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ORIGINAL CONTRIBUTION

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Flocculation of dilute titanium dioxide suspensions by graft cationic polyelectrolytes

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Abstract The flocculation of a dilute titanium dioxide (TiO_2) suspension using homopolymers and graft copolymers of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC) was investigated. The graft copolymers produced by γ-irradiating the mixtures of polyacrylamide (PAM) and polyDADMAC gave better flocculating performance than homopolymers, reflecting the higher fractions of large particles and bigger floc size. A kinetic delay in the onset of flocculation was observed after adding the copolymers in the dose range 5–30 [mg polymer]/[g TiO_2]. Increasing dosage resulted in a longer delay period. No significant flocculation was observed when the dose was above 50 [mg polymer]/[g TiO_2]. This delay was interpreted in terms of the re-conformation of polymer chains driven by charge neutralization, between the positively charged polymer branches and the negative particle surface. Depending on the dosage used, the flocculation behavior of the graft copolymer has been suggested to be equilibrium and non-equilibrium flocculation. It was also observed that re-conformation is not affected by the ion strength of the media, but a strong shear force significantly reduces the chain reconformation time.

Key words Water-soluble polymer – Polyelectrolyte – Graft copolymer – Flocculation – Chain re-conformation

Introduction

Water-soluble polymeric flocculants play an important role in papermaking, mineral processing and wastewater treatment. In principle, these applications are all governed by the principles of flocculating colloidal particles via the mechanisms of chain bridging, charge neutralization and patch flocculation [1, 2]. These flocculation mechanisms can act alone or in combination, depending on the properties of particles and polymers in solution.

The formation of flocs by a polymeric flocculant is often kinetically controlled [3–5]. The kinetic aspects include mixing and diffusion of polymer molecules with colloidal particles, adsorption of polymer chains or segments onto the particle surface, re-conformation of adsorbed chains or segments from their initial state to an equilibrium configuration, collisions between particles with adsorbed polymers to form flocs and breakage of aggregated particles [1, 3–5]. It has been suggested that, in a dilute suspension system, the mixing and diffusion of polymers with colloidal particles are often quick and therefore are not rate-determining steps in the formation of flocs [6]. It is also generally believed that the flocs formed by polyelectrolytes show more resistance to breakage than those formed by inorganic coagulants [7]. In the current view of polymer-induced flocculation, the flocculant adsorbs at the interface with a configuration similar to that in solution. With time the polymer chain re-configures to a more collapsed conformation which may or may not be an effective flocculant. Therefore, adsorption, re-conformation and collisions are predominant factors affecting flocculation and have recently drawn great attention both theoretically and experimentally [5, 7–13]. In practice, all these elementary steps often proceed simultaneously. If a collision occurs before the adsorbed polymer chain reaches an equilibrium state, as illustrated in Fig. 1, flocs can also be formed. This type of flocculation was firstly described as non-equilibrium flocculation [14, 15]. A few experimental investigations of this aspect have been reported [16–18].

The size and structure of polymers in aqueous solution have been found to be predominant factors in influencing the adsorption and flocculation. Depending on the relative magnitudes of the polymer coil and colloidal particle dimensions, three cases can be identified.

1. If the polymer coil size (hydrodynamic volume) is much smaller than that of the colloidal particle, the polymers in solution are adsorbed onto the particle surfaces. Collisions between the particles adsorbed with polymers lead to flocculation. Kinetic aspects of this type of flocculation have been well established [8–11].

2. When the polymer is much larger than the particle, it was observed that many particles were adsorbed onto a single macromolecule. This polymer-particle aggregation leads to flocculation [19–21]. Recently, a few models have been developed to describe this type of flocculation [22, 23].

3. When the polymer and particle sizes are comparable, particles can be bridged by polymer chains, resulting in a three-dimensional network structure of particles linked by polymer coils [24]. However, the flocculation behavior of this three-dimensional network is not well understood.

