Preparation and Flocculation Behavior of Cellulose-g-PMOTAC Copolymer

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ABSTRACT: As a contribution to the wider use of biodegradable materials, this article reports the synthesis and testing of cationic polyelectrolyte cellulose derivatives for use as flocculation chemicals. Cellulose macroinitiator is synthesized in DMAc/LiCl solvent system by direct acylation of cellulose with 2-bromoisobutyryl bromide. Cellulose-*graft*-poly(N,N-dimethyl aminoethyl methacrylate) (cellulose-*g*-PDMAEMA) copolymers are prepared by copper-mediated radical polymerization in homogeneous medium. Formation of the macroinitiator and graft copolymers is confirmed by ATR-FTIR and ^{1}H NMR. Quaternization of the graft chains to poly(methacryloxyethyl trimethylammonium chloride) (PMOTAC) produces cellulose-*g*-PMOTAC, which performs similarly to a commercial product in flocculation of pulp and kaolin. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40448.

INTRODUCTION

Polymeric flocculants are widely used to promote the aggregation of small particles in retention applications, surface sizing, and wastewater treatment. Polyelectrolytes, especially synthetic cationic polymers such as polydiallyldimethylammonium chloride (polyDADMAC), polyethyleneimine, and cationic polyacrylamides, are widely used as flocculants for dewatering and wastewater treatment in the paper industry.[1,2] Modified starches are used in papermaking applications as a means of increasing the use of renewable resources, and cationized starches have attracted attention as potential biodegradable flocculants.[3,4] Relevant to this, cationic cellulose derivatives are interesting biodegradable alternatives to the flocculants needed in papermaking. Cellulose has been directly cationized with 2,3-epoxypropyltrimethylammonium chloride in NaOH/urea aqueous solution,[5] and dialdehyde cellulose has been cationized to produce a cellulose-based water-soluble flocculant.[6]

A special type of biopolymer-based material is a copolymer consisting of a biopolymer grafted with synthetic polymer. The use of biopolymer-based graft copolymers and other copolymers in flocculation was recently reviewed by Lee et al.[7] Cellulose and cellulose derivatives have been grafted with vinyl or acrylic monomers via free radical mechanism. The reaction is initiated by creating free radical sites on the cellulose backbone, and monomer reacts with these sites to propagate new polymer chains covalently anchored to the backbone.[8] The free radicals can be formed by irradiation of the cellulose with gamma rays[9] or the use of chemical initiators.[10–12] Both methods have the drawback that the molecular weight and molecular weight distribution of the graft chains cannot be controlled. The polysaccharide backbone may also be degraded.

Controlled radical polymerization techniques, such as atom transfer radical polymerization (ATRP) and single-electron transfer living radical polymerization (SET–LRP), are versatile techniques that allow grafting with controlled and well-defined chain length while preventing homopolymer formation. Controlled radical polymerization can be used to graft polysaccharides, such as cellulose or cellulose derivatives, in both homogeneous and heterogeneous media.[13,14] First, however, the cellulose or cellulose derivative must be modified into a macroinitiator (MI) through attachment of alkyl bromide (or chloride) groups along the cellulose chain.

Macroinitiators have been prepared by dissolving unmodified cellulose in dimethylacetamide/LiCl (DMAc/LiCl) solvent system and directly acylating it with 2-bromoisobutyryl bromide in the presence of pyridine[15–17] or triethylamine and 4-dimethylaminopyridine.[18] Cellulose MIs have also been prepared in a mixture of ionic liquid 1-allyl-3-methylimidazolium chloride (AmimCl) and dimethylformamide and acylated with 2-bromopropionyl bromide[19,20] or 2-bromoisobutyryl bromide.[21] Further, cellulose has been dissolved in ionic liquid 1-N-butyl-3-methylimidazolium chloride (BmimCl) and acetylated with chloroacetyl chloride.[22]

We dissolved pulp cellulose in DMAc/LiCl solvent system at elevated temperature.[23] DMAc/LiCl was used in our laboratory previously to dissolve cellulose for preparation of cellulose MIs, but the cellulose was then dissolved by solvent exchange.[15] Elevated temperature allows a good cellulose solution to be achieved in shorter time. N,N-Dimethyl aminoethyl methacrylate (DMAEMA) monomer was chosen for graft copolymerization of the cellulose. Poly(N,N-dimethyl amino-ethyl methacrylate) (PDMAEMA) is a pH- and temperature-sensitive weak cationic polyelectrolyte that can be modified into a strong polyelectrolyte [poly(methacryloxyethyl trimethylam-monium chloride)] (PMOTAC). PDMAEMA homopolymers have earlier been synthesized by copper-mediated controlled LRP in various solvents, including dimethyl sulfoxide (DMSO).[24] Copolymerizations of DMAEMA and hydroxyethyl methacrylate have been conducted in DMSO by ATRP.[25]

