

Chitosan-graft-Acrylamide Polyelectrolytes: Synthesis, Flocculation, and Modeling

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ABSTRACT: A series of chitosans have been grafted with quaternary ammonium cationic monomers, as well as acrylamide using Ce(IV) to induce macroradical formation on the polysaccharide backbone. The materials, which have long chain branches per molecule between 0.3 and 5.5, are shown to provide very high specific flocculation efficiency, at the very least equal to the entirely synthetic materials which have been previously documented in the literature. A charge ratio, determined from the polymer concentration at which flocculation takes place, the charge density of the polymer, and the surface charge of the suspended matter are proposed as metrics to evaluate the occurrence of charge neutralization and bridging or charge patch flocculation mechanism. Furthermore, a window of application (WA) for flocculants,

which characterizes the region of concentration wherein the polyelectrolyte can remove 99% of the supernatant turbidity, has been defined. It was shown to depend on the square root of the ionic strength and varies inversely with the Debye length, providing a fundamental basis for the concept of the WA. A mathematical expression is presented which links the WA with the salt concentration and the number of branches of the grafted polymer. Grafted chitosans have been shown to be more robust than polyacrylamides in testing against model kaolin suspensions. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 885–896, 2006

Key words: acrylamide; chitosan; flocculation

INTRODUCTION

Polymeric flocculants are typically synthetic water-soluble macromolecules, often of high molar mass. For municipal water treatment, synthetic cationic polymers are almost exclusively employed, with charges in the 2–3 mequiv range. However, in the pulp and paper industry, the consumption of modified natural polymers, including cationic starches, is nearly twice that of the acrylic flocculants, and cationicity below 1 mequiv is common.

Charge, charge density, molar mass, and molar mass distribution distinguish polymeric flocculants. Charge type provides the basis for classification into anionic, cationic, and nonionic polymers. The charged polymers are commonly referred to as polyelectrolyte. More than half of all synthetic polymeric flocculants and all those of high and very high molar mass are copolymers in which the principal monomer is acrylamide.

Cationic copolymers based on acrylamide consist, frequently, of a quaternary ammonium acrylic comonomer. These include trimethyl ammonium

ethyl acrylate chloride (Fig. 1, left, R=H: TMAA), trimethyl ammonium ethyl methacrylate chloride (Fig. 1, left, R=CH₃: TMAM), acrylamidopropyl trimethyl ammonium chloride (Fig. 1, middle, R=H), methacrylamidopropyltrimethylammonium (Fig. 1, middle, R=CH₃), and diallyldimethylammonium chloride (Fig. 1, right) (DADMAC).^{1–5} The proportion of cationic or anionic monomer determines the charge density of the polyelectrolyte.

Flocculation

Flocculation of suspended particles by polymeric flocculants is a multistep process. Gregory⁶ has measured relative flocculation rates as a function of polymer concentration for three cationic polyelectrolytes differing only in molar mass. He defined three polymer concentration regimes:

1. a stable region which occurs at very low polymer concentration.
2. a flocculation region.
3. a region of restabilization at high polymer concentration.

Within the boundaries of the flocculation region, which the critical flocculation concentration (CFC) and the restabilization concentration (RSC) demarcate, lies

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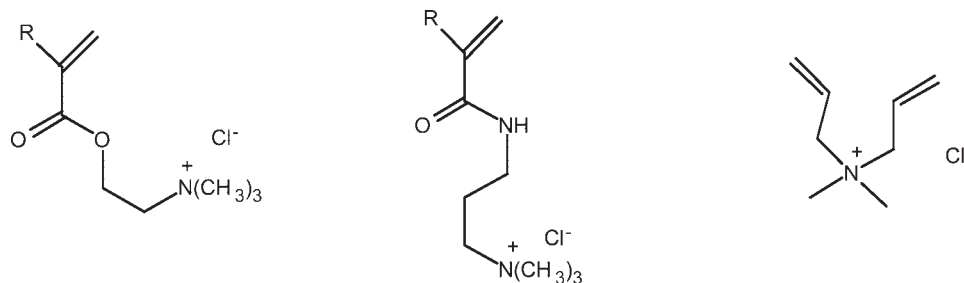


Figure 1 Frequently used cationic monomers as part of polymeric flocculants. These are, specifically, trimethyl ammonium ethyl acrylate chloride (left, R=H: TMAA), trimethyl ammonium ethyl methacrylate chloride (Fig. 1, left, R=CH₃: TMAM), acrylamidopropyl trimethyl ammonium chloride (middle, R=H) methacrylamidopropyltrimethylammonium (middle, R=CH₃), and diallyldimethylammonium chloride (right) (DADMAC).

the optimum flocculation concentration (OFC) in Figure 2. Values of any of these three characteristic concentrations need not be identical if determined by the different flocculation tests mentioned earlier.⁷ While attempts have been undertaken to define the OFC, no means were reported to unambiguously determine CFC and RSC.⁷ It was found that the OFC has approximately the same value for different molar masses. Optimum flocculation occurred when a certain amount of an opposite charge had been adsorbed by the particle, regardless of the length of the polymer chain carrying the charge. It was observed, however, that as the molar mass increased, the flocculation region broadened. The window of application (WA) is also shown in Figure 2 and can be considered as the concentration range between the limits CFC and RSC.

Types of polycation-based flocculants

The polymers that are widely used to destabilize colloidal suspensions of industrial and municipal provenance have historically been primarily of linear structure, though recently a shift to lightly branched poly-

mers for flocculation purposes are reported.^{8–12} These branched polymers consisted of poly(acrylamide) chains grafted with poly(DADMAC),^{8,9} cationic poly(acrylamide) including methylenebisacrylamide as crosslinker,^{10,12} or a partially quaternized poly(*N*-glycidylpiperazine) as backbone grafted with 1,3-bis(dimethylamino)-2-propanol and 1,4-dichloro-2-butene.¹¹ Compared to reference materials these graft-copolymers revealed a reduced supernatant turbidity over a broad range of concentration,⁸ or higher cake solids,¹² and an improved drainage volume.¹⁰

Polysaccharide-based flocculants

Polysaccharides are interesting as potentially natural polymers, which could provide advantages in terms of flocculation efficiency or reductions in the life cycle environmental burdens associated with synthetic flocculants. However, as the majority of commodity polysaccharides are of limited charge, and flocculation, for many applications, requires molar charge densities above 50%, means to increase the charge on polysaccharides are of interest. To graft monomers onto an inert polysaccharide backbone, several methods are possible, though all require the generation of a radical on the polysaccharide. One method involves the use of a Ce(IV) cation which, in equilibrium with an acceptor, forms a complex which decomposes into a radical and Ce(III). This macroradical can then add monomer in solution, hence providing long-chain branches to the polysaccharide backbone.