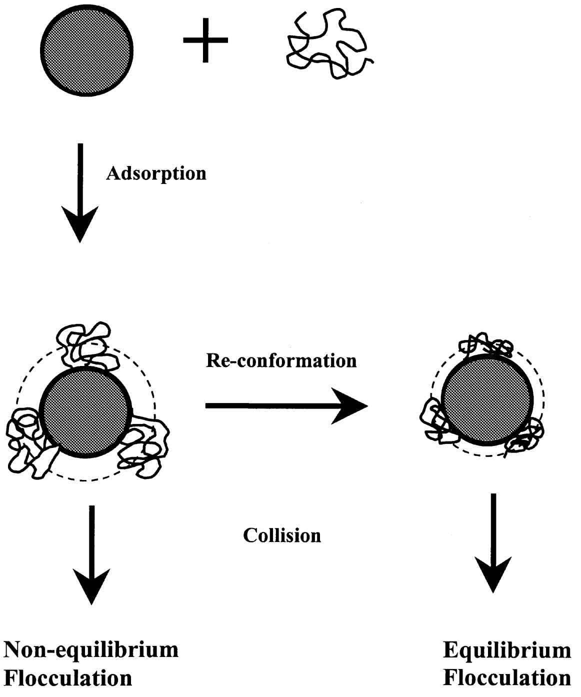

Fig. 1 Schematic diagram of equilibrium and non-equilibrium flocculation of colloidal particles by polymers (from Ref. [3])

Polymer structure influences adsorption. Using a Monte Carlo simulation, Balazs and Siemasko [11] compared the adsorption of comb and linear polymers. They concluded that the comb polymers, which contain 'stickly' teeth, have greater polymer-surface affinity than the equivalent linear chains. This contradicts the results of van der Linden et al. [25], who found that the backbone segments of comb polymers adsorb preferentially over the tooth segments, using self-consistent field theory.

In this work, comb graft copolymers were synthesized using a grafting technique. Flocculation of titanium dioxide (TiO_2) particles, in a dilute suspension, was investigated regarding polymer chain structure, molecular weight, charge density and distribution of charge units. The flocculation behavior was examined in terms of equilibrium and non-equilibrium flocculation theories.

Experimental

Materials

TiO_2 (Anatase) with a density of 3.9 g/ml was purchased from Aldrich. The volume-average diameter of TiO_2 particles was 0.248 ± 0.155 μm from the particle size distribution (PSD) measurement. Polyacrylamide (PAM) and polydiallyldimethyl ammonium chloride (polyDADMAC) were supplied by Nalco Canada. Their molecular weights were 1×10^7 and 8.4×10^4 g/mol, respectively, by viscosity measurement [26, 27]. The mean size of polymer coils in aqueous solution was determined from the intrinsic viscosity $[\eta]$, based on the equation [28]:

$$[\eta]M_w = 6^{3/2}\Phi\langle S^2\rangle^{3/2} ,$$

where $\langle S^2\rangle^{1/2}$ is the roo-mean-square radius of gyration of the polymer coil and Φ is the Flory-Fox parameter [29]. The polymer properties calculated are listed in Table 1.

Table 1 Properties of the polymers used in this study

	M_w (g/mol)	$[\eta]$ (dl/g)	$\langle S^2\rangle^{1/2}$ (μm)
PAM	1×10^7	15.1	0.17
PolyDADMAC	8.4×10^4	0.71	0.012

Synthesis and characterization of graft copolymers

PolyDADMAC was grafted onto PAM by γ-irradiation (100 krad/h, within a 5% variation). An aqueous solution of 0.5 wt% of total polymers with a weight ratio of 3 PAM to 7 polyDADMAC, was prepared as described in our previous paper [30]. After γ-irradiation, the polymer was precipitated with fivefold acetone. The precipitated polymer samples were then subjected to Soxhlet extraction with methanol for 48 h to remove residual homopolyDADMAC. A blend with the same proportions of PAM and polyDADMAC was compared, to assure complete separation of homopolyDADMAC from PAM and the graft copolymer.

A proton nuclear magnetic resonance (NMR) spectrometer, AC-200, was used to estimate the amount of polyDADMAC grafted onto PAM. The ratio of PAM to polyDADMAC was calculated by integration of the peak at 2.51 ppm (related to the β-proton on the PAM backbone) and also of peak's between 3.2 and 4.5 ppm (attributed to the methyl protons and the ethyl protons adjacent to the nitrogen atom of polyDADMAC). The experimental errors from NMR were within 3%, calculated by measuring blends of polyDADMAC and PAM in the range 0–50 wt% polyDADMAC. The results of the weight percentage of polyDADMAC of graft copolymers pertaining to the γ-irradiation time are presented in Table 2.

