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ORIGINAL CONTRIBUTION

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Synthesis and flocculation performance of graft and random copolymer microgels of acrylamide and diallyldimethylammonium chloride

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Abstract Graft (from linear homopolymers) and random (from a linear random copolymer) copolymer microgels of diallyldimethylammonium chloride (DADMAC) and acrylamide were synthesized via a free-radical mechanism using a γ-radiation technique. These copolymer microgels were evaluated as flocculants on a model dilute TiO_2 colloid suspension using a turbidimeter and a disc centrifuge photosedimentometer, and their performances were compared with the linear homopolymers and their blends. It was found that microgels produced after an appropriate irradiation time showed improved flocculation behavior over their nonirradiated linear counterparts. The graft microgels performed better than the corresponding random microgels. For a γ-radiation dosage of 100 krad/h, the graft microgels obtained by irradiating a 30% DADMAC (by weight) homopolymer blend for 3 h showed the maximum reduction in the relative turbidity of the TiO_2 suspension as well as the largest fraction of larger particles flocculated.

Key words Polyacrylamide · Polydiallyldimethylammonium chloride · Graft copolymer · Random copolymer · Microgel

Introduction

Water-soluble polymers (polyelectrolytes) play an important role as flocculants in industries such as wastewater treatment, mineral processing, and papermaking [1–7]. Synthetic organic polyelectrolytes have been developed and used extensively in the past 40 years and they have largely replaced inorganic chemicals such as alum, lime, and ferric chloride, and natural products such as starch and gums in some applications.

There are two major mechanisms involved in the flocculation of charged particles: charge neutralization and chain bridging [1, 8]. Depending on the mechanism involved, repulsive forces between similarly charged particles are either reduced, and thus natural attractive forces bring about destabilization, or the repulsive forces are overcome by polymer chain bridging. In the charge neutralization mechanism, the charges on the particles are neutralized by the addition of counterions. For simple charge neutralization, optimum flocculation occurs near the point of total neutralization on particle surfaces, i.e., when the electrophoretic mobility of the particles has been reduced to nearly zero [9–13]. In the chain bridging mechanism, polymer chains are attached to the surface of particles at several points by adsorption with unattached segments that extend into the bulk of the liquid [14]. The chain may loop back and attach to the same particle at more than one site. If a polymer chain can be attached to more than one particle, the polymer links particles together to form an aggregate. For adsorption to occur, there must be a favorable interaction between polymer segments and a particle surface. If particles and polymers have opposite charges, the counterions will have a strong interaction and will facilitate adsorption of the polymer.

In reality, most polyelectrolyte flocculants function by both mechanisms, i.e., ionic centers (charge units) provide adsorption points on the surface of particles while polymer backbones hold the particles together; therefore, both charge density and high molecular weight are essential for a polymer to be effective as a flocculant. Many commercial polyelectrolytes are cationic polymers prepared by modifying polyacrylamide (PAM) or copolymerizing acrylamide (AM) with comonomers having cationic charge groups [1, 15–18]. This is because it is difficult to synthesize high-molecular-weight charged polymers such as polyquats, polyimines, and polyamines due to strong repulsion between monomer units, and they are expensive. On the other hand, PAMs are usually inexpensive and have high molecular weights, but they are nonionic. Current commercial polyelectrolyte flocculants are mainly AM copolymers and they are manufactured via a free-radical polymerization mechanism or by postreaction modification of PAMs by Mannich- and Hoffman-type reactions to give cationic flocculants with relatively high molecular weight [1, 19–22].

Most commercial flocculants contain up to 50% charge densities of the cationic polymer. These ionic centers are randomly distributed along backbone of the polymer chains. A schematic diagram of a random cationic copolymer chain holding two anionic particles together is shown in Fig. 1a. The cationic centers located on the bridging segments of the polymer chain are wasted while there are insufficient cationic centers at the adsorption site to neutralize counterions. An additional problem is the control of charge density. Polymer chains with too few charges will not provide adequate adsorption while excessive charges will make adsorbed loops too small [23]; therefore, to be more effective for flocculation, the charge units should be concentrated on several sections on the polymer chain (Fig. 1b). The chain will consist of a long backbone bearing short pendant-type cationic oligomers. Highly concentrated charge clusters provide stronger adsorption points on the particles. This type of copolymer can be synthesized by grafting monomers from the polymer backbone [24] or by grafting preformed polymer chains onto the polymer backbone [25–27].

