexamethylated tris(2-aminoethyl)amine (Me₆Tren) as catalyst. The successful synthesis of the macroinitiator and St-g-PAM was proved by NMR, FT-IR, SEM, XRD and TGA analysis. The molecular weight and polydispersity of PAM chains were analyzed by gel permeation chromatography (GPC) after hydrolyzing the starch backbone. Monomer conversion was monitored by gas chromatography (GC), on the basis of which the kinetics were determined. A preliminarily rheological study was performed on aqueous solutions of the prepared materials.

1. Introduction

Despite the decreasing share of oil in the total fuel mix in the past decades, the oil consumption has increased by more than sixty percent since 1973 (IEA, 2015). For the stable development of economy, enhanced oil recovery (EOR) technology is needed to get more oil out from the reservoir. Polymer flooding is one of the commonly used EOR technologies in which partially hydrolyzed polyacrylamide (HPAM) is used as viscosifier (Wei, Romero-Zerón, & Rodrigue, 2013). However, its performance will deteriorate significantly under high temperature and (or) high salinity water (Zhu, Zhang, Han, Wang, & Feng, 2013). To overcome this problem, efforts have been made to increase the hydrodynamic volume of polymers under such conditions. Besides the successful application of ultra-high molecular weight PAM (UHMW PAM) in oil fields, investigation on branched PAM has also been reported because its large hydrodynamic volume resulting from steric hindrance renders it a potential viscosifier for EOR (Dalsania & Doda, 2015; Wever, Picchioni, & Broekhuis, 2011; Wever, Picchioni, & Broekhuis, 2013; Wever, Polgar, Stuart, Picchioni, & Broekhuis, 2013). Apart from EOR, branched acrylamide homopolymers and its copolymers can also be used in wastewater treatment and mining as flocculants (Blanco,

2009; Wang, Wang, Li, & Zhu, 2013), in the preparation of nanoparticles as stabilizer (Chumachenko, Kutsevol, Rawiso, Schmutz, & Blanck, 2014) because of their higher efficiency compared with linear ones.

Several methods are available for the synthesis of branched polymers. Direct controlled synthesis of star-like and hyperbranched PAM by reversible addition-fragmentation chain transfer (RAFT) polymerization has been reported (Wang, Wang, Li, & Zhu, 2013; Wang, Wang, Li, & Zhu, 2010). Other PAM products with different topologies, star-like or comb-like, have also been synthesized by grafting PAM side chains from “core” polymers like dextran and polyketone (Kutsevol, Bezuglyi, Bezugla, & Rawiso, 2014; Wever, Polgar, et al., 2013). Compared with these reported “core” polymers, which are either non-biodegradable or relatively expensive, waxy potato starch, as a naturally occurring low-cost renewable polysaccharide, is a promising alternative as the backbone for branched PAM. It contains more than 95 percent amylopectin, which has a highly branched structure that is composed of 10⁵–10⁶ anhydroglucose units (AGU) (Jane, 2004; Yoo & Jane, 2002; Zobel, 1988). Thus, branched PAM based on waxy potato starch is supposed to have a high hydrodynamic volume because of the steric hindrance inherent to its structure. Besides, the use of starch

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could also endow the copolymer with biodegradability, which is important for environmental protection.

The copolymerization of starch with PAM generally is carried out in water with ceric salts as initiator (Eutamene, Benbakhti, Khodja, & Jada, 2009; Song, Zhang, Ma, Wang, & Yang, 2007; Zou et al., 2012). These polymerizations, depending on the type of ceric salts, are usually carried out in the temperature range of 30–60 °C with more than 90% monomer conversion within 4 h (optimum condition) as opposed to the highest 66% conversion within 2 h at 0 °C in the present study (Eutamene et al., 2009; Song et al., 2007). The lower conversion is inherent to the strategy for controlled radical polymerization, which entails relative slower kinetics for achieving control over the structure. Although the above mentioned conventional free radical polymerization has higher conversion, drawbacks are that their initiators are expensive and the homopolymerization of acrylamide is uncontrollable (e.g. around 10 up to 46 wt.% of monomer may form homopolymer during grafting) (Song et al., 2007). Furthermore, products produced with this method are not suitable for studying the relationship between rheology and macromolecular structure due to the uncontrollable chain length (normally PDI > 2) and time-consuming purification (e.g. removing the homopolymer) (Pabon, Selb, Candau, & Gilbert, 1999). On the contrary, the use of controlled polymerization, like atom transfer radical polymerization (ATRP) or Cu⁰-mediated living radical polymerization (Cu⁰-mediated LRP), can avoid the formation of homopolymer and achieve tailor-made structures (e.g. PDI around 1.5) (Jones et al., 2016; Wang, Zhong, Zhang, Magenau, & Matyjaszewski, 2012; Weber, Picchioni, et al., 2013). Few researches on the homogeneous copolymerization of starch with monomers like styrene, methyl methacrylate and *N*-isopropylacrylamide have been reported in recent years (Wang, Shen, et al., 2015; Wang, Wu, Men, Shen, & Liu, 2015). Although St-g-PAM has also been synthesized with ATRP, only the surface of starch granules was grafted, which limited the graft density and thus limited the performance of the final product (Najafi Moghaddam, Fareghi, Entezami, & Ghaffari Mehr, 2013).