PSD measurement

TiO_2 (50 mg) was dispersed in 1 l deionized water with 0.001 M NaCl overnight, to ensure complete wetting of the particles. The TiO_2 suspension was then treated in an ultrasonic bath for at least 3 h, to break up the self-aggregated particles. At room temperature, the pH value of the suspension was carefully adjusted to 8 ± 0.2 by adding 0.001 N NaOH solution.

To avoid heterogeneous particle aggregation, polyelectrolyte was first diluted to 2.5×10^{-5} g/ml. Flocculation was performed by adding polyelectrolyte solution to the TiO_2 suspension, slowly stirring for 3 min. Polymer doses were based on the weight of TiO_2 in the suspension in terms of [mg polymer]/[g TiO_2]. The PSD of the suspensions was examined by Disc Centrifuge Photosedimentometer (DCP, Brookhaven Instruments Corporation) at 3000 rpm with a homogeneous start. The fraction of large particles, f, was calculated by integrating the PSD curve. The relative fraction of large particles, f_r, was defined as the ratio of f with polymer to that of a blank suspension, as in our previous papers [30].

Table 2 Amount of polyDADMAC grafted onto polyacrylamide varying with γ-irradiation time

Sample	ME4	ME6
γ-irradiation time (hours)	4	6
PolyDADMAC wt%	35	40

Turbidity measurement

A stock suspension was prepared by dispersing 5 g TiO_2 powder into 95 g deionized water. After mixing overnight, the suspension was placed in an ultrasonic bath for 3 h. A 0.5 ml TiO_2 stock solution was added to a 500 ml beaker containing 250 ml water for turbidity measurement.

The turbidity of the TiO_2 suspension (100 mg/l) after polymer addition was continuously monitored by Photometric Dispersion Analyzer (PDA 2000, Rank Brothers, Cambridge, UK). The suspension was re-circulated with a peristaltic pump through the PDA at a rate of 0.75 ml/s and the DC output voltage was recorded. The measuring cell of the turbidimeter is 1 mm^3; it is equipped with a high-intensity light emitting diode (wavelength 820 nm) and a sensitive photodiode to detect the transmitted light. The output amplifer of the PDA was adjusted to give an output voltage $V_0 = 10$ for pure water. The turbidity, τ, is related to the DC output voltage, V, by the following expression: $V = V_0 \exp(-\tau L)$, where L is the path length [31, 32].

Results

In our previous work we described the preparation and characterization of a series of copolymers obtained using γ-irradiation grafting of polyDADMAC onto polyacrylamide [30]. Although hydrogels would form at longer γ-irradiation times and higher PAM concentrations, the current experimental conditions yielded a polymer solution of sol character. The graft polyelectrolytes have a comb structure as illustrated in Fig. 2. The following sections compare flocculation performance induced by the graft copolymers, with the corresponding homopolymers.

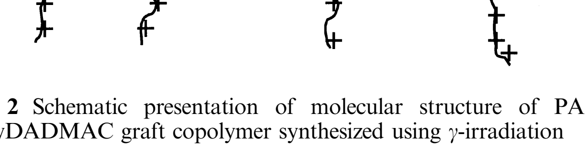

Fig. 2 Schematic presentation of molecular structure of PAM/polyDADMAC graft copolymer synthesized using γ-irradiation

A dilute TiO_2 suspension was chosen as the model colloid. In 0.001 M NaCl the electrophoretic mobility of TiO_2 particles was about 4 μm cm/V s at pH 8 [30]. The TiO_2 PSD, measured by disk centrifuge, is shown in Fig. 3. The distribution was bimodal; the sharpest peak was at ~0.1 μm and a broader peak was centered around 0.4 μm. The fraction of large particles, f, is defined as the fractional area of the large peak. When flocculation occurs, the f value increases because small particles are converted to large agglomerates. The extent of flocculation is expressed as the relative fraction of large particles, f_r, which is defined as the ratio of f after flocculation to that of the initial suspension [30].