Graft copolymerization of cellulose or cellulose derivatives with DMAEMA has been achieved via controlled radical polymerization. Sui et al.[19] carried out homogeneous ATRP of a cellulose MI prepared from pulp with DMAEMA in DMF solvent. The graft copolymers were soluble in water, and the authors investigated the aggregation and self-assembly of the copolymers at various pH values. Ma et al.[26] prepared MIs from hydroxy-propyl cellulose and grafted them with DMAEMA by ATRP in methanol–water mixture. The graft copolymerization was living and controllable. Yan et al.[27] prepared MIs from ethyl cellulose and used them to synthesize dual graft molecular brushes of PDMAEMA and poly(ε-caprolactone) (PCL). The ethyl cellulose MIs were first grafted with PCL via ring-opening polymerization and then with PDMAEMA via ATRP in THF solvent.

In this study, graft copolymerization was conducted in DMSO because the MI, monomer, and copper salts could all be dissolved in DMSO. As catalyst system, CuBr/CuBr$_2$ was used with a ligand. Recent reports[18,28–30] of controlled radical copolymerization in DMSO suggest that the mechanism of the polymerization is Cu(0)-mediated SET–LRP. Nitrogen-containing ligands in protic solvents and dipolar aprotic solvents such as DMSO disproportionate Cu(I) into Cu(0) and Cu(II).

The aim of our research was to prepare cationic, water-soluble cellulose derivatives for use as flocculation chemicals in papermaking. A cellulose MI for controlled radical polymerization was prepared and used in the synthesis of cellulose-PDMAEMA graft copolymers and their quaternized derivatives. The ability of the quaternized derivatives to perform as flocculants was demonstrated.

EXPERIMENTAL

Materials

The starting material for the cellulose MI was softwood dissolving pulp (Domsjö, Sweden), prepared from spruce and pine (60 : 40) by a modified two-stage sulfite cooking with totally chlorine-free bleaching. The pulp was reported to contain 3.5% hemicelluloses (2.1% glucomannan and 1.4% xylan) and to have low lignin content (<0.5%). N,N-Dimethylacetamide (DMAc 99%), LiCl (99%), 2-bromoisobutyryl bromide (BiB, 99%), CuBr (99.999%), CuBr$_2$ (99.999%), N,N,N′,N″,N‴-pen-

tamethyldiethylenetriamine (PMDETA, 99%), 1,1,4,7,10,10-hexa methyltriethylenetetramine (HMTETA, 97%), and kaolin clay were purchased from Aldrich. DMAEMA was from Acros Organics and HCl and NaOH standard solutions were from Oy FF-Chemicals Ab. Other reagents were DMSO (99.5% Lab-Scan), NaCl (J.T. Baker), iodomethane (Fluka, ≥99%), acetic acid (VWR International, 100%), and sodium acetate (Riedel-de Haën, purum).

Two commercial cationized polyacrylamides (c-PAM) were provided by Kemira: c-PAM1 (MW 6M g mol^{-1}, 1.2 meq g^{-1}) and c-PAM2 (MW 6M g mol^{-1}, 4.0 meq g^{-1}). Eucalyptus pulp was used in flocculation experiments. Solvents (DMAc and DMSO) were dried over 4Å molecular sieves. The inhibitor was removed by passing DMAEMA through a column of basic alumina. Other reagents were used as received.

Characterization

Infrared Spectroscopy. ATR-FTIR spectra were measured with a PerkinElmer Spectrum One FT-IR spectrometer equipped with Spectrum One FT-IR software and an ATR sampling accessory.

Spectrophotometry. Transmittance of samples in flocculation tests was measured at room temperature with a Shimadzu 1601PC UV–Vis spectrophotometer at wavelength of 600 nm.

Nuclear Magnetic Resonance Spectroscopy. The ^{1}H NMR spectrum of the MI was measured in d_6-DMSO at 80°C, and spectra of cellulose graft copolymers dissolved in D$_2$O were measured at room temperature. The spectra were acquired with a Bruker Avance III 500 MHz NMR spectrometer.

Dynamic Light Scattering. Dynamic light scattering measurements of two cellulose graft copolymers and a commercial flocculant were conducted on aqueous solutions at a concentration of 0.1 mg mL^{-1}. Measurements were made with a Brookhaven Instruments BIC-200SM goniometer, a BIC-TurboCorr digital auto/crosscorrelator, and a BIC-CrossCorr detector equipped with two BIC-DS1 detectors. A Sapphire 488-100 CDRH laser from Coherent GmbH operating at wavelength $\lambda_0 = 488$ nm (vertically polarized) was used, and the time-correlation functions of the scattered light were analyzed with the inverse Laplace transform program CONTIN. The temperature of the sample was controlled with a Lauda RC 6C thermostat. Scattered light was collected at 90° scattering angle and 25°C. Samples were passed through 0.45 μm ø 13 mm PVDF filters.