In our recent research, waxy potato starch-based macroinitiator was synthesized homogeneously in dimethylacetamide and lithium chloride (DMAc/LiCl) (El Seoud, Nawaz, & Areas, 2013; Zhang, Liu, Xiang, Kang, Liu, & Huang, 2014). Cu⁰-mediated LRP of acrylamide was then carried out in aqueous phase at molecular level (Jones et al., 2016). Both of the macroinitiator and St-g-PAM were characterized by NMR, FT-IR, SEM and XRD. The molecular weight and polydispersity index (PDI) of grafted PAM chains were determined, after hydrolyzing the starch backbone, by aqueous gel permeation chromatography (GPC) equipped with a differential refractive index (DRI) detector.

2. Experimental section

2.1. Materials

Waxy potato starch (> 95% amylopectin) was kindly provided by Avebe (The Netherlands) and dried under vacuum at 60 °C for 48 h before use. Lithium chloride was purchased from Sigma-Aldrich and dried under vacuum at 80 °C for 24 h prior to use. Anhydrous *N,N*-dimethylacetamide (DMAc) was purchased from Sigma-Aldrich in Sure/Seal™. 2-bromopropionyl bromide (BpB), acrylamide (AM), formaldehyde solution (37%) and formic acid (> 95%) were purchased from Sigma-Aldrich and used as received. Tris(2-aminoethyl)amine (Tren) was purchased from TCI and used as received. Tris[2-(dimethylamino)ethyl]amine (Me₆Tren) was synthesized following the procedures reported by Roland, Wisegarver, and Alles (1945). CuBr was stirred in sulfuric acid solution for 2 h, then filtered, washed with ethanol and acetone respectively for three times and dried under vacuum at room temperature for 24 h, followed by storage under N₂ atmosphere.

2.2. Instruments and analysis

Fourier Transform Infrared (FT-IR) spectra were recorded with attenuated total reflection (ATR) accessories on an IRTracer-100 SHIMADZU Fourier Transform Infrared Spectrophotometer and data were processed with LabSolutions IR software. NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer using deuterated solvents purchased from Sigma-Aldrich. Monomer conversion was measured with Hewlett Packard 5890 Gas Chromatography (GC) with an Elite-Wax ETR column. Aqueous gel permeation chromatography (GPC) was conducted on an Agilent 1200 system equipped with a differential refractive index (DRI) detector and Polymer Standard Service (PSS) column set (PSS SUPREMA 100 Å, 1000 Å, 3000 Å). The mobile phase used was 0.05 M NaNO₃. Column oven and detector temperatures were regulated to 40 °C, the flow rate was set to 1 mL/min. Polyacrylamide standards from PSS were used for calibration. Samples were filtered through a membrane with 0.22 µm pore size before injection. Experimental molar mass and dispersity (PDI) values of synthesized polymers were determined by conventional calibration using Agilent GPC/SEC software. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Phaser X-Ray diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406 \text{ Å}$) in the 2θ range between 5° and 40°. Microstructure morphology was obtained by environmental scanning electron microscope (FEI XL30-FEG ESEM) with a low voltage of 3 kV. Differential Scanning Calorimetry (DSC) analysis was carried on a PerkinElmer Diamond Differential Scanning Calorimeter. Samples were heated from 20 °C to 200 °C at a heating rate of 10 °C/min in a nitrogen atmosphere and data were processed with Pyris thermal analysis software. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 4000 Thermogravimetric Analyzer. Samples were heated from 30 °C to 950 °C at a heating rate of 10 °C/min in a nitrogen atmosphere and data were processed with Pyris thermal analysis software. Rheological properties were measured on a HAAKE Mars III (ThermoScientific) rheometer equipped with a cone-and-plate geometry (diameter 60 mm, angle 2°). Shear rate for flow curve measurement was varied from 0.1 to 1750 s⁻¹ and the shear stress was increased by regular steps. Dynamic measurements were carried out with sweep frequencies between 0.04–100 rad/s. Oscillation stress sweep measurements were employed first to assure the dynamic measurements were conducted in the linear response region of the samples. A Brookhaven ZetaPALS Zeta Potential Analyzer with Dynamic light scattering (DLS) function model was used to measure the hydrodynamic radius of polymers. Measurements were performed at 20 °C with a scattering angle of 90°. The device was calibrated with Nanosphere™ Size Standard (90 nm) from Thermo Scientific. Ten runs for each sample were performed at the concentration of 0.0005 wt.%. Data were obtained and processed with MAS OPTION software.