Flocculation by homopolymers

Figure 4 shows the f_r values versus the dose of homopolymers at pH 8. No significant flocculation was observed up to 10 [mg polymer]/[g TiO_2] for the PAM homopolymer. When pure polyDADMAC, with M_w of 8.4×10^4, was employed as a flocculant, an increase in f_r was observed at low doses. PolyDADMAC reaches an optimal flocculating dose (OFD) at 1.25 [mg polymer]/[g TiO_2]. No flocculation was observed above 10 [mg polymer]/[g TiO_2]. Flocculation using the homopolymers was not dependent on time, for times longer than the minimum time required to conduct the experiment (less than 1 min).

Flocculation by graft copolymers

The graft copolymers showed a more complicated flocculation, depending not only on polyelectrolyte dosage but also on time. ME4 with 35 wt% of grafted polyDADMAC was chosen for the kinetic investigation. From the measurement of the PSD profiles, the flocculation of the graft copolymer as a function of the dose used can be divided into three groups, as shown in Fig. 5. At doses < 2.5 [mg polymers]/[g TiO_2], flocculation was rapid, and the relative intensity of large

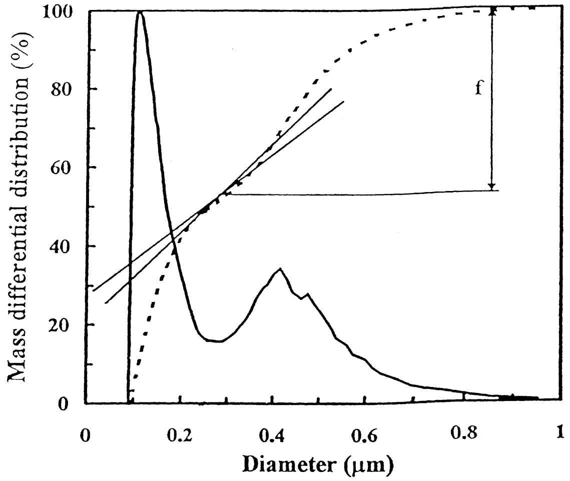

Fig. 3 Differential (*solid line*), cumulative (*dashed line*) mass particle size distribution of TiO_2, and the fraction of large particles, f

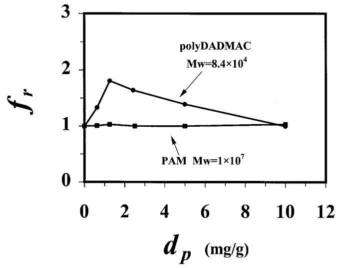

Fig. 4 Relative fraction of large particles f_r versus polymer dosage d_p for PAM and polyDADMAC homopolymers measured at pH = 8 in dilute TiO_2 suspension system (50 mg TiO_2/l 10^{-3} M NaCl)