Dissolution of Cellulose Pulp

Softwood dissolving pulp was dissolved in DMAc/LiCl by the method of Rahn et al.[23] The pulp was cut into small pieces and dried at 110°C. Dry pulp (4 g) was stirred into 400 mL DMAc and heated to 130°C. After 2 h, the temperature was lowered to 100°C and dry LiCl (5 wt %) was added. Stirring was continued overnight without heating. The following day the solution was transparent.

Synthesis of Cellulose Macroinitiator

The MI was synthesized as described by Hiltunen et al.[15] Pyridine was added to the cellulose solution to neutralize the HBr formed in the reaction, after which 2-bromoisobutyryl bromide (BiB) was added dropwise in an ice/water bath with stirring.

Table I. Polymerizations with Macroinitiator MI

No.	Ligand	Reaction time (h)	Monomer conversion[b] (%)	Cellulose in product[b] (%)	Quaternized/Reaction time (h)
1	PMDETA	1	13	18	Yes/5
2	PMDETA	4	18	14	No
3	HMTETA	6	12	19	No
4	HMTETA	23	22	11	Yes/21

The ratio of [I][a]:[M]:[Cu(I)]:[ligand] was 0.5 : 100 : 1 : 2 and monomer concentration 0.27M.
[a] Concentration of 2-bromoisobutyryl groups.
[b] Estimated from weight gain.

The ratio of BiB to cellulose anhydroglucose units was 1 : 1. When the addition was complete, the reaction was allowed to proceed for 20 h at room temperature, after which the product was precipitated into distilled water, carefully washed with water, and dried under vacuum.

Synthesis of Cellulose-PDMAEMA Graft Copolymers

The cellulose MI was used to initiate the polymerization of DMAEMA via SET-LRP with the use of CuBr/CuBr$_2$ and a ligand as the catalyst system. Ligands tested were PMDETA and HMTETA. Polymerizations were conducted in DMSO at 60°C. Reaction times were varied (see Table I). The polymerization procedure was the following: MI was dissolved in DMSO (25% of total solvent volume). Copper bromides were weighed and dissolved in DMSO, and DMAEMA was added. The [Cu$^+$] : [Cu^{2+}] ratio was 4 : 1. Ligand was added to the MI solution, and the mixture was bubbled with nitrogen for 10 min. The copper bromide-DMAEMA solution was also bubbled with nitrogen, for at least 40 min, and then placed in an oil bath. The MI–ligand solution was added drop-wise to the copper bromide-DMAEMA solution over ~10 min.

After reaction the reaction mixtures were cooled and purified by dialysis through a regenerated cellulose tubular membrane (dialysis membrane nominal molecular weight cut-off of 3500 g mol^{-1}; Orange Scientific). The reaction mixture was first dialyzed against acetic acid/sodium acetate buffer and then against neutral distilled water. After a few days of dialysis, the products were freeze-dried. The acidic buffer was used because of the poor stability of DMAEMA in neutral water.[31] Buffer lowers the risk of unreacted monomer hydrolyzing and reacting with the polymer.

Quaternization of Cellulose-PDMAEMA Graft Copolymers

Graft copolymers were dispersed in water and iodomethane was added. The molar ratio of iodomethane to DMAEMA units of the copolymers was 5 : 1. The mixture was stirred, protected from light, for a prescribed time. Iodide ions were exchanged for chloride ions by adding concentrated NaCl solution to the reaction mixture and then dialyzing against NaCl solution. The pure cellulose-*g*-PMOTAC was obtained by changing the dialysis solution to distilled water and freeze-drying.

Flocculation Tests

Flocculation tests were performed with the quaternized cellulose derivatives and the results were compared with those for commercial flocculants. Dispersions of kaolin clay were prepared with and without eucalyptus pulp. The concentration of kaolin was 3 g L^{-1} and the concentration of pulp was 5 g L^{-1}. Before the flocculation tests the pH of the dispersion was adjusted with dilute HCl or NaOH solution. The dispersion (99 mL) was measured in a 100 mL beaker and flocculant was added in solution form (1 mL in water) with stirring. The mixture was stirred for 1 min and allowed to settle for 1 min (when only kaolin was used) or 2 min (when both kaolin and pulp were used). After the settling period, a sample of the supernatant liquid was drawn off and transmittance of the supernatant was measured with a spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of Macroinitiator

Cellulose MI was prepared by partial acylation of the hydroxyl groups of the cellulose with BiB (Scheme 1). Characterization by ATR-FTIR and ^{1}H-NMR confirmed the success of the acylation.