2.3. Synthesis of starch-based macroinitiator (StBr)

2.3.1. Typical procedure for water-soluble StBr

Waxy potato starch (2.59 g, 16 mmol) and lithium chloride (1.02 g, 24 mmol) were added to a 250 mL three-necked flask (dried overnight at 100 °C before use) connected to a mechanical stirrer. The system was vacuumed under heat and backfilled with N₂ three times to remove residual water. Anhydrous DMAc (100 mL) was transferred to the flask and the mixture was stirred at 130 °C for about 1 h under N₂ atmosphere. A transparent solution formed when the mixture was cooled down to room temperature naturally. The solution was subsequently cooled down with an ice bath and then 0.42 mL (4 mmol) BpB was added dropwise within 30 min under the protection of N₂. The mixture was then warmed up naturally to room temperature and stirred for 3 h. The final products were precipitated in tenfold acetone and then filtered, washed, and dried under vacuum at 45 °C for 24 h. The resulting white powder was then purified by Soxhlet extraction for 24 h (final yield 87%). For StBr with high degree of substitution (DS), product was

precipitated out with Milli-Q water and then filtered, washed, dried under vacuum at 45 °C for 24 h.

2.4. Aqueous Cu^0 -mediated LRP of acrylamide onto starch

The polymerization of acrylamide followed the procedures reported by Jones et al. (Jones et al., 2016).

2.4.1. Typical polymerization protocol

H_2O (5 mL) and Me_6TREN (16 μL , 0.06 mmol) were charged to a 100 mL three-neck round-bottom flask with a magnetic stirrer bar and rubber septums. The solution was vacuumed and backfilled with N_2 three times to remove O_2 . CuBr (11.5 mg, 0.08 mmol) was added under vigorous stirring. The solution was cooled down with ice bath. Simultaneously, another 100 mL three-neck round-bottom flask was charged with StBr (121.5 mg, 0.1 mmol equiv. Br), acrylamide (3.55 g, 50 mmol), and 25 mL of Milli-Q water. The flask was degassed with three cycles of vacuum and N_2 backfill in ice bath. This monomer/macromolecule solution was then transferred to the flask containing catalyst solution via a degassed syringe. The mixture was allowed to react for 30 min. The resulting solution was passed through a basic alumina column to remove catalyst residue and then precipitated out with tenfold methanol. The product was filtered, washed with methanol and then dried in vacuum oven at 60 °C for 24 h.

2.5. Cleaving of graft polymer chains from the starch backbone

St-g-PAM (0.5 g) was dissolved in 25 mL Milli-Q water in a round bottom flask and then 0.25 mL concentrated hydrochloric acid was added. The mixture was stirred and refluxed at 100 °C for 2 h. The resulting free polyacrylamide (PAM) was precipitated out with methanol, filtered, and washed with methanol for three times. The product was dried under vacuum at 60 °C for 24 h.