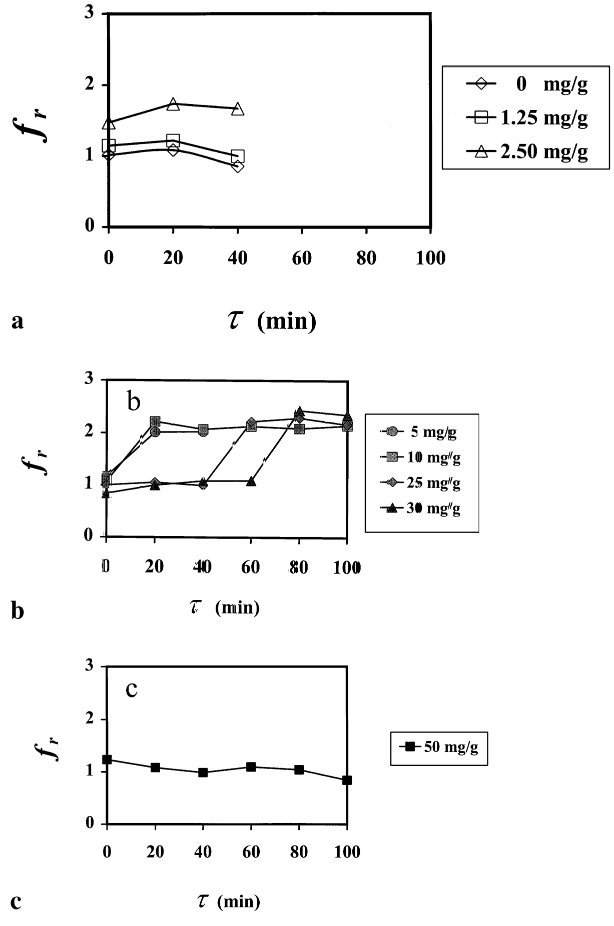

Fig. 5a–c Relative fraction of large particles f_r versus time for ME4 sample at different copolymer dosages: **a** no delay time, **b** delay time related to dosage, and **c** no flocculation

particles slightly increased with more ME4 added (Fig. 5a). At doses > 5 [mg polymer]/[g TiO_2], flocculation was not observed immediately after adding polyelectrolyte to the TiO_2 suspension. There appeared to be a delay period before flocculation occurred. It is interesting to note that the length of delay was a strong function of polymer dose: the more polyelectrolyte was added, the longer the delay period observed in the dose range 5–30 [mg polymer]/[g TiO_2] (Fig. 5b). When the doses were > 50 [mg polymer]/[g TiO_2], no flocculation was observed under the current experimental conditions (Fig. 5c).

To analyze the flocculation ability of various graft copolymers quantitatively, the average relative fractions of large particles after the delay period $(f_r)_{av}$ were used. Figure 6 shows the $(f_r)_{av}$ values as a function of the graft copolymer dose. It was clearly observed that ME6 with 6 h of γ-irradiation gave better flocculation performance than ME4, with higher $(f_r)_{av}$ and a lower optimal dose.

Turbidity measurement

The turbidity measured by PDA was also used to evaluate the flocculation ability of the polymers. According to the equation $V = V_0 \exp(-\tau L)$ [31, 32], the turbidity (τ) is inversely proportional to the amplified mean voltage V. Flocculation was investigated as a function of polymer dose, ion strength, pH value and shear force. When pH was adjusted to 8 ± 0.2 and the stir speed was 400 rpm, no significant change in the PDA profile was observed as the salt concentration was varied from 0 to 10^{-3} M NaCl. However, the voltage versus stir speed experiments, as shown in Fig. 7 for ME4, revealed that shear force plays an important role in flocculation.

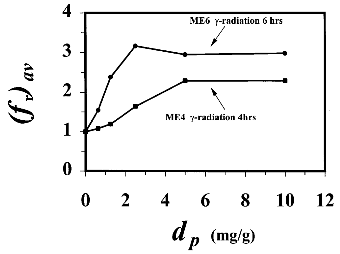

Fig. 6 Average relative fraction of large particles $(f_r)_{av}$ after delay time versus polymer dosage for two graft copolymer samples

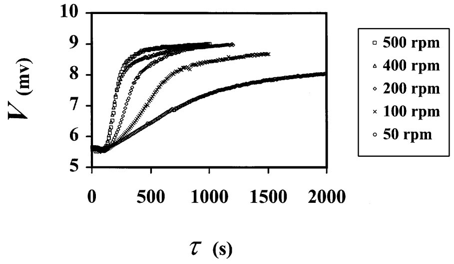

Fig. 7 Influence of shear force on the turbidity profile measured by Photometric Dispersion Analyzer

Discussion

The PAM used in this study has a high molecular weight and low degree of hydrolysis (less than 1%). No significant flocculation was observed for the TiO_2 suspension when PAM doses of up to 10 mg/g TiO_2 were used, as shown in Fig. 4. This showed that bridging by long polymer chains was not effective in this system, which we attribute to the weak adsorption of non-ionic chains onto charged particle surfaces. In the case of polyDADMAC, the OFD was observed at 1.25 mg/g; there were no significant delays. PolyDADMAC has a relatively small radius of gyration compared with the TiO_2 particles, 0.012 μm and 0.248 μm respectively. These factors imply that case I flocculation, mentioned in the Introduction section, occurs. The adsorption, reconformation and collision are very fast, leading to the quick formation of flocs. This type of particle collision could be due mainly to the attraction between positively and negatively charged domains on the different particles. Partial coverage of the negatively charged particles interacts with the adsorbed cationic polyelectrolytes in a rather flat conformation on particle surface [12].