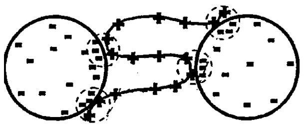
Poly (diallyldimethyl ammonium chloride) (polyDADMAC) is one of the most popular quaternary cationic polyelectrolytes used commercially. The overall objective of this work is to identify superior structures of polymer chains for flocculation applications. In this paper, we used a γ-radiation technique

1. To synthesize graft copolymer microgels (Fig. 2a) of two different low-molecular-weight, high-charge-density polyDADMACs and a high-molecular-weight, nonionic PAM.

2. To synthesize random microgels (Fig. 2b) from a linear random copolymer of DADMAC and AM.

3. To investigate the flocculation performance of the graft and random copolymer microgels on a model TiO_2 colloid suspension as a function of polymer dose and flocculation time. The flocculation performances of the microgels were then compared with those of the homo-

(a) Random Copolymer



(b) Graft Copolymer

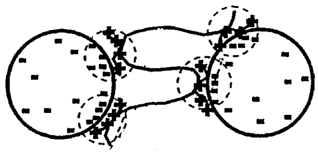
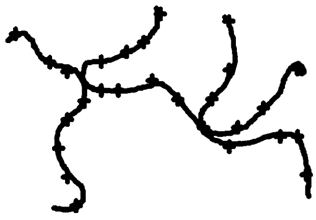


Fig. 1 Schematic representation of flocculation by a polyelectrolyte chain: **a** random copolymer and **b** graft copolymer

(a) Random Copolymer Microgel



(b) Graft Copolymer Microgel

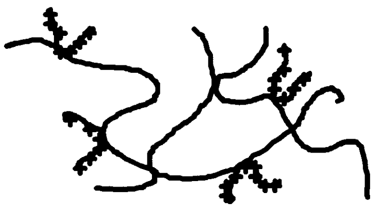


Fig. 2 Schematic representation of **a** random and **b** graft copolymer microgels

polymers and their blends. The chemical structures of the polymers used in this study are shown in Figure 3.

Experimental

Materials

PAM (M_w 5×10^6 g/mol) containing 1.5% by weight polyacrylic acid was supplied in granular form by the Sigma-Aldrich Chemical Company. PolyDADMAC (M_w 1×10^5 and 2.4×10^5 g/mol) solutions were supplied by Ciba Specialty Chemicals, and they were vacuum-dried at room temperature to obtain solid powders. The charge densities were determined (by conductometric titration) to be 3.14 mEq/g for the 1×10^5 g/mol polyDADMAC and 3.71 mEq/g for the 2.4×10^5 g/mol polyDADMAC. A commercial linear random copolymer of DADMAC and AM was obtained from Calgon Canada in the form of a 3.8 wt% solution in water. The linear copolymer was extracted by precipitating the solution in large quantities of acetone. The precipitate (containing the copolymer along with some water and acetone) was separated from the supernatant (containing acetone and other additives) and dried in a fume hood overnight to remove traces of acetone. It was subsequently vacuum-dried for 3 days to remove traces of water. The linear copolymer samples contained 30% DADMAC by weight and had a weight-average molecular weight of about 1×10^6 g/mol.

TiO_2 powder (ρ = 3.9 g/ml) was obtained from the Sigma-Aldrich Chemical Company. Stock solutions of the suspension were prepared by dispersing 50 mg TiO_2 in 1 l deionized water with an ionic strength of 0.001 M NaCl and were left overnight to ensure complete wetting of the particles. Prior to the flocculation tests, an ultrasonic bath was used for at least 3 h in order to completely disperse the TiO_2 particles.

All experiments were carried out at room temperature (25 °C). Deionized water was used in the preparation of all solutions. Since PAM is prone to stick to glass, only polyethylene bottles were used. All bottles were washed and rinsed with deionized water prior to use.