3. Results and discussion

3.1. Synthesis of waxy potato based macroinitiator StBr

The starch-based macroinitiator StBr was prepared homogeneously via a one-step esterification reaction with 2-bromopropionyl bromide (BpB) in DMAC/LiCl as depicted in Scheme 1. Both FT-IR (Fig. 1 Left) and NMR gHSQC (Fig. 1 Right), ^1H NMR and ^{13}C NMR (Fig. S1a and b, respectively, in the support information) were employed to demonstrate the successful preparation of the macroinitiator. The absorption peak at 1743 cm^{-1} in the FT-IR spectrum was assigned to the stretching of the $\text{C}=\text{O}$ group from the grafted BpB moiety while the peak at 1281 cm^{-1} was attributed to the $\text{C}-\text{O}$ bond in the ester group. The successful synthesis of StBr was further proved by NMR analysis. In Fig. S1a, the peak at 5.4 ppm is assigned to the proton attached to the anomeric carbon and peaks in the range of 3.3–4.2 ppm are attributed to the rest protons of the anhydroglucose unit (AGU) (Cheng & Neiss, 2012). Peaks around 1.7 ppm and 4.7 ppm belong to methyl and methine groups of the 2-bromopropionyl group, respectively. The DS of

StBr could be quantified with the peaks at 5.4 ppm and 1.7 ppm (see equation S1 in the support information). In the ^{13}C NMR spectrum (Fig. S1b), the peak at 100 ppm belongs to the anomeric carbon and the peaks ranging from 60 ppm to 80 ppm can be assigned to the rest AGU carbons (Cheng & Neiss, 2012). The resonances of methyl and methine carbon are located at 22 ppm and 54 ppm, respectively. These assignments are verified by the gHSQC spectrum (Fig. 1 Right). The weak signal (due to long relaxation time and reduced nuclear Overhauser effect) from carbonyl carbon can also be seen at 173 ppm (Fig. S1b), which further indicates the successful synthesis of StBr (Pavia, Lampman, Kriz, & Vyvyan, 2014).

Three StBr with different DS were synthesized to study the esterification efficiency and the influence of DS on the solubility of the macroinitiator in water. As reported, homogeneous esterification of corn starch was carried out in ionic liquid 1-allyl-3-methylimidazolium chloride ([AMIM]Cl) with 2-bromoisobutyryl bromide (BiBB) as bromination reagent (Wang, Shen, et al., 2015; Wang, Wu, et al., 2015). When the AGU/BiBB ratio was set to 1:5, different DS (0.12, 0.83 and 0.93) could be obtained within different reaction time (0.15 h, 1.0 h and 2.5 h correspondingly). As summarized in Table 1, compared with the above-mentioned results (Wang, Shen, et al., 2015; Wang, Wu, et al., 2015), the apparent esterification efficiency of waxy potato starch in DMAC/LiCl is higher, although the reaction time is longer. The differences in the DS values between this work and others (Wang, Shen, et al., 2015; Wang, Wu, et al., 2015) could be due to the difference in chemical structure (i.e. steric hindrance) of the brominating agent, the structure (and thus botanical source of the starch), as well as the used solvent. Table 1 also indicates that macroinitiators with DS lower than 0.15 should be water soluble. Given the molecular weight of waxy potato starch (ca. 10^7 – 10^8) (Jane, 2004; Yoo & Jane, 2002; Zobel, 1988), there should be roughly 1000 initiation sites per macroinitiator molecule. When the DS is higher than 0.26, StBr becomes insoluble in water but soluble in organic solvents like acetone and DMSO.

3.2. Aqueous Cu^0 -mediated LRP of acrylamide onto starch

Cu^0 -mediated LRP, usually known as single electron transfer living radical polymerization (SET-LRP) or supplemental activator and reducing agent (SARA) ATRP, could accomplish controlled living radical polymerization with much lower catalyst concentration while obtaining higher conversion rate (Konkolewicz et al., 2014). Recent research also showed that Cu^0 -mediated LRP is a very effective technique for the aqueous polymerization of monomers like acrylamide (Jones et al., 2016) and methacrylic acid (Fantin, Isse, Venzo, Gennaro & Matyjaszewski, 2016), which have been the challenge of normal ATRP for a long time. In this research, the grafting of acrylamide onto starch was carried out with this technique.

As depicted in Scheme 1, Cu^0 -mediated LRP of acrylamide was carried out with StBr (DS = 0.15) as initiator and $\text{CuBr}/\text{Me}_6\text{Tren}$ as the catalyst system. Series of St-g-PAM copolymer with the degree of polymerization (DP) of PAM chains ranging from 200 to 600 were synthesized (see Table 2). The copolymer was characterized by FT-IR (Fig. 2, Left) and ^1H NMR (Fig. 2, Right). The absorption peak at

Scheme 1. Synthesis of waxy potato starch-based ATRP macroinitiator and St-g-PAM.