In this work, hybrid natural/synthetic graft-copolymers with a chitosan backbone were used in the flocculation experiments. The present study also introduces a new evaluation metric. Its aim is to unambiguously determine the limits of polymer concentration needed for effective flocculation. From these borders the WA was derived. This evaluation method has been applied for the chitosan based cationic graft-copolymers. As colloidal particles a kaolin suspension was employed. The stability of the suspension was evaluated under various conditions. The determination of a

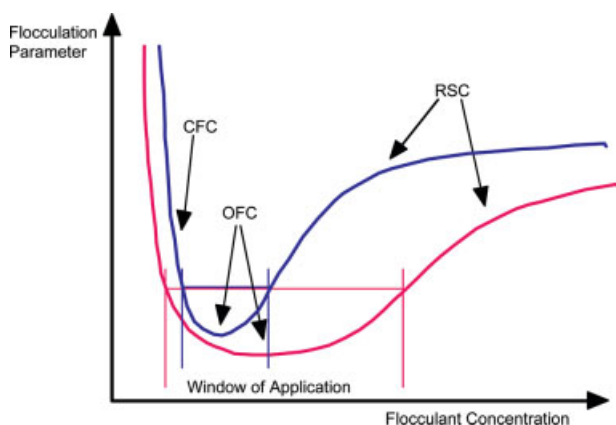


Figure 2 Schematic plot of a flocculation parameter versus amount of two flocculants with their CFC, OFC, RSC, and the WA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

discrete OFC was not included. It will be located within the polymer concentration limit, however, its value depends on the specific flocculation problem.

EXPERIMENTAL

Chemicals

All chemicals used in this study were of p.a. grade and used as received (Fluka, Switzerland). The polymer and graft-copolymer synthesis and characterization is described elsewhere.¹³ 2-Methacroyloxyethyl trimethyl ammonium chloride (TMAM) was received as a 75% solution in water, (Ageflex, FM1Q75MC, Ciba). Acrylamide and ceric ammonium nitrate (purris, p.a. >99%) were purchased from Fluka.

Chitosan purification

The purchased chitosan (molar mass of 1.15×10^6 g/mol, Aldrich 41,941-9) was dissolved over a period of 24 h in a 0.01M acetic acid/0.01M sodium acetate buffer to yield a 1% solution. Undissolved product was removed by filtering the solution. A 10-fold excess of NaCl with respect to glucosamine units was added and the mixture was dialyzed in a 10-fold excess of NaCl with respect to glucosamide units (Amicon CH2A Concentrator) through hollow fibers (Diaflo™ Hollow Fiber Cartridge, cut off 30,000 g/mol). The purified chitosan was freeze-dried for 24 h and stored at room temperature. Freeze drying of the polymers was performed in a β 1-16 Freeze Dryer (Christ, Germany). The water content of the product was determined by drying a sample at 80°C under vacuum.

Solution polymerization

Chitosan was used as the backbone for all graft copolymerizations. The desired amount of solid chitosan powder was dissolved in 200 mL 0.1M acetic acid/0.1M sodium acetate buffer solution by agitation. Subsequently, the 2-methacroyloxyethyl trimethyl ammonium chloride and, for selected syntheses, the acrylamide were added. The reactor was then purged with nitrogen while the mixture was heated to 30°C. The nitrogen stream was guided through a solvent bath, to reduce the loss of acetic acid from the reaction mixture due to the nitrogen flux. After 30 min stirring under N₂ the Ce(IV) initiator was added in form of 1 mL of a 0.058 mM ceric ammonium nitrate aqueous solution. Three hours of reaction at 30°C under N₂ followed the initiation. Opening the reactor, diluting it with water, and cooling the mixture to room temperature stopped the polymerization. The product was purified by hollow fiber ultrafiltration and freeze-dried prior to use. Complete details of the Ce(IV) based grafting are provided elsewhere.¹³

Characterization

Light scattering measurements were performed on a Malvern Autosizer Spectrophotometer operating on a dynamic light scattering principle (Malvern, Worcestershire, UK). The measurements were taken over a 2-min period. The measurements were repeated five times and the average value of these measurements was calculated. The digital correlator was acquired from Brookhaven (Brookhaven Instrument, Holtsville, NY). For the estimation of molar mass of the graft arms the one-concentration light scattering method was used.¹⁴

An ATI Mattson Genesis Series FTIR (Henri Sarasin AG, Basel) equipped with a single reflection diamond attenuated total reflection system (P/N 10,500 Graseby Specac, Aartselaar, Belgium) was employed. A total of 32 scans were recorded with a resolution of 4 cm⁻¹ between 4000 and 624 cm⁻¹. WINFIRST software was employed for the Fourier transformation.

The capillary viscosity measurements were conducted on an automated TII Ubbelodhe dilution viscosimeter (Sematech, Nice, France). The intrinsic viscosity was determined from the intercept of a Huggins plot.

Specific surface areas of kaolin used were determined by nitrogen adsorption (77 K) employing BET method via Sorptomatic 1900 (Carlo-Erba, Milan, Italy).

The turbidity of the supernatant was measured by the 90° scattering of an 880-nm IR beam with a CUS41 detector (Endress+Hauser, Weil am Rhein, Germany). The calibration of the turbidimeter revealed that the turbidity of the supernatant is a linear function of the kaolin concentration up to 5 g/L Kaolin at an ionic strength of 0.01M. At an ionic strength of 0.1M the calibration curve was linear and similar to the aforementioned calibration up to a Kaolin concentration of 2 g/L. Above this concentration the measured turbidity was lower than for 0.01M ionic strength.

Grafted chitosan characterization

The composition of the chitosan, after grafting with synthetic monomers, was determined by FTIR by comparing the absorbance at wave numbers of 1065 (glucosamine peak) and 1722 (TMAM) cm⁻¹. Though a series of control experiments, with known compositions, the average deviation for the FTIR calculation was deemed to be 1.3% for chitosan, 0.9% for the cationic monomer TMAM, and 2.5% for acrylamide.

To assess the length and number of graft chains, the grafted chains were first decoupled from the backbone polysaccharide. The most effective means to do this was the treatment of the graft polymers via HCl for 72 h at ambient temperatures. This yielded a transparent, slightly yellow solution, and a white powder from

TABLE I
Characteristics of the Polymer Flocculants Investigated

Polymer	$[\eta]$ (mL/g)	Chitosan content X_c (FTIR; wt %)	M (10^6 g/mol)	Charge density (mmol equiv/g)	σ (No. of grafts/chitosan chain)
SA2-2	574	13	2.0	4.43	1.9
SA4-1.8	593	12	1.8	4.45	4
SB1-3	642	12	2.9	4.45	1.2
SC5.5-1.6	599	16	1.6	4.18	5.5
PTMAM	688	0	4.8	4.77	—
MA0.6-2.6	800	25	2.6	2.71	0.6
MA2-0.7	667	26	0.7	3.02	2.2
MA2-4.1	726	18	0.9	2.70	2.4
MA2-3.6	912	14	3.6	3.09	—
MA-X	708	25	—	2.58	—
MA-Y	445	>55	—	2.78	—
MAG	486	0	—	2.51	—
Floerger saron 4000	869	0	—	<5%	—
Cytec superfloc C498	1196	0	—	3.02	—

which the graft could be obtained. The freeze-dried polymers were then hydrolyzed for 180 min in an acid environment, with a pH below 2. As the polymers degraded during this period, that is the average molar masses decreased, the kinetics in the reduction in average molar mass were monitored by SEC and this was used to calculate a corrected molar mass.¹³ This correction was minimal for polymers with molar masses below 1 million Daltons. From the SEC-based number average molar mass, as well as the composition of the polymer, determined by FTIR, the average number of grafts per backbone chain could be estimated.