To understand this quantitatively, we calculated that at the OFD of 1.25 [mg polymer]/[g TiO_2], the ratio of polymer chains to TiO_2 particles was about 280:1. (The number of polyDADMAC chains in 1 gTiO_2 is: 1.25×10^{-3} g polyDADMAC/8.4×10^4 g/mol $\times 6.023 \times 10^{23}$#/mol $= 8.96 \times 10^{15}$; the number of TiO_2 particles is: 1 g TiO_2/3.9 g/ml/((3.14/6) $\times 0.248^3 \times 10^{-12}$)ml $= 3.21 \times 10^{13}$). If all the monomeric units of the polyDADMAC chains are adsorbed onto the surface of the particles, the coverage area of the 280 polyelectrolyte chains is 2.33×10^{-10} cm^2 (the number of DADMAC units of each chain is 8.4×10^4 g/mol/161.5 g/mol $= 520$, the area of each unit is $3.2 \times 5.0 \times 10^{-16} = 1.6 \times 10^{-15}$ cm^2). The surface coverage of the TiO_2 particles is about 12% (the area of each particle is $3.14 \times 0.248^2 \times 10^{-8} = 1.93 \times 10^{-9}$ cm^2). The projected area of the 280 polyelectrolyte coils is ($3.14 \times 0.012^2 \times 10^{-8} \times 280 =$) 1.27×10^{-9} cm^2, which is equivalent to 66% surface coverage. This calculated value corresponds to La Mer's model, which shows that the optimal surface coverage for flocculation to be effective is about 50% [33, 34].

When more polyDADMAC is added to the TiO_2 suspension, the charge of the TiO_2 particle surface is probably be converted from negative to positive, due to nearly complete coverage by polyDADMAC. This makes it difficult for the particles to form flocs because of electric repulsion caused by the adsorbed cationic polyelectrolytes. This over-dose phenomenon has been demonstrated in many colloidal flocculation system [18, 35]. It is the main reason why f_r gradually decreased with more polyDADMAC was used over the optimum dose. At a dose of 10 [mg polymer]/[g TiO_2], no particle sediment was observed.

When the graft copolymer was used for flocculation, a delay period was observed at high polymer doses. Before we start analyzing flocculation by the graft copolymer, we should examine the chain structure of this copolymer. For the ME4 sample with 35 wt% polyDADMAC chains randomly grafted onto PAM backbones, it is estimated that each PAM backbone bears about 50 polyDADMAC branches. This comb-type structure is illustrated in Fig. 2. When this type of graft copolymer is dissolved in water, the size of the polymer coil changes due to the grafting branches. Let us assume that the grafted side chains do not significantly increase the coil size of PAM due to the low molecular weight of polyDADMAC. The graft polymer coil is slightly smaller than that of TiO_2 particles (30% less in diameter).

At low polymer doses, for example 1.25 [mg polymer]/[g TiO_2], the copolymer concentration in the suspension is 6.25×10^{-8} g/cm^3 ($=1.25$ mg polymer/g $TiO_2 \times 50$ mg TiO_2/l), corresponding to the number of graft polymer chains of 2.65×10^9/cm^3 (6.25×10^{-8} g/cm^3 $\times 6.023 \times 10^{23}$ #/mol/($10^7 + 50 \times 8.4 \times 10^4$)g/mol). This is of the same order as the number of TiO_2 particles in suspension, 1.6×10^9/cm^3 (50 mg TiO_2/l H_2O). It can be estimated that, at this concentration, the average distance between two copolymer coils in the suspension is about 7.23 μm ($=(2.65 \times 10^9$/cm$^3)^{-1/3}$). Within such a space, the graft copolymer chains could exist as isolated coils without serious entanglement with each other. When mixed with the particles, the graft copolymers are adsorbed on the particle surfaces. Since on average only 1.66 copolymer chains are adsorbed per particle, most of the particle surface remains empty. With the help of shear force (stirring when the polymer solution is added to the suspension, and spinning when the suspension is injected into the high-speed disk), some aggregated flocs form. The conformation of the adsorbed chains on the surface is believed to be in a high energy state. This flocculation can be considered as non-equilibrium flocculation according to Gregory's model, as shown in Fig. 1.