Fig. 1. FT-IR spectra of StBr with different DS (Left) and gHSQC spectrum of StBr (DS = 0.15) in D₂O (Right).

Table 1

Experimental data of esterification of starch at various molar ratios of AGU/BpB.

Entry	AGU/BpB ratio	DS ^a	Time/h	Solubility in water ^b
1	4:1	0.15	3	+
2	3:1	0.26	3	–
3	1:1.2	0.86	3	–

^a DS is calculated from ¹H NMR.

^b +, water soluble; –, not soluble in water.

3188 cm^{−1} in the FT-IR spectrum was assigned to the stretching of the N–H bond in the amine group. Typical amide group peaks at 1652 cm^{−1} (amide I) and 1610 cm^{−1} (amide II) could also be seen in the spectrum. The successful synthesis of St-g-PAM was further verified with ¹H NMR. In Fig. 2 (Right), peaks in the range of 1.3–1.9 ppm and 2.0–2.5 ppm were attributed to protons attached to the secondary and tertiary carbon atoms on the backbone of polyacrylamide, respectively. The inset spectrum shows the resonance signals from the AGU of starch in the range of 3.4–5.5 ppm.

Besides the obvious changes in the macromolecular structure as highlighted above, also the morphology of the material is clearly affected by the grafting reaction. In particular, as expected from the dissolution in DMAc, the starch granule structure is lost as evident from the corresponding SEM images (Fig. 3(a–c)). This is in turn coupled with the disappearance of the crystalline structure as evidenced by XRD analysis (Fig. 3(d, e, f)). In the case of thermal analysis, DSC results (Fig. S2) show no relevant difference in the transition temperature between pristine and modified starch. This is possibly due to the low heat capacity of starch and other various parameters (e.g. water content) (Averous & Boquillon, 2004; Wang & Copeland, 2013). The TGA results as shown in Fig. 4, however, clearly indicate that StBr has a lower initial decomposition temperature (IDT = 236 °C) compared with

pristine starch (300 °C). This is quite similar to other systems for which chemically modified starches display a lower IDT (Kaushik, Singh, & Verma, 2010). For St-g-PAM the TGA curve changes in shape and clearly displays a two-stage degradation step, closely resembling the behavior of pure PAM as expected from the relatively low percentage of starch in St-g-PAM.

A clear evidence for the grafting as opposed to AM homopolymerization, yielding a physical mixture of the two polymers, can be derived, although indirectly, from the chemistry of the system. Indeed, ATRP relies on the presence of the halogen atom (in this case Br), which only presents as grafted group onto the starch (*vide supra*), for the chain growth (Fantin et al., 2016; Wang et al., 2012).

As shown in entry 1 (Table 2), the initial homogeneous Cu⁰-mediated LRP of acrylamide was carried out with a ratio of [AM]:[Initiator]:[CuBr]:[Me₆Tren] of 600:1:0.8:0.6. A monomer conversion of 66% was achieved within 80 min with a narrow PDI of 1.36, which indicates a reasonably good control over the polymerization (Wang, Shen, et al., 2015; Wang, Wu, et al., 2015; Wever, Raffa, Picchioni, & Broekhuis, 2012). This was further proved by the GPC results which showed very high correspondence between experimental and theoretical molecular weight. Unlike other works stating that the polymerization could finish within 15 min with almost 99% conversion (Jones et al., 2016), the polymerization rate of AM onto starch was slower and the conversion rate was relatively lower with a larger PDI of PAM chains under similar initial conditions. One possible reason for the lower polymerization rate could be related to the difference in initiator structure. In Jones' work tertiary α-bromoester was used as the initiator, the activation rate constant of which is about 8 times of the secondary α-bromoester used in the present work (Tang, 2007; Zhou & Luo, 2014). Besides the initiator structure, viscosity may be another factor influencing the polymerization. According to the modeling, diffusion-controlled deactivation resulting from high viscosity may cause the increase in molecular

Table 2

Experimental data of Cu⁰-mediated LRP of AM onto starch.