Polymer solution preparation

The polymers were dissolved in distilled water to give a 0.2 wt-% solution. Known volumes of polymer solution were added to 200 mL of Kaolin suspension, stirred with a two-blade stirrer at 350 rpm. Stirring was maintained for 15 min. Subsequently, the flocculated Kaolin was allowed to settle for 15 min before the turbidity of the supernatant was measured. The turbidimeter was dipped in the liquid during settling time.

Kaolin characterization

The Kaolin employed herein had a diameter of 239 nm, as determined by dynamic light scattering. The surface area was 14.9 m²/g as assessed by BET with a charge density of 1.9×10^{-5} molequiv/g, as measured by acid-base titration.

Flocculation

Kaolin suspensions were prepared by the addition of an appropriate amount of Kaolin powder in distilled

water. A 5-g/L kaolin/water mixture was vigorously stirred and used directly in the flocculation experiments if not stated otherwise. The ionic force was adjusted by the addition of appropriate amounts of NaCl. The pH was adjusted to 11 by the addition of 4M NaOH solution. The solution was allowed to stir overnight, and prior to the experiments the pH was controlled and, if necessary, adjusted to the desired value.

A 200-mL sample of kaolin suspension was stirred at 350 rpm at the laboratory flocculation testing platform (Armfield W1, Ringwood, Great Britain, maximum stirring speed). After the addition of a certain amount of 2-g/L polymer aqueous solution, a pre-defined time of stirring and another of floc settling were observed. Subsequently the turbidity of the supernatant was measured quantitatively by the 90° scattering of a 880-nm IR light and compared to the turbidity of the kaolin suspension without flocculant, however, after the same settling time. The lower and upper limit concentration (LLC and ULC) were determined by fitting the flocculation curve obtained with an appropriate equation from which the values for LLC and ULC were derived.

RESULTS AND DISCUSSION

The linear polymers and graft-copolymers, which were used in the flocculation experiments herein, are summarized in Table I. The polymers named SA, SB, or SC, consist of chitosan grafted exclusively with TMAM. As a measure for the size of the polymeric flocculant the intrinsic viscosity $[\eta]$ is given and ranges from 445 to 1196 mL/g determined in 0.5M acetic acid/0.5M sodium acetate buffer. The chitosan content of the graft-copolymers varied from 0 to 30 wt-%. PTMAM stands for a homopolymer of TMAM

units. Table I also shows that graft-copolymers with approximately 0.6–5.5 branches have been prepared.

Choice of kaolin as a reference colloid

The flocculation of colloids is highly dependent on the size of the colloid, its density in suspension, as well as the surface charge. For colloids of natural origin, for example, those based on bacteria, the sizes and, in particular, charges, often vary as a function of time. The selection of a reference colloid, therefore, should be limited to a material of a specific charge (we selected a negatively charged material to evaluate polycations). Furthermore, flocculation mechanism can differ if the colloid is low, moderately or highly anionic. Therefore, a flocculant, or the optimization of a flocculant for a given colloid, will, in all cases, be specific to the charge on the colloid and we cannot consider the identification of a general flocculant as feasible, with charge and molar mass optimization required for each specific colloid surface. Kaolin was, therefore, selected as a model as, by varying the pH of the suspension, the surface charge could be modified, and, thereby, the behavior of flocculants, including the novel chitosan-based grafts, could be evaluated over a broad range. We elected to represent the robustivity of a flocculant by its WA, as will be discussed below.

The highest Kaolin concentration forming a stable suspension at pH 11, and an ionic strength of 0.01M, was 5 g/L. This kaolin concentration has been applied for flocculation experiments. Since the charges on the kaolin surface strongly depend on the suspension pH, the pH had to be fixed prior to all measurements. Therefore, the pH was adjusted from the initial level of 5 to the desired value with 4M NaOH. Preliminary experiments conducted at pH 7 revealed that, under these conditions, the kaolin suspension pH slowly varied in time. Moreover, kaolin slowly settled. This had the effect that the measured residual turbidity reflected both the forced flocculation and the spontaneous settling without selectivity. Furthermore, the measured differences in turbidities were small, which emphasized the importance of the measurement uncertainties. It has been observed, on the contrary, that at pH 11 the suspension was more stable (i.e., the natural settling of kaolin was negligible), which allowed us to notice finer differences between the flocculants.

Influence of pH on flocculation

Figure 3 shows the supernatant turbidities of destabilized kaolin suspension at various pH (4, 7, 7.3, and 11). In all measurements the ionic strength was maintained at 0.01M NaCl. The NaOH concentration to adjust the pH was at maximum 1×10^{-3} M for pH 11 and less for lower pH. The contribution of NaOH to

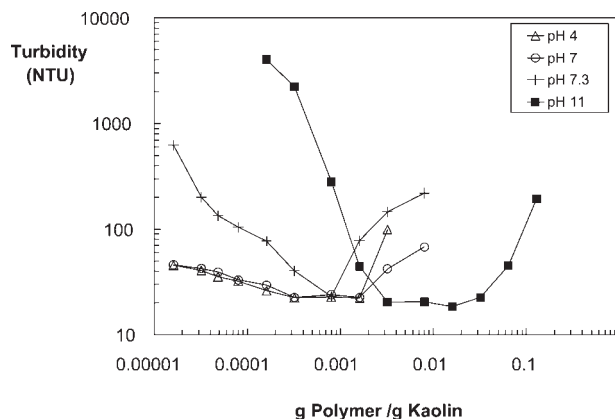


Figure 3 Variation of flocculation performance with the pH of the kaolin suspension; 5 g/L kaolin, 0.01M NaCl, 3 mL of 2 g/L flocculant solution, 15 min stirring time, 15 min settling time (Polymer MA 2–3.6).

the ionic strength therefore, is 10%. The polymer concentration is given as weight ratio between polymer and kaolin. Since, in the majority of experiments the kaolin concentration was maintained constant at 5 g/L, this ratio is directly proportional to the polymer concentration. The following description summarizes the effect of pH on the polymer-induced destabilization of kaolin suspensions.