As the polyelectrolyte concentration increases, the number of polymer coils per particle increases. It was experimentally observed that the delay period was correlated to the polymer dosage. The higher the dose used, the longer the delay time observed. In terms of flocculation kinetic theory, this can be related to the processes of adsorption, re-conformation and stabilization. Firstly, with the increase of polymer concentration, the fraction of particle surface covered by the adsorbed polymer chains on the particles increases. In the limiting situation when the surface is completely covered, the colloidal particle is stabilized by an adsorbed polymer layer; no flocculation can be observed at this moment. Secondly, it can be speculated that some polymer chains may remain in the media, especially at high polymer concentrations.

The adsorption of copolymer coils onto surfaces is different from the adsorption of low-molecular-weight polymer chains, because the copolymer coils are of comparable size with the particles. The adsorption layer on the surface is therefore much thicker. Because polyDADMAC branches on the PAM backbone are favorably extended as rods [36], the graft copolymer is likely to assume a brush-like coil, in which polyDADMAC branches preferentially occupy the outside of the coil. Using a Monte Carlo computer simulation, Balazs and Siemasko [11] modeled the adsorption behaviors of comb-like copolymers and their linear counterparts. They predicted that the branch points of the copolymer adsorb preferentially onto particle surfaces compared with the backbone, especially for comb copolymers containing long 'sticky' teeth. In the present case, the adsorption of branch segments by charge neutralization is more likely than that of PAM backbone segments. These highly charged branches could act as the 'sticky' teeth to be adsorbed onto particle surfaces. The energy of ion bonding (1–10 kcal/mol) is much higher than that of PAM backbone rotation (0.2 kcal/mol). As a result of adsorption via charge neutralization, the conformation of PAM-based polyelectrolyte changes from its original one, experiencing shrinkage of the PAM backbone to allow more polyDADMAC branches be adsorbed onto the particle. The adsorption of polyDADMAC branches by charge neutralization is a predominant driving force causing the re-conformation of copolymer chains on the surface. This slow re-conformation process is believed to be the main reason for the delay in flocculation at high polymer doses. In our experiments, the delay period for a given polymer dosage was reproducible.

It is interesting to note that this chain re-conformation depends strongly on the shear force, as shown in Fig. 7. If the transition point on a PDA curve is taken as the re-conformation time t_{rc}, the plot of t_{rc} versus shear speed is shown in Fig. 8. High shear speeds significantly reduce the re-conformation time.

At high polyelectrolyte doses, for example 50 [mg polymer]/[g TiO_2], the ratio of polyDADMAC branches on the PAM backbone to TiO_2 particles is much higher than the optimal adsorption of polyDADMAC onto the TiO_2 surface. As mentioned above, the driving force for chain re-conformation is charge neutralization. When the iso-electric point of the particle reaches zero, chain

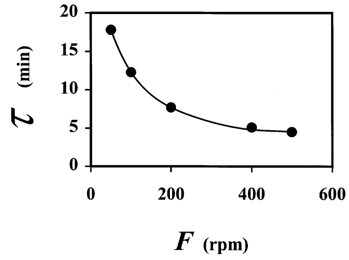

Fig. 8 Influence of shear force on the chain re-conformation time from the turbidity measurements

re-conformation induced by charge neutralization almost stops. In this situation, no flocculation can be observed.

The sample ME6 was exposed to γ-irradiation for a longer time and therefore has a higher charge density, as shown in Table 2. This could be the reason why ME6 has lower OFD compared to ME4, shown in Fig. 6. On the other hand, longer γ-irradiation time also leads to chain crosslinking between two PAM chains. In this case, ME6 will have a large average molecular weight, and therefore act as a better flocculant than ME4.

Conclusions

Based on the experimental flocculation of TiO_2 suspensions using homopolymers and graft copolymers of PAM and polyDADMAC, the following conclusions can be drawn:

1. Compared with the homopolymers of PAM and polyDADMAC, the graft copolymers produced by γ-irradiation showed improved flocculating abilities, giving higher large particle fractions in PSD measurements.