Entry	[M]:[I]:[Cu(I)]:[Me ₆ Tren] ^a	M/water ^b (wt:vol)	Time (min)	Conv. ^{GC} (%)	M _n ^{GPC}	M _n th	PDI
1	600:1:0.8:0.6	1:9	80	66	2.83 × 10 ⁴	2.81 × 10 ⁴	1.36
2	1000:1:0.8:0.6	1:8	60	63	4.27 × 10 ⁴	4.48 × 10 ⁴	1.64
3	1000:1:1.0:0.6	1:8	90	50	3.70 × 10 ⁴	3.55 × 10 ⁴	1.67
4	1000:1:1.2:0.6	1:8	120	25	1.55 × 10 ⁴	1.78 × 10 ⁴	1.49
5	1000:1:1.2:0.6	1:5	80	37	2.35 × 10 ⁴	2.63 × 10 ⁴	1.45
6	1000:1:1.2:0.6	1:4	80	42	2.55 × 10 ⁴	2.98 × 10 ⁴	1.31
7	1000:1:1.2:0.6	1:3	120	25	1.74 × 10 ⁴	1.78 × 10 ⁴	1.35

^a Molar ratio of monomer/initiator/catalyst.

^b Ratio of monomer to water.

Fig. 2. FT-IR spectra of St-g-PAM (Left) and ^1H NMR spectra of St-g-PAM in D_2O (Right).

weight distribution (Rabea & Zhu, 2015). Considering the higher viscosity of St-g-PAM compared with PAM homopolymer (see Fig. 6c), larger PDIs in the present work could be explained.

When the targeted degree of polymerization was increased to 1000 (entry 2, Table 2), the same monomer conversion could be achieved within around 60 min, which implies a higher polymerization rate compared with entry 1 (Table 2). Although the experimental and theoretical molecular weight are in good correspondence, a higher PDI value indicated relatively insufficient deactivation of the propagating polymer chains. The concentration of copper was increased by 25% to $[\text{AM}]:[\text{Initiator}]:[\text{CuBr}]:[\text{Me}_6\text{Tren}]$ of 1000:1:1.0:0.6 (entry 3, Table 2). When comparing the conversion rate and corresponding reaction time with entry 2, there is a clear decrease in the polymerization rate with no apparent improvement on the molecular weight distribution. When the ratio of $[\text{AM}]:[\text{Initiator}]:[\text{CuBr}]:[\text{Me}_6\text{Tren}]$ was set to 1000:1:1.2:0.6

(entry 4, Table 2), a better controlled polymerization with final PDI of 1.49 was achieved. The reaction was stopped at 120 min to prevent the loss of chain end bromide, which usually leads to a broad molecular weight distribution (Lutz & Matyjaszewski, 2005; Nguyen, Rodriguez-Emmenegger, Brynda, Sedlakova, & Percec, 2013; Rademacher, Baum, Pallack, & Brittain, 2000). It is clear that high concentration of deactivator in the solution resulted in a lower polymerization rate compared with entry 2 and entry 3 (Table 2). The living polymerization process was also monitored with a kinetic study (detail in Support information Figs. S3–S5). In Fig. 5 (Left), where the $[\text{M}]_0$ and $[\text{M}]_t$ correspond to the monomer concentration at the beginning of polymerization and at time t , the linear temporal evolution of $\ln([\text{M}]_0/[\text{M}]_t)$ demonstrated a first-order polymerization process.

Besides the concentration of catalyst, the influence of monomer to solvent ratio was also studied in this research. When decrease the

Fig. 3. SEM micrograph of starch (a), StBr (b), St-g-PAM (c) and corresponding XRD patterns of starch (d), StBr (e), St-g-PAM (f).

Fig. 4. Thermogravimetric analysis of Starch, St-Br, PAM, and St-g-PAM.

volume of water to a ratio of 1:5 with respect to the monomer mass (entry 5, Table 2), a 48% increase in the conversion rate was found at a shorter reaction time compared with entry 4 with a ratio of 1:8. This implies a significant increase in the polymerization rate which may be attributed to the increase of monomer concentration, although the concentration of deactivator was also increased. A further decrease in the water volume (entry 6, Table 2) led to a 13.5% increase in the monomer conversion on the basis of entry 5 (Table 2). The molecular weight distribution was also improved which was related to efficient deactivation of propagation polymer chains resulting from the increase of deactivator concentration. When the ratio was set to 1:3, a significant drop on the polymerization rate was observed. This indicated that the activation/deactivation equilibrium was predominated by Cu(II) because of its high concentration. The comparison also hints that there should be an optimum monomer to solvent ratio for the controlled living aqueous polymerization of acrylamide. A simple kinetic study was carried out during the polymerization as shown in Fig. 5 (Right) (detail in support information Figs. S6 and S7). The linear dependence of $\ln([M]_0/[M]_t)$ on time illustrates a controlled living polymerization of acrylamide onto waxy potato starch.