pH 4 and 7

It can be seen from Figure 3 that between pH 4 and 7 only marginal differences in supernatant turbidity were observed. The addition of 1.3×10^{-5} – 1.6×10^{-3} g polymer/g kaolin reduced the turbidity marginally between 46 NTU and 24 NTU (nephelometric turbidity units). The low turbidities, at polymer concentrations of 1.3×10^{-5} g polymer/g kaolin, were due to the unconstrained settling of kaolin which took place even without polymer. When at, pH 4 and 7, more than 1.6×10^{-3} g polymer/g kaolin was added, the turbidity increased strongly. Adsorbed polymer chains were likely responsible for this effect, providing a cationic net charge on the surface of the suspended kaolin or causing a steric stabilization.

pH 7.3

The increase of pH to 7.3 stabilized the kaolin suspension. Apparently, the small difference in pH provoked important changes in surface charge, which stabilized the suspension prior to the polymer addition and at low polymer dosage. The turbidities decreased continuously with increasing polymer addition up to 8×10^{-3} g polymer/g kaolin. The differences in turbidity at the lowest polymer concentration and 8×10^{-3} g polymer/g kaolin were larger than at pH 4 and 7. In

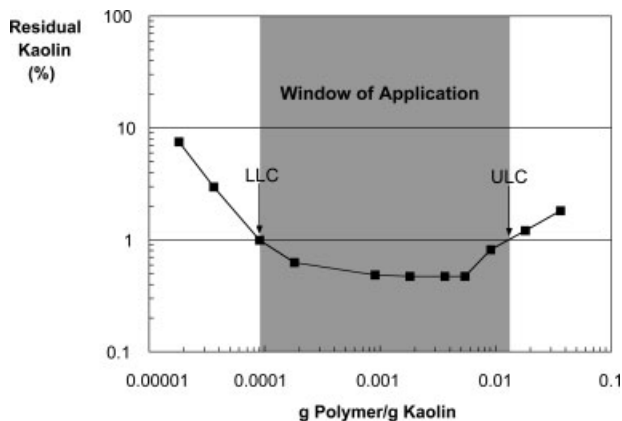


Figure 4 An example to illustrate the determination of the LLC, ULC, and the WA.

addition, restabilization occurred at concentrations as low as 1.6×10^{-3} g polymer/g kaolin, likely provoked by charge inversion or steric reasons due to adsorbed polymer molecules.

pH 11

At pH 11 the kaolin suspensions revealed a much higher supernatant turbidity at low polymer dosage ($<1 \times 10^{-3}$ g polymer/g kaolin). According to the aforementioned surface reactions, the surface charge is much larger than at lower pH. Therefore, more polymer was needed to effectively destabilize the kaolin suspension. Above 3.2×10^{-2} g polymer/g kaolin restabilization was observed.

Stirring and settling time were chosen in a way that their influence on the turbidity could be neglected.¹³

Flocculation evaluation method

Figure 4 shows a typical plot obtained from a flocculation experiment. Following the addition of the polymer to the kaolin suspension, and appropriate mixing and settling times, the turbidity of the supernatant was determined. The measured supernatant turbidity is directly proportional to the kaolin concentration though this is only valid over a specific range and is not true in general. The points plotted in Figure 4 represent the residual kaolin concentration in the supernatant as a function of gram polymer per gram kaolin initially present in the suspension. The line of connected data points is referred to, herein, as the flocculation curve. In general terms, it can be stated that, when no, or little, polymer was added, a remarkable residual turbidity was observed. On the other hand, a large amount of added polymer tended to restabilize the suspension which was resulted in higher turbidities. It was only within a more or less narrow range of polymer/kaolin ratio where floccula-

tion occurred and the polymer fulfilled his purpose as clarifying agent. Comparable flocculation curves have been obtained by other workers.^{6,8,15-22} While attempts were reported to define the point of optimum polymer dosage,⁷ a description of the flocculation performance including the limits of beginning flocculation and restabilization, based on plots such as shown in Figure 4, are commonplace in testing laboratories.

To evaluate and compare flocculation performance of different polymers, an arbitrary limit of 1% residual kaolin concentration was fixed. A residual kaolin concentration of 1% provided a transparent supernatant and implies that 99% of the initial kaolin particles have been removed. If the residual kaolin concentration was smaller than 1% of the initial value the polymer was considered to be effective as flocculant. From plots such as the one shown in Figure 4 and by applying an arbitrary threshold of 1% residual kaolin concentration, three parameters could be deduced as will be defined in the following paragraphs.

The polymer/kaolin ratio at the lower polymer concentration where the turbidity becomes smaller than 1% was referred to as the LLC. With increasing polymer concentration, and thus increasing polymer/kaolin ratio, the supernatant turbidities began to increase again and passed the limit of 1% kaolin concentration, indicating that a restabilization of the suspension occurred. The polymer/kaolin ratio where this limit was passed was defined as ULC. The logarithm of the ratio between ULC and LLC provided a measure of the relative concentration range in which a polymer is effective as clarifying agent.

$$WA = \log \frac{ULC}{LLC} \quad (1)$$

The parameter WA, referring to the window of application, is independent from the absolute values of ULC and LLC. A value of unity represents a WA where the polymer concentration can vary over one order of magnitude without occurrence of restabilization of the suspension. This novel approach allows one to compare values of different systems such as variation of the kaolin concentration or ionic strength. Furthermore, the WA can be discussed independently from the LLC.

Standard flocculation experiments

As standard conditions for the evaluation of the graft-copolymers as flocculants, a 5 g/L kaolin suspension at pH 11 with an ionic strength of 0.01M NaCl, was selected. The residual kaolin concentration was based on the 5 g/L initial kaolin. The stirring time was 15 min at 350 rpm. The flocs were allowed to settle 15 min after the stirring. The flocculation tests were con-

TABLE II
Charge Ratio ξ at LLC for Various Ionic Strengths

NaCl concentration (mol/L)	PTMAM	SA2-2	SA4-2	SB1-3	SC5.5-2
1×10^{-1}	0.05	0.02	0.02	0.02	0.02
1×10^{-2}	0.07	0.12	0.08	0.08	0.09
1×10^{-3}	0.08	0.14	0.09	0.12	0.07

ducted with graft-copolymers with exclusively TMAM graft arms (S-series) and with TMAM-AAM copolymer graft arms (MA series). Additionally, two commercial products of various charge densities have been tested for kaolin flocculation. The tested graft-copolymers differed in graft arm length, graft density, and chitosan content. Details of the graft-copolymer characteristics can be found in Table II. Within a class of graft-copolymers the charge density was approximately constant.