The ^{1}H NMR spectrum of the cellulose MI was measured at 80°C (Figure 1). The protons of the methyl groups are detected at 1.5–2.0 ppm (integral value 10.2) and cellulose backbone protons at 3.1–5.5 ppm (integral value 89.8). The assignment of protons in unsubstituted glucose units is included in the spectrum. All other peaks are due to the acylation in positions 2, 3, or 6. The degree of substitution (DS) of OH groups with 2-bromoisobutyryl groups was ~0.2, estimated from the ^{1}H NMR spectrum (Figure 1) as ratio of the integral of the protons of the methyl groups (I_{methyl}) to the integral of the protons of the cellulose backbone ($I_{cellulose}$) (eq. 1). Note that eq. 1 is valid only for low DS macroinitiator.

$$DS = \frac{I_{methyl}/6}{I_{cellulose}/10} \qquad (1)$$

The MI was designed to have low DS but also sufficient solubility for homogeneous polymerization. Higher DS would allow better solubility, but probably some initiator groups would not
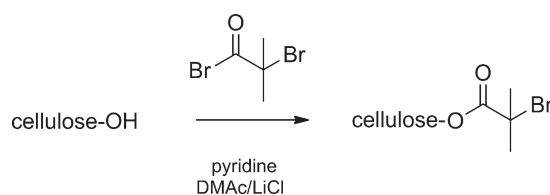
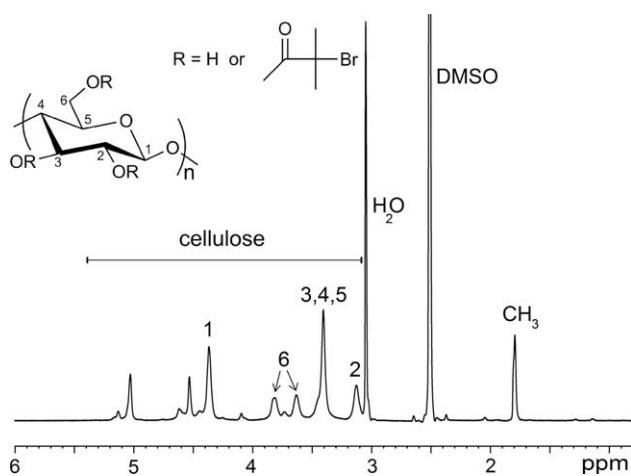**Scheme 1.** Synthesis of MI: reaction of BiB with cellulose.

Figure 1. ^{1}H NMR spectrum of MI 7 mg mL^{-1}.

Scheme 2. Reaction schematic for grafting of MI with DMAEMA.

be able to initiate polymerization because of steric hindrance. Hiltunen et al.[15] prepared cellulose MIs with different degrees of substitution by varying the reaction time and the feed ratio of BiB to anhydroglucose units.

ATR-FTIR spectra of the unmodified softwood dissolving pulp and cellulose MI are shown in Figure 2. Formation of the MI is confirmed by the carbonyl ester stretching band at 1743 cm^{-1} [Figure 2(b)]. The broad band at ~3400 cm^{-1} is the stretching band of cellulose hydroxyl groups.[15]

Graft Copolymerizations

The cellulose MI was used to prepare cellulose-PDMAEMA graft copolymers by SET–LRP in DMSO solvent (Scheme 2). The SET–LRP was catalyzed by CuBr/CuBr$_2$ and ligand PMDETA or HMTETA. Polymerization parameters are shown in Table I. The solubility of MI was too low for it to dissolve properly in DMSO in high concentrations. The grafting was therefore conducted in dilute MI solution, and the cellulose content in the grafted products was low. With ligand PMDETA the reaction proceeded fast, but apparently there was considerable cross-linking due to intermolecular recombination reactions, in which two growing side chains react with each other. Cross-linking explains why the products were not readily soluble in water. With HMTETA the reaction was slow and longer reaction times
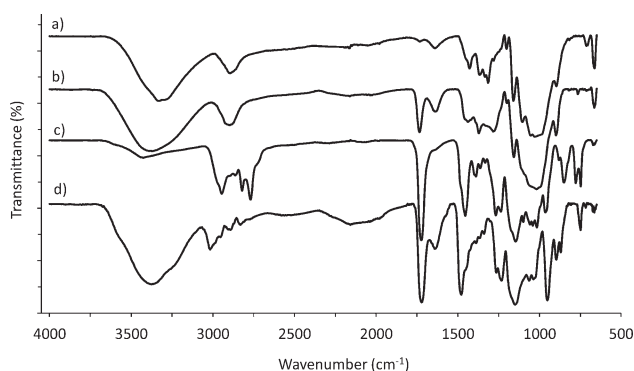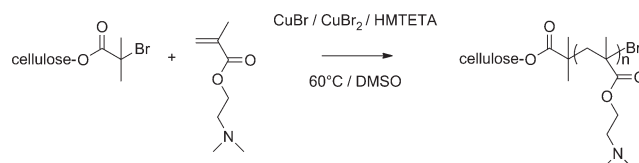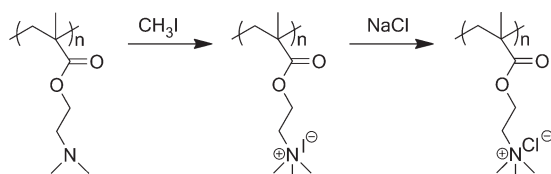
were needed, but the products were more soluble than with PMDETA, indicating less cross-linking. The ATR-FTIR spectrum of MI grafted with DMAEMA [Figure 2(c)] shows C—H stretching bands at 3000–2700 cm^{-1}, a C═O stretching band at 1724 cm^{-1}, CH$_2$-bending band at 1457 cm^{-1}, and C—N stretching at 1148 cm^{-1}.[19,32] Similar spectra were obtained for all PDMAEMA-grafted celluloses prepared. The the cellulose backbone appears as a band at 672 cm^{-1} and as a shoulder at ~1600 cm^{-1}.