A preliminary study on the influence of PAM chain length on the rheological properties of St-g-PAM was also carried out at the same concentration (5.0 wt.%). According to the DP of PAM side chains and the result shown in Fig. 6c, St-g-PAM copolymers were divided into three groups, thus only comparison of entry 1 (group DP 300–400, Table 2), entry 2 (group DP 500–600, Table 2) and entry 4 (group DP 200–300, Table 2) with that of starch was shown in the other subgraphs of Fig. 5 for the purpose of clarity.

Fig. 5. Kinetic plot of Cu^0 -mediated LRP of AM onto starch.

As shown in Fig. 6a and b, both storage (G') and loss (G'') modulus of St-g-PAM increase with the increasing of PAM chains' DP. When the chain length goes up to DP 500 (entry 2, Table 2), there is a significant increase in the storage modulus compared with the other two groups, especially at the low frequency (Fig. 6a). This indicates that there should be a critical chain length for the considerable improvement of polymer solution's elastic behavior which is important for efficient EOR (Zhu et al., 2013). Different from G' , the influence of chain length on the loss modulus (G'') which represents viscous properties seems to be more gradual (Fig. 6b), given the absence of result from copolymers with DP around 400–500. The same trend could also be seen in Fig. 6d, which shows the relationship of modulus (G' and G'') at the highest frequency) with the hydrodynamic volume (R_h) of copolymers. Considering the hydrodynamic volume of PAM chains that are cleaved from the St-g-PAM copolymers and PAM homopolymer with similar DP synthesized by RAFT in our group ($R_h < 15$ nm), the increase in the R_h of copolymers should be mainly attributed to the increase of steric hindrance which results in the stretching of amylopectin molecules. This could prove the successful grafting of PAM onto starch at the molecular level. Besides G' and G'' , finely tuned solution viscosity was obtained through varying polymers' graft chain length as well (Fig. 6c). Moreover, experimental results in Fig. 6c also show a significant difference between St-g-PAM (Table 2, entry 2) and the mixture of starch and PAM homopolymer (St/PAM600, being prepared according to the graft ratio of entry 2 (Table 2); PAM600 had the same DP with the PAM side chains of entry 2 (Table 2)). This is also a persuasive proof for the successful synthesis of St-g-PAM.

4. Conclusion

In the present study, waxy potato starch-based macroinitiator (StBr) was synthesized homogeneously in DMAc/LiCl and characterized by ^1H NMR, ^{13}C NMR, gHSQC and FT-IR. Starch-g-polyacrylamide (St-g-PAM) was then synthesized, for the first time to the author's best knowledge, by aqueous Cu^0 -mediated LRP at the molecular level. The macromolecular structure changes (as highlighted by NMR and FT-IR), the morphology evolution (as evidenced by SEM and XRD), the differences in TGA analysis as well as the comparison of flow curves of St-g-PAM with a starch/PAM mixture proved the successful synthesis of StBr and St-g-PAM. The difference in the hydrodynamic volume of starch with St-g-PAM indicated that polyacrylamide was grafted onto starch at molecular level. The agreement of PAM molecular weight (GPC) with theoretical values and corresponding PDIs as well as kinetic plot demonstrated well-controlled graft polymerization. Investigation on the influence of monomer to solvent (wt.:vol.) ratio implied that an optimal monomer concentration exists for efficient and controlled polymerization. Good tunability of Cu^0 -mediated LRP on copolymers' rheological properties was also demonstrated by a primary rheological study. Besides that, a critical PAM chain length for significant improvement of

Fig. 6. Storage modulus G' (a), loss modulus G'' (b), solution viscosity vs shear rate (1-StPAM400, 1 is the entry number and StPAM400 stands for starch-g-PAM with DP of 400 for PAM side chains, the rest is similar) (c) for starch and St-g-PAM copolymers at the concentration of 5.0 wt % and their relationship with hydrodynamic volume (d).

copolymers' elastic properties was suggested by dynamic rheology analysis.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.carbpol.2018.03.041>.

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