2. Besides the polymer dosage, the flocculation of graft copolymers is a strong function of time. A delay period was observed for the polymer dose range of 5–30 [mg polymer]/[g TiO_2]. The higher the dose used, the longer the delay time. This delay is believed to be mainly attributable to the polymer chain re-conformation. Flocculation behavior was interpreted in terms of equilibrium and non-equilibrium flocculation theory.

3. It was observed that the chain re-conformation of graft copolymers was not affected by the ionic strength of the solution. However, strong shear forces significantly reduced the chain re-conformation time.

4. The sample ME6 was a superior flocculant to ME4 because of its high charge density and large molecular weight.

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References

1. Rose DR, St. John MR (1990) In: Mark HF (ed) Encycl Polym Sci Eng Ed, vol 7. J Wiley, New York, p 212
2. Bolto BA (1995) Prog Polym Sci 20:987
3. Adachi Y (1995) Adv Colloid Interf Sci 56:1
4. Gregory J (1988) Colloids Surf 31:231
5. Van de Ven TGM (1994) Adv Colloid Interf Sci 48:121
6. Yu X, Somasundaran P (1996) J Colloid Interf Sci 178:770
7. Ray DT, Hogg R (1987) J Colloid Interf Sci 116:256
8. Adachi Y, Cohen Stuart MA, Fokkink R (1994) J Colloid Interf Sci 165:310
9. Halab L, Ricard A (1996) J Colloid Interf Sci 179:265
10. Barany S, Cohen Stuart MA, Fleer GJ (1996) Colloid Surf A: Physicochem Eng Aspects 106:213
11. Balazs AC, Siemasko CP (1991) J Chem Phys 95:3798
12. Eriksson L, Alm B, Stenius P (1993) Colloid Surf A: Physicochem Eng Aspects 70:47
13. Tripp CP, Hair ML (1996) Langmuir 12:3952
14. Gregory J (1988) Colloid Surf 31:231
15. Gregory J (1973) J Colloid Interf Sci 42:448
16. Pelssers EGM, Cohen Stuart MA, Fleer GJ (1989) Colloid Surf 38:15
17. Pelssers EGM, Cohen Stuart MA, Fleer GJ (1990) J Chem Soc Faraday Trans 86:1355
18. Chaplain V, Janex ML, Lafuma F, Graillat C, Audebert R (1995) Colloid Polym Sci 273:984
19. Tripp CP, Hair ML (1993) Langmuir 9:3523
20. Spalla O, Cabane B (1993) Colloid Polym Sci 271:357
21. Furusawa K, Shou Z, Nagahashi N (1992) Colloid Polym Sci 270:212
22. Nowicki W, Nowicha G (1995) Colloid Polym Sci 273:298
23. Hsu J-P, Lin D-P (1995) Colloid Polym Sci 274:172
24. Otsubo Y (1993) J Rheol 37:799
25. Van der linden CC, Leermakers FAM, Fleer GJ (1996) Macromolecules 29:1000
26. Munk P, Aminabhavi TM, Williams P, Hoffman DE, Chmelir M Macromolecules 13:871
27. Ioan S, Dumitriu E, Maxim S, Carpov A (1977) Eur Polym J 13:109
28. Flory PJ (1953) Principle of polymer chemistry. Cornell University, Ithaca, NY
29. Fried JR (1995) Polymer science and technology. Prentice Hall, Englewood Cliffs, NJ
30. Ma M, Zhu S (1998) Colloid Polym Sci 277:115–122, 123–129
31. Gregory J (1985) J Colloid Interf Sci 105:357
32. Järnström L, Lason L, Rigdahl M (1995) Colloids Sci A: Physiochem Eng Aspects 104:191
33. Smellie RH Jr, La Mer VK (1958) J Colloid Sci 23:589
34. Healy TW, La Mer VK (1964) J Colloid Interf Sci 19:322
35. Tanaka H, Ödberg L, Wägberg L, Lindström T (1990) J Colloid Interf Sci 134, 219
36. Fuoss RM (1952) Discuss Faraday Soc 11:125