As is typical for graft copolymerization of cellulose, monomer conversions were low (see Table I). In copolymerization of DMAEMA with a cellulose MI in DMF, Sui et al.[19] obtained 34.7% conversion. The highest conversion for cellulose grafting using a MI system in homogeneous medium (60%) is reported by Yan & Tao,[33] who grafted N,N-dimethylacrylamide to cellulose in DMSO solution. To determine molecular weights of the grafts, we attempted to cleave graft chains off the cellulose backbone by stirring overnight in 2M HCl at 110°C, but we were unable to analyze the hydrolysis products. Difficulties with graft chain cleavage have been reported for cellulose-g-PDMAEMA by Sui et al.[19] and for hydroxypropyl cellulose-g-PDMAEMA by Ma et al.[26] The problems with graft cleavage were attributed to a thick PDMAEMA layer wrapped around the cellulose backbone that prevents the hydrolysis[19] and to ester groups of the side chains hydrolyzing simultaneously with the cellulose backbone.[26]

When conversion in the grafting of MI with PDMAEMA (HMTETA as ligand) was followed by NMR, the conversion was found to increase up to 3 h and then remain more or less constant. In the case of PDMAEMA homopolymerization (1-ethylbromoisobutyrate initiator, CuBr/CuBr$_2$/HMTETA catalyst system), conversion increased up to ~1 h and then leveled off. We can conclude that the control of polymerization in our study was poor. Even without controlled grafting, the method was nevertheless necessary in preventing homopolymer formation and degradation of the cellulose backbone during polymerization. The limited conversion indicates either the occurrence of termination reactions or loss in activity of the catalyst.[28,34]

Quaternization

PDMAEMA is a weak cationic polyelectrolyte, which can be modified to the strong polyelectrolyte PMOTAC. The PDMAEMA grafts were first modified with iodomethane to PMETAI [poly(methacryloxyethyl trimethylammonium iodide)] and then with NaCl to PMOTAC (Scheme 3). The ^{1}H-NMR spectra of a cellulose-PDMAEMA graft copolymer before (Table I, No.4) and after (MI-g-PMOTAC-4) quaternization are shown in Figure 3. The spectra were recorded at room temperature. The peak at 4.8 ppm is the solvent peak.

Figure 2. ATR-FTIR spectra of (a) untreated pulp, (b) cellulose MI, (c) grafting product No. 4, MI-g-PDMAEMA-4, and (d) quaternized product MI-g-PMOTAC-4.

Scheme 3. Modification of PDMAEMA to PMOTAC.

Figure 4. Hydrodynamic diameter distributions of two MI-*g*-PMOTAC copolymers and a commercial flocculant.

In the spectrum of MI-*g*-PDMAEMA-4 [Figure 3(A)] the peak at ~4.2 ppm is from a, the peak at ~2.7 ppm from b, and the strong peak at ~2.3 ppm from c methyl groups as referenced in the structure.[35] The peaks at ~2 ppm and at 1.2–0.9 ppm are from the polymer backbone d and e, respectively. The small peaks in the spectrum between 5 and 6 ppm and at ~1.8 ppm are attributed to the hydrolysis products of residual DMAEMA monomer. Since the copolymer had been purified by dialysis against acidic buffer solution to prevent hydrolysis of unreacted DMAEMA, possibly DMAEMA hydrolyzed even in acidic medium, or perhaps some DMAEMA was left in the dialysis membranes after the dialysis liquid was changed to neutral distilled water. Minor indications of cellulose peaks are evident between 3 and 4 ppm. The cellulose peaks are weak because the cellulose backbone is not soluble in D_2O. The spectrum of PDMAEMA homopolymer (not shown) was nearly identical confirming that the amount of cellulose in the graft copolymer was low.