Chitosan polymers grafted with cationic monomers

Cationic grafted polymers consist of a chitosan backbone and side chains in which each monomer unit bears a positive charge, in this case from trimethylaminoethylmethacrylate. From the plot depicted in Figure 4 the LLC, ULC, and the WA were determined for each measured polymer. The results are compared to the flocculation performance of the linear homopolymer PTMAM in Figure 5. The important values for the application of a polymer as flocculant are its LLC and WA. For sake of clarity, the values of the ULC are not shown in the following sections since the flocculation performance is sufficiently characterized

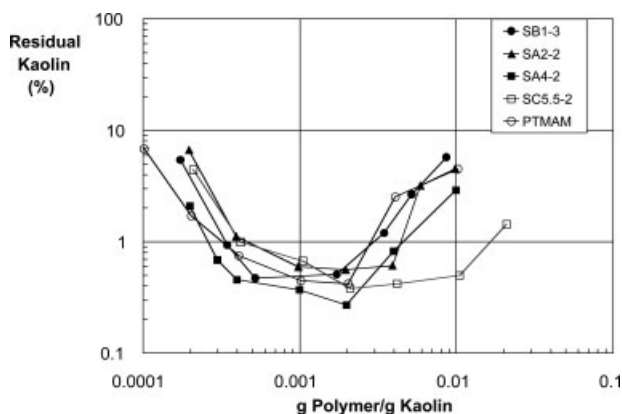


Figure 5 Flocculation curves of exclusively TMAM grafted chitosan and linear PTMAM. The flocculation conditions were a kaolin suspension, at pH 11 with an ionic strength of 0.01M NaCl, at a kaolin level of 5 g/L. The agitation time was 15 min, at 350 rpm. The flocs were permitted to settle 15 min after stirring.

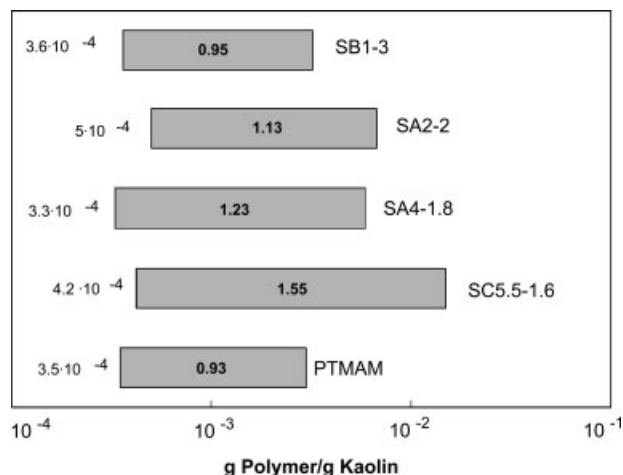


Figure 6 Illustration of LLC and WA of exclusively TMAM grafted copolymers and linear PTMAM determined from figure; value left beside the bars: LLC; values in the bars: WA.

by the LLC and the WA. The ULC can easily be deduced from the LLC and WA.

The LLC value for exclusively TMAM grafted chitosan were found to be in the range of $(3.3\text{--}5.0) \times 10^{-4}$ g polymer/g kaolin. A LLC of 3.5×10^{-4} g polymer/g kaolin was determined for the linear PTMAM. The differences in these values have not been significant with respect to the precision of the LLC determination ($\pm 15\%$) as it has been shown in the preceding section. Therefore, it has been concluded that all graft-copolymers with exclusively TMAM graft arms provoked a destabilization of a kaolin suspension, indicated by the LLC, at $\sim 4.1 (\pm 0.9) \times 10^{-4}$ g polymer/g kaolin.

Figure 6 illustrates the results for the LLC and the WA of TMAM grafted chitosan in comparison to the linear PTMAM. The graft-copolymers SA4-1.8, SA2-2, and SB1-3 are composed of 4, 1.9, and 1.2 branches, respectively. They provided a WA of 0.95–1.23 which was comparable with the WA of the linear PTMAM (WA = 0.93). Only for the graft-copolymer sample with the highest number of branches (SC5.5-1.6; 5.5 branches of 2×10^6 g/mol) was the WA larger than for the other samples. Since the LLC was identical to the linear PTMAM pushing the ULC to higher values enlarged the WA. Apparently, the graft-copolymer with the shortest branches ($M_w = 1.6 \times 10^6$ g/mol) and the highest number of branches was able to destabilize the kaolin suspension at polymer concentrations where other graft-copolymers and the linear polymer induced already a restabilization in the suspension.

Effect of kaolin concentration on flocculation

The quality of waste streams, with respect to the solid content in clarification processes, often changes with

time. Applied as clarifying agent in wastewater treatment, the flocculant concentration may not change until several minutes after. If the polymer dosage is maintained constant, and the solid content changes, the ratio of polymer to solids also changes. A change in the polymer/solid ratio can easily be simulated by varying the polymer concentration and holding the solid concentration at the same level. Therefore, the flocculation performance of polymers has often been evaluated with experiments in which the added polymer concentration to a suspension was varied.^{2,4,6,23} However, the validity of this approach has not been demonstrated to date.

At lower kaolin concentrations, the mean distance between two suspended particles is larger. As a consequence, the number of collisions between to particles is reduced at constant temperature and agitation. Large polymers are expected to span easier the gap between two particles and increase the effective collision diameter of the particles if bridging is the predominant mechanism.⁶

To evaluate the influence of changes in solid content of the suspension, three kaolin concentrations were employed. The concentrations varied by a factor of ten (0.05, 0.5, 5 g/L). The polymer concentration was, as in preceding discussion, calculated as the ratio of polymer to kaolin. If the aforementioned approach were valid, the obtained curves would be expected to superimpose. Since the kaolin concentration was given as a percentage of the initial kaolin concentration, the curves obtained should vary in turbidity by a factor of ten. This has been obtained, as can be seen in Figure 7. For the determination of WA the kaolin concentration threshold for 0.5 g/L kaolin has been set to 10% to take into account that the kaolin concentration was 10-fold reduced. The results for the LLC and the WA are summarized in Figure 8.

In Figure 7, the flocculation curves for the three kaolin concentrations (5, 0.5, and 0.05 g/L) are de-

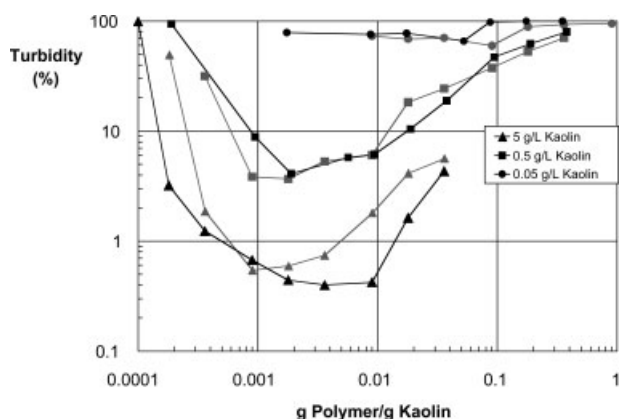


Figure 7 Comparison of flocculation curves for various kaolin concentrations of MAG (gray curve) and MA2-0.7 (black curve). The flocculant physical-chemical data is given in Table I.