The spectrum of MI-*g*-PMOTAC-4 [Figure 3(B)] differs from that of MI-*g*-PDMAEMA-4 [Figure 3(A)]. The strong peak at ~3.3 ppm comes from the three methyl groups attached to nitrogen and the peak at ~3.8 ppm from the methylene group at nitrogen. The small peaks in the spectrum of MI-*g*-PDMAEMA-4 attributed to hydrolysis products are not present in the spectrum of MI-*g*-PMOTAC-4. According to the ^{1}H-NMR spectra, the quaternization was successful. Quaternization increased the solubility of the copolymers, which was also seen as greater sensitivity in the spectrum measured after quaterniza-
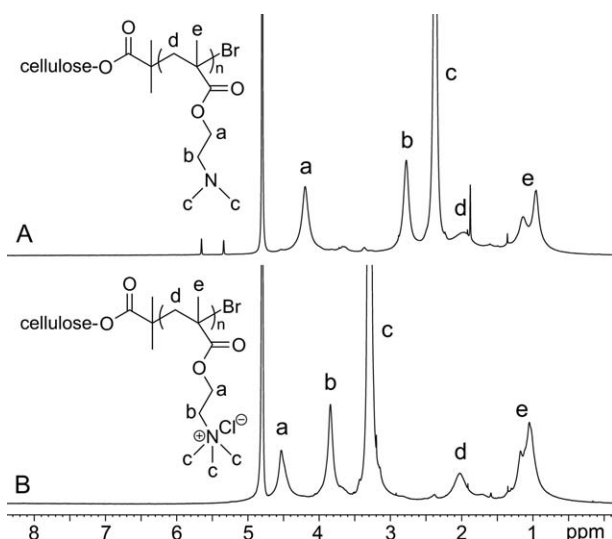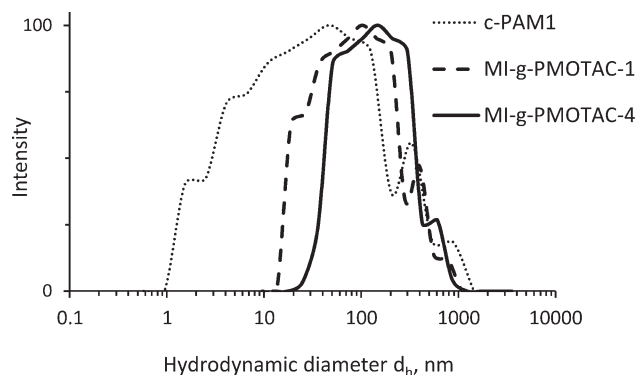
tion. The ATR-FTIR spectrum of the quaternized sample is presented in Figure 2(d). The quaternized sample contains more moisture than the unquaternized one, even though it was freeze-dried the same way. The moisture gives rise to the broad band at 3400 cm^{-1} and the band at ~1640 cm^{-1}, which are assigned to OH-stretching and bending modes of water, respectively. The quaternized sample also shows the C=O stretching band. The band at 1480 cm^{-1} is assigned to methyl groups of the quaternary ammonium.[5]

Dynamic Light Scattering
Dynamic light scattering was used to measure the sizes of cellulose-graft-PMOTAC copolymers and a commercial flocculant in water at a concentration of 0.1 mg mL^{-1} [Figure 4]. All measurements were conducted with 90° scattering angle. The hydrodynamic diameter distributions of the MI-graft-PMOTAC copolymers ranged from ~10 nm to 1000 nm. For c-PAM1 the distribution was still broader, ranging from 1 nm to ~1000 nm. The purification of the graft copolymers by dialysis may have removed the smallest particles.

Flocculation Tests
The flocculation performance of two quaternized graft copolymers and two commercial cationic flocculants (c-PAM1 and c-PAM2, with charge densities 1.2 meq g^{-1} and 4 meq g^{-1}, respectively) was tested in kaolin and kaolin-cellulose pulp dispersions. Kaolin clay, which is frequently used as paper filler, has an anionic charge. The flocculation mechanism of the polymers likely involves bridging, which can be described as the adsorption of a single high-molecular-weight polymer molecule onto two or more particles, forming bridges between them.[36] When graft copolymer or c-PAM is added to the dispersion, the polymer coils are adsorbed on kaolin and cellulose fiber surfaces, leading to aggregation. The pH was adjusted to 5 or 6. The results are shown in Figures 5 and 6. In each case, transmittance of the supernatant solution after an appropriate settling period was plotted against flocculant concentration in ppm. For the kaolin dispersions (without pulp) at pH 5 [Figure 5(A)], the transmittance values were highest at flocculant concentrations between 1 and 3 ppm for c-PAM2 and MI-*g*-PMOTAC-4 and between 2 and 5 ppm for c-PAM1 and MI-*g*-PMOTAC-1. Under these conditions 3 ppm flocculant dosage means that 1 kg of flocculant would be needed to flocculate 1000 kg of kaolin

Figure 3. ^{1}H-NMR spectra of A: MI-*g*-PDMAEMA-4 and B: MI-*g*-PMO-TAC-4 in D_2O, 5 mg mL^{-1}.
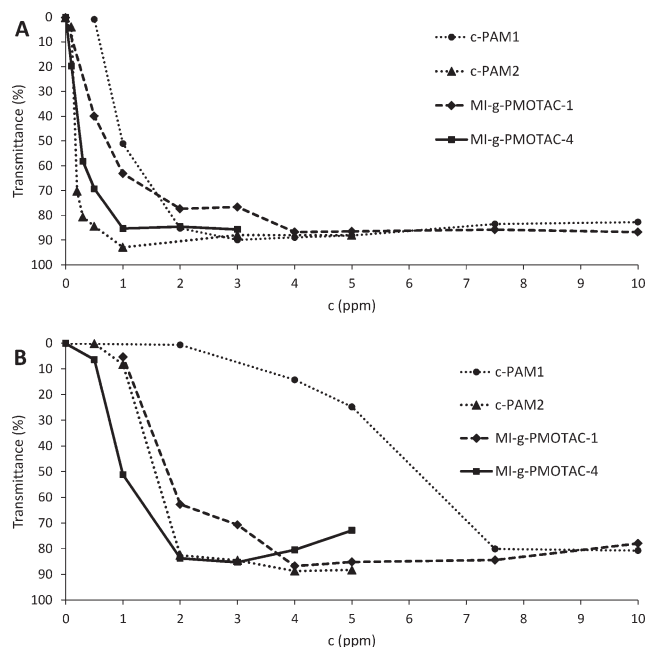
Figure 5. Transmittance of supernatant kaolin dispersions after 1 min settling period as a function of flocculant concentration A: at pH 5 B: at pH 6.

dispersed in water. With higher concentrations (7.5 and 10 ppm), the transmittance values were sometimes lower, probably because above a certain concentration, the cationic flocculant causes the surface to become positive and aggregation is less likely. Increase in pH stabilized the kaolin dispersion. The kaolin dispersion was more difficult to flocculate at pH 6 [Figure 5(B)]. For all samples, the supernatant liquid was turbid up to higher flocculant concentrations as compared with tests performed at pH 5.

The polymers were further tested in flocculation of kaolin-cellulose pulp dispersions at pH 5. Flocculation was more difficult for these dispersions than for dispersions of kaolin alone. c-PAM2 and MI-*g*-PMOTAC-4, which gave the best performance in kaolin dispersions, also performed best in kaolin-pulp dispersions. For both samples the optimal flocculant dosage was 5 ppm. MI-*g*-PMOTAC-1 was somewhat less efficient. With c-
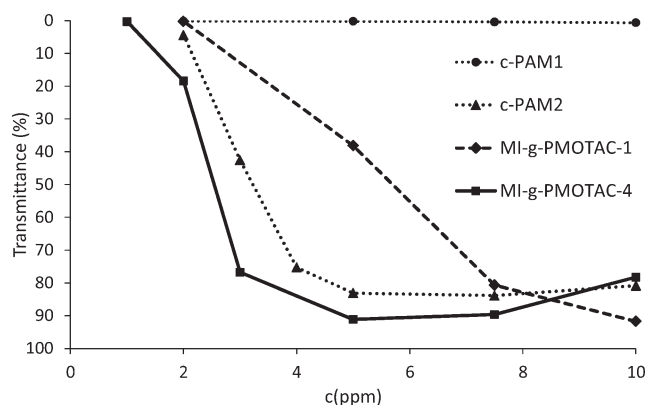

Figure 6. Transmittance of supernatant kaolin-eucalyptus pulp dispersions at pH 5 after 2 min settling period as a function of flocculant concentration.

PAM1, though part of the dispersion was flocculated, the supernatant remained turbid over the whole concentration range used.

CONCLUSIONS

Softwood dissolving pulp was successfully converted to a MI for graft copolymerization by direct homogeneous acylation in DMAc/LiCl solution. Cellulose-PDMAEMA graft copolymers were synthesized in DMSO solvent under mild conditions. Copolymerization was successful, though evidently not controlled. Two cellulose-*g*-PDMAEMA copolymers were quaternized to cellulose-*g*-PMOTAC to increase the cationic charge and improve water solubility. Flocculation performance of the cationized graft copolymers was tested and compared with that of commercial cationic polyacrylamides. The effectiveness of the cationized graft copolymers was similar to that of the commercial flocculants as demonstrated with kaolin and kaolin-pulp suspensions.

ACKNOWLEDGMENTS

REFERENCES

1. Norell, M.; Johansson, K.; Persson, M. In Papermaking Science and Technology; Neimo, L., Ed.; Fapet: Helsinki, **1999**; Book 4, pp 43−51.

2. Leiviskä, T.; Rämö, J. *J. Hazard. Mater.* **2008**, *153*, 525.

3. Bratskaya, S.; Schwarz, S.; Liebert, T.; Heinze, T. *Colloids Surf., A* **2005**, *254*, 75.

4. Kuutti, L.; Haavisto, S.; Hyvärinen, S.; Mikkonen, H.; Koski, R.; Peltonen, S.; Suortti, T.; Kyllönen, H. *Bioresources* **2011**, *6*, 2836.