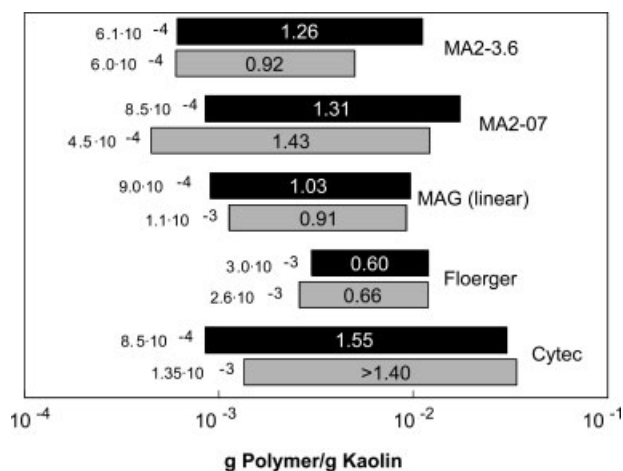


Figure 8 Influence of kaolin concentration on LLC and WA; gray bars: 5 g/L kaolin; dark bars 0.5 g/L kaolin; value left beside the bars: LLC; values in the bars: WA. The commercial polymers are Cytec Superfloc C498 and Floerger Sarron 4000.

picted for the linear MAG (gray curves) and the graft-copolymer MA2-0.7 (black curves). At high kaolin concentrations (5 g/L) the graft-copolymer MA2-0.7 clearly outperformed the linear polymer in terms of LLC and WA. While at 0.5 g/L kaolin the LLC and WA for the linear MAG were found to be approximately the same as for 5 g/L kaolin, the graft-copolymer MA2-0.7 showed a higher LLC (8.5×10^{-4} g polymer/g kaolin) at 0.5 g/L kaolin. The WA of MA2-0.7 was influenced by the kaolin concentration. For 0.05 g/L kaolin the differences in turbidity between the flocculated and unflocculated samples were too small to permit a reliable interpretation of the data.

The calculated values of LLC and WA for various kaolin concentrations are depicted in Figure 8 for two graft-copolymers (MA2-0.7 and MA2-3.6) with different graft arm lengths, the linear MAG, and the acrylamide-based commercial flocculants from two commercial manufacturers of synthetic flocculants (Cytec and SNF Floerger). It can be seen that the polymer with longer graft arms (MA2-3.6) was less influenced by a variation in kaolin concentration. The LLC was almost identical for 5 and 0.5 g/L kaolin whereas the WA increased from 0.92 to 1.26 with decreasing kaolin concentration. When the initial kaolin concentration was reduced to 0.5 g/L, the LLC for the graft-copolymers MA2-0.7 and MA2-3.6 was in the range of $(7-9) \times 10^{-4}$ g polymer/g kaolin. Differences in the flocculation performance between MA2-0.7 and MA2-3.6 could only be observed at high polymer concentrations, however, these were less important than with 5 g/L kaolin concentration. Both graft-copolymers provided a larger WA than the linear copolymer MAG and the Floerger commercial flocculant (1.3 and 1.2 for MA2-0.7 and MA2-3.6). The graft-copolymer with

longer branches (MA2-3.6) should perform better than the one with shorter branches if exclusively bridging between particles lead to flocculation. The WA of MA2-3.6 was increased with respect to the experiment at higher Kaolin concentration, however, it did not outperform the polymer with shorter grafts, indicating that bridging is not the predominant mechanism.^{4,6}

The commercial products showed relatively small changes in flocculation performance as a function of varying kaolin concentrations. LLC and WA varied by a minor extent. Their performance as clarifying agent was not affected by the larger distance of the particles. This was true both at lower kaolin concentration or the lower number of collisions. Similar results were observed for the linear MAG. These findings indicated that, for the two commercial polymers and at kaolin concentrations between 0.5 and 5 g/L, the variation of polymer concentration is a means to simulate the changes in the ratio polymer/solids.

Effect of ionic strength on flocculation

In applications such as wastewater treatment of sewage, or pulp and paper effluents, the ionic strength can vary more than two orders of magnitude.²⁴ The flocculant addition is not adjusted to ion concentration in these effluents and it is, therefore, desirable that polymers perform well at various salt and solid concentrations. Additionally, to design polymeric flocculants that are less sensitive to ionic strength, a general relationship between salt concentration, polymer structure, and flocculation performance would be useful. Since it has also been reported that the flocculation performance is affected by the ionic strength of model suspensions,⁶ the influence of this parameter on the flocculation performance of graft-copolymers was evaluated by varying the ionic strength from $1 \times 10^{-4}M$ to $1 \times 10^{-1}M$. The influence of ionic strength

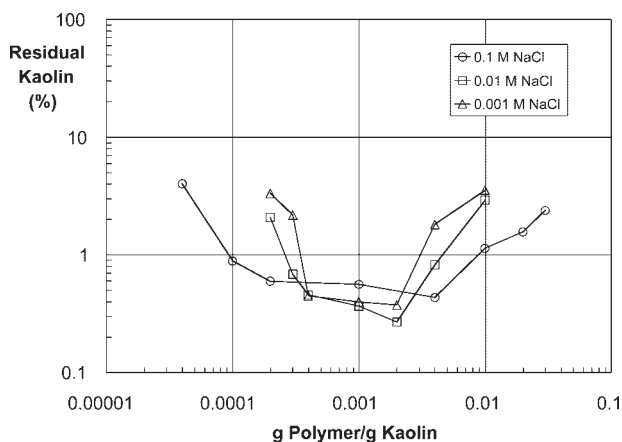


Figure 9 Flocculation curves of SA4-1.8 for various salt concentrations.

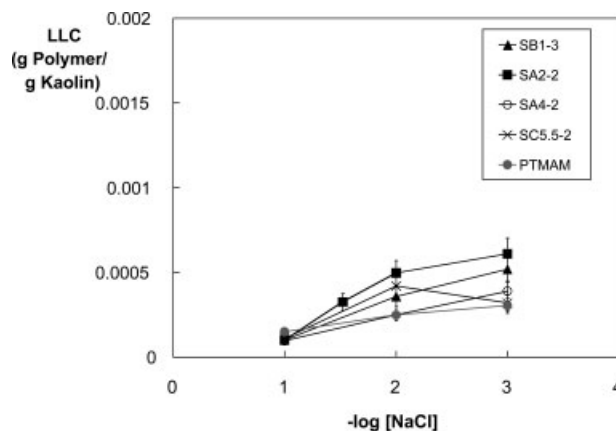


Figure 10 Influence of ionic strength of the kaolin suspension on LLC for exclusively TMAM grafted polymers.

has been tested on selected graft-copolymers. The kaolin concentration was maintained constant at 5 g/L and the standard procedure was applied.