5. Yan, L.; Tao, H.; Bangal, P. R. *Clean* **2009**, *37*, 39.

6. Sirviö, J.; Honka, A.; Liimatainen, H.; Niinimäki, J.; Hormi, O. *Carbohydr. Polym.* **2011**, *86*, 266.

7. Lee, K. E.; Morad, N.; Teng, T. T.; Poh, B. T. *Chem. Eng. J.*, **2012**, *203*, 370.

8. Roy, D.; Semsarilar, M.; Guthrie, J. T.; Perrier, S. *Chem. Soc. Rev.*, **2009**, *38*, 2046.

9. Takács, E.; Wojnárovits, L.; Borsa, J.; Papp, J.; Hargittai, P.; Korecz, L. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2005**, *236*, 259.

10. Okieimen, F. E. *J. Appl. Polym. Sci.* **2003**, *89*, 913.

11. Dahou, W.; Ghemati, D.; Oudia, A.; Aliouche, D. *Biochem. Eng. J.* **2010**, *48*, 187.

12. Graczyk, T.; Hornof, V. *J. Polym. Sci. Part A: Polym. Chem.* **1988**, *26*, 2019.

13. Tizzotti, M.; Charlot, A.; Fleury, E.; Stenzel, M.; Bernard, J. *Macromol. Rapid Commun.* **2010**, *31*, 1751.

14. Malmström, E.; Carlmark, A. *Polym. Chem.* **2012**, *3*, 1702.

15. Hiltunen, M.; Raula, J.; Maunu, S. L. *Polym. Int.* **2011**, *60*, 1370.

16. Hiltunen, M.; Siirilä, J.; Aseyev, V.; Maunu, S.L. *Eur. Polym. J.* **2012**, *48*, 136.

17. Yan, L.; Ishihara, K. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 3306.

18. Raus, V.; Stepanek, M.; Uchman, M.; Šlouf, M.; Látalová, P.; Čadová, E.; Netopilik, M.; Kriz, J.; Dybal, J.; Vlček, P. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 4353.

19. Sui, X.; Yuan, J.; Zhou, M.; Zhang, J.; Yang, H.; Yuan, W.; Wei, Y.; Pan, C. *Biomacromolecules* **2008**, *9*, 2615.

20. Xin, T.T.; Yuan, T.; Xiao, S.; He, J. *Bioresources* **2011**, *6*, 2941.

21. Meng, T.; Gao, X.; Zhang, J.; Yuan, J.; Zhang, Y.; He, J. *Polymer* **2009**, *50*, 447.

22. Chun-xiang, L.; Huai-yu, Z.; Ming-hua, L.; Shi-yu, F.; Jia-jun, Z. *Carbohydr. Polym.* **2009**, *78*, 432.

23. Rahn, K.; Diamantoglou, M.; Klemm, D.; Berghmans, H.; Heinze, T. *Die Angew. Makromol. Chem.* **1996**, *238*, 143.

24. Monge, S.; Darcos, V.; Haddleton, D.M. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 6299.

25. Teoh, R. L.; Guice, K. B.; Loo, Y. L. *Macromolecules* **2006**, *39*, 8609.

26. Ma, L.; Liu, R.; Tan, J.; Wang, D.; Jin, X.; Kang, H.; Wu, M.; Huang, Y. *Langmuir* **2009**, *26*, 8697.

27. Yan, Q.; Yuan, J.; Zhang, F.; Sui, X.; Xie, X.; Yin, Y.; Wang, S.; Wei, Y. *Biomacromolecules* **2009**, *10*, 2033.

28. Voepel, J.; Edlund, U.; Albertsson, A. C. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2366.

29. Nguyen, N. H.; Rosen, B.; Percec, V. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 1752.

30. Percec, V.; Guliashvili, T.; Ladislaw, J.; Wistrand, A.; Stjerndahl, A.; Sienkowska, M. J.; Monteiro, M. J.; Sahoo, S. *J. Am. Chem. Soc.* **2006**, *128*, 14156.

31. van de Wetering, P.; Zuidam, N. J.; van Steenbergen, M. J.; van der Houwen, O. A. G. J.; Underberg, W. J. M.; Hennink, W. E. *Macromolecules*, **1998**, *31*, 8063.

32. Roy, D.; Knapp, J. S.; Guthrie, J. T.; Perrier, S. *Biomacromolecules*, **2008**, *9*, 91.

33. Yan, L. F.; Tao, W. *J. Biomed. Sci. Eng.* **2008**, *1*, 37.

34. Neugebauer, D.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 2598.

35. Zeng, F.; Shen, Y.; Zhu, S.; Pelton, R. *Macromolecules* **2000**, *33*, 1628.

36. Fellows, C. M.; Doherty, W. O. S. *Macromol. Symp.* **2006**, *231*, 1.