Figure 9 shows the flocculation curves of two graft-copolymers destabilizing kaolin suspensions of various ionic strength. In both cases the LLC decreased with increasing ionic strength, whereas the WA broadened with increased ionic strength. The ULC for the graft-copolymer SA4-1.8 and for the graft-copolymer MA2-0.7 a decrease in ULC with decreasing ionic strength was observed.

Chitosan exclusively grafted with cationic monomers

A parameter influencing the environment of suspended particles is the ionic strength (or salt concentration) of the suspension. With increasing salt concentration the repulsive surface potential decreases following an exponential expression. The lower this repulsive force is, the easier two particles can be brought into close proximity. The plots of LLC and WA against ionic strength are shown in Figures 10 and 11 for exclusively TMAM-grafted polymers. The scales of both plots are identical to permit better comparison of the two series of polymers. Error bars are included to illustrate the uncertainties of the LLC determination (15% relative deviation). Thus, only significant differences in LLC for the three presented polymers will be discussed in the following paragraphs.

For the TMAM-grafted polymers and the linear PTMAM it can be seen in Figure 10 that the necessary minimum amount of polymer to provoke a destabilization of the kaolin suspension increased with decreasing ionic strength. The LLC for the graft-copolymers SA2-2, SA4-1.8, SB1-3, and SC 5.5-1.6 were similar taking into account the precision of the LLC determination. The minimum polymer concentration

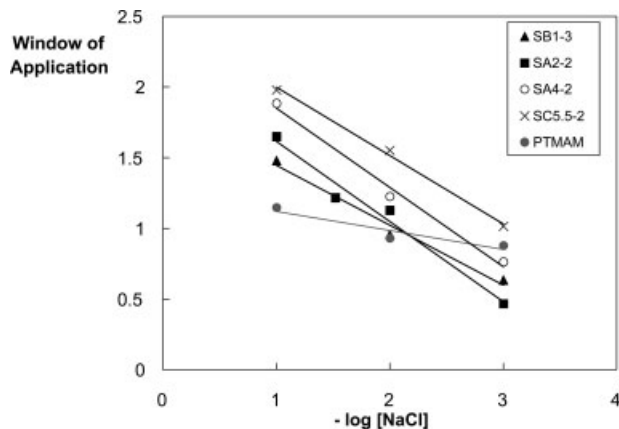


Figure 11 Influence of ionic strength of the kaolin suspension on WA of exclusively TMAM grafted polymers.

at high ionic strength was 9.7×10^{-5} g polymer/g kaolin. The maximum polymer concentration at low ionic strength was 6.1×10^{-4} g polymer/g kaolin. Decreasing the ionic strength over two orders of magnitude increased the LLC approximately six times.

At low polymer concentration up to LLC it can be assumed that the added polymer is completely adsorbed to the kaolin surface. The ratio between the amount of negative charges on the particle surface and the positive charges added with the polymer provides a measure of the net particle charge. A useful parameter for the understanding of flocculation processes is, therefore, proposed in this work. The critical charge ratio for flocculation ξ , which is the charge ratio at LLC to the original surface charge, can be calculated by the following equation:

$$\xi = \frac{\text{LLC } CD_p}{\sigma_{\text{Kaolin}}} \quad (2)$$

where CD_p is the polymer charge density and σ_{kaolin} is the surface charge of kaolin, both given in molequiv/g. When, at the point where flocculation starts to proceed (LLC), this ratio of charges is one or close to one the case of simple charge neutralization can be affirmed. For bridging and charge patch neutralization smaller values for this ratio are expected.^{4,6}

Table II summarizes the charge ratios at LLC for the TMAM graft-copolymers. Independent of the ionic strength, all charge ratio values are substantially smaller than unity, clearly indicating that simple charge neutralization is not the destabilization mechanism at LLC. While the differences in LLC between the graft-copolymers with TMAM graft arms and the linear homopolymer PTMAM were found to be marginal over the range of measured ionic strengths, the determined WA for these samples reveal significant differences as can be seen in Figure 11. The linear polymer showed an almost unchanged WA with vary-

ing ionic strength. The WA of graft-copolymers were lower at a salt concentration of $1 \times 10^{-3}M$ and increased with increasing ionic strength. The graft-copolymers with an average of 1.2 and 1.9 graft arms per chitosan chain (SB1-3 and SA2-2) showed a lower WA than the graft-copolymers with 4 and 5.5 branches (SA4-1.8 and SC5.5-1.6). The largest WA was observed for SC5.5-1.6 ranging from 1.1 to 2 with increasing ionic strength.

Broader flocculation curves with respect to LLC-ULC distance have been observed by Gregory,⁶ when the salt concentration was increased. Gregory proposed the charge patch mechanism to explain this dependence of flocculation performance on ionic strength. The charge patch mechanism is, therefore, considered to be responsible for the destabilization of kaolin suspension by the graft-copolymers. Because of the almost unchanged WA of the linear PTMAM, at various salt concentrations, another mechanism seems to be responsible for this polymer. The WA increased for all graft-copolymers with increasing ionic strength as it has also been reported by Gregory⁶ for linear polymers. The dependence of WA on ionic strength can quantitatively be expressed by the slope α of the regressions in Figure 11 for TMAM grafted polymers using:

$$WA = \alpha c^* + b \quad (3)$$

with $c^* = -\log[\text{NaCl}]$.

From these equations it can be derived that the ratio of ULC to LLC is proportional to the salt concentration to the power of α as shown in eq. (4). Table III lists the values of α for the graft-copolymers and the linear PTMAM.

$$\frac{\text{ULC}}{\text{LLC}} \propto [\text{NaCl}]^\alpha \quad (4)$$

A mean value and the 95% confidence interval (CI) of 0.51 ± 0.06 are given for the exclusively TMAM graft-copolymers in Table III. The PTMAM homopolymer provided an exponent of 0.13, much lower than the

TABLE III
Salt Concentration Exponent α for Graft-Copolymers and Linear Polymers

Polymer	Exponent α
PTMAM	0.13
SB1-3	0.57
SA2-2	0.42
SA4-2	0.56
SC5.5-2	0.48
Mean value* and 95% Confidence interval	0.51 ± 0.06

* Mean value for graft-copolymers SB1-3, SA2-2, SA4-2, SC5.5-2.

graft-copolymers with TMAM graft arms. Since this is, to the authors' knowledge, the first time that a dependence of the WA on ionic strength has been revealed, these results can not be compared to literature data. However, another important parameter in colloid theory is the Debye screening length which describes the length scale of the potential around charge that is surrounded with other charges that cause a screening of the interaction. This length is generally referred to as the double layer thickness. It is the distance at which the surface potential has dropped to $1/e$ of its value at the solid surface:

$$\lambda_D = \frac{1}{\kappa} = \left(\frac{\epsilon_r \epsilon_0 k_B T}{\sum_i (z_i e)^2 n_{i,\infty}} \right)^{0.5} \quad (5)$$

where n_∞ is the number concentration of ions far from the particle, thus directly proportional to [NaCl]. From the dependence of λ_D on ion concentration and the approximation that α in eq. (6) is equal to 0.5, which is very close to the experimental result of 0.51 ± 0.06 for the exclusively TMAM graft-copolymers, a relationship between the ratio ULC/LLC and the Debye length can be concluded:

$$\frac{1}{\lambda_D} \propto \frac{ULC}{LLC} \quad (6)$$

The proportionality in eq. (6) implies that the WA, which is just the logarithm of ULC/LLC, increases when the Debye length decreases. Since the Debye length describes the fall of the potential with the distance from the surface it follows that the WA increases, the faster the potential decreases with the distance.

Dependence of the window of application on the polymer structure

The WA not only depends on the salt concentration of the suspension. In Figure 12 WA is plotted as a func-

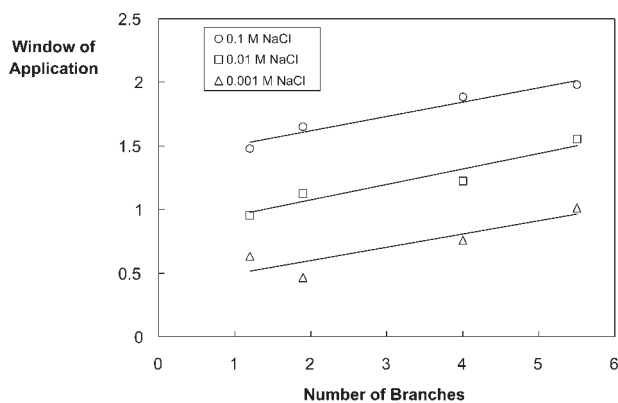


Figure 12 WA as a function of the number of exclusive TMAM branches per chitosan chain.

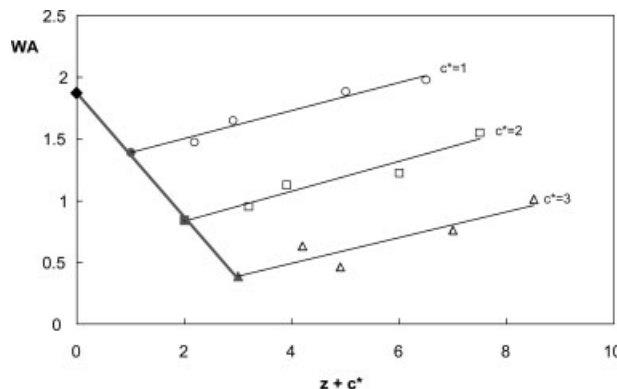


Figure 13 Zimm-like plot which serves to obtain an expression for WA.

tion of the number of graft arms per chitosan chain. It can be seen that with increasing number of branches, WA increased for all applied salt concentrations. This increase in WA with the number of branches was similar for all salt concentrations and can be manifested by the slope of the linear regressions which yield 0.113 ± 0.008 (95% CI for all three salt concentrations).

From Figure 12 the following equation has been deduced where d is the intercept of the regressions in Figure 11 which is a function of c^* :

$$WA = mz + d(c^*) \quad (7)$$

The number of branches is given by z , while m is the slope of the linear regression. Equation (8) reveals:

$$WA = \alpha c^* + b(z) \quad (8)$$

where $b(z)$ is the intercept in Figure 12 which is a function of the number of branches. Eqs. (7) and (8) include three unknowns, WA, $d(c^*)$, and $b(z)$. To solve this system of equations the boundary conditions are considered. A plot of $z + c^*$ versus WA, as it is depicted in Figure 13, is helpful in this sense. This way of plotting data is comparable with the classical Zimm plot in light scattering data processing.²⁵ Each series of measurements with graft-copolymers of various number of branches at the same salt concentration is given as hollow symbols. The full symbols represent the extrapolation to zero number of branches for the corresponding salt concentrations. The linear regression to the extrapolated values yield an expression for the limit of no branches, which is in the specific case:

$$WA_{z=0} = -0.5 c^* + 1.87 \quad (9)$$

This is the third equation necessary to solve the equation system. By combining eqs. (8) and (9) expression

can be derived from which WA as a function of ionic strength and the number of branches follows:

$$WA = 0.113 z - 0.5 c^* + 1.87 \quad (10 a)$$

or

$$WA = 0.113 z + 0.5 \log[\text{NaCl}] + 1.87 \quad (10 b)$$

This empirical equation is valid for TMAM grafted chitosan of an average of 1.2–5.5 branches and at salt concentrations of 0.001–0.1M of an 1:1 electrolyte such as sodium chloride. The linear PTMAM, which is in principle a polymer with zero number of branches, showed a behavior which is not in accordance to eq. (10a). This could be due to the lack of chitosan in PTMAM which was present in all other samples. Chitosan itself was only applied to flocculation experiments at $c^* = 2$ and a WA of 0.72 was found. From eq. (10b) a predicted WA of 0.84 is obtained, which is in quite reasonable agreement.

CONCLUSIONS

Graft-copolymers based on chitosan with quaternary ammonium and nonionic synthetic monomers added on side chain long branches clearly provide a large WA and a clean supernatant turbidity within this WA. These results appear to be at least as good as obtained with one commercial flocculant. Therefore, it seems that the graft-copolymers better capture the suspension particles and let them agglomerate to a critical size, so that their settling velocity was increased. The best performing of the chitosan-grafted polymers also had lower specific concentration requirements than traditional synthetic acrylic polyelectrolytes, in controlled flocculation experiments. Therefore, chitosan-based grafted copolymers, appear more robust, as well as functioning more effectively at specific dosages, compared to completely synthetic polycations with the same charge density. This is likely the result of the long chain branches and rigid nature of the backbone, which provides a more extended conformation in solution with a higher charge density.

A novel method has been presented which permits one to determine the polymer concentration limits within which the product functioned as clarifying agent. By introducing an arbitrary performance limit at 1% residual kaolin concentration, a LLC and ULC were defined from which the WA was deduced. It could be shown that the variation of polymer concentration in flocculation experiments is a valuable ap-

proach to simulate the particle concentration variation of a suspension. The WA provides a concentration independent measure of the performance width of a flocculant. The salt dependence of the WA could be linked to the Debye length. This shows that the WA is a parameter which can be derived from theoretical values.

A novel parameter has been introduced with the critical charge ratio for flocculation ξ , obtained from the product of LLC and the polymer charge density divided by the surface charge density of the suspended particles. At the point of incipient flocculation, this ratio was found to be much smaller than unity, thus strongly indicating that bridging and/or charge patch mechanism can be assumed as flocculation mechanism.

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