Synthesis of graft copolymers and microgels

The grafting of polyDADMAC onto PAM and microgelation of the linear random copolymer of DADMAC and AM were done by irradiation with γ-rays from a ^{60}Co source. The γ-rays, which act as free-radical initiators, extract hydrogen atoms from the backbone of polyDADMAC and PAM. These backbone radicals are then terminated by combination. It has been found from viscosity measurements that a polyDADMAC radical does not easily combine with its own kind, i.e., crosslinking between cationic chains is limited [25]; however, a PAM radical is prone to termination with either another PAM radical or with a polyDADMAC radical. Due to the high activity of PAM radicals, macrogel formation becomes an important feature of the grafting process, and it must be carefully controlled. Significant levels of gelation (crosslinking) tend to occur at high radiation doses and high polymer concentrations, leading to the formation of water-insoluble copolymers. Therefore, grafting and microgelation have to be carried out at a relatively low polymer concentrations in order to minimize macrogel formation.

For this study, a feed concentration of 0.8 wt% polymer in deionized water was used. The polyDADMAC content was 10, 20, 30, 40, and 50% by weight of the total homopolymer blend for grafting and 30% by weight for microgelation of the linear random copolymer. The samples were exposed to γ-radiation for 1, 2, 3, 4, and 5 h at a dosage of 100 krad/h. After irradiation, stock solutions (25 mg polymer/l H_2O) of the graft and random microgels were prepared by adding 1 ml irradiated product (containing 8 mg copolymer) to 319 ml deionized water and were stored in a refrigerator prior to the flocculation experiments.

Surface charge of TiO_2 particles

The zeta potentials (surface charge) of TiO_2 colloidal particles were measured in terms of electrophoretic mobility using a Coulter Delsa 440 Doppler electrophoretic light scattering analyzer at 25 °C (Fig. 4). Samples (1 ml) from the stock solution of the suspension containing 50 mg TiO_2 in 1 l deionized water with an ionic strength of 0.001 M NaCl were used. The isoelectric point (the point at which the particle surface charge changes from positive to negative) was at pH 4.3, and the electrophoretic mobility was nearly constant (about -4.2×10^{-8} m^2/Vs) above pH 7. For this study, a pH value of 8 was used for the flocculation

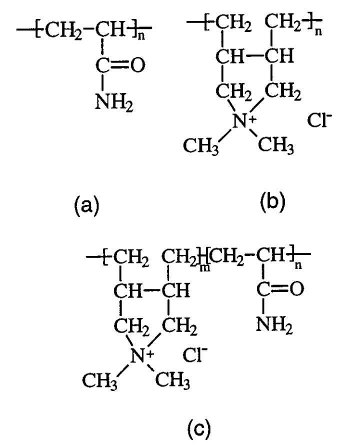


Fig. 3 Chemical structures of polymers used in this study: **a** polyacrylamide (*PAM*), **b** poly(diallyldimethylammonium chloride) (*polyDADMAC*), and **c** DADMAC-*co*-acrylamide

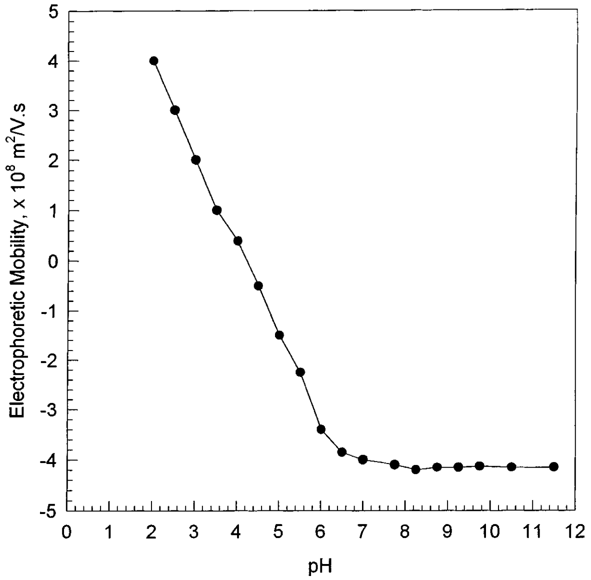


Fig. 4 Electrophoretic mobility of TiO_2 particles as a function of pH in a 10^{-3} M NaCl solution

tests to assure a negative charge on the TiO_2 particle surface. The pH of the colloid suspension was carefully adjusted by adding a small amount of 0.01 M NaOH solution.

Turbidity measurements

The turbidities of TiO_2 suspension samples with and without polymer were measured using a Hach 2100P portable turbidimeter (Hach, Loveland, Colo.). This is based on the nephelometric principle of turbidity measurement and it meets the design criteria specified by the United States Environmental Protection Agency, method 180.1. This method calculates the ratio of the intensity of scattered light to transmitted light as the light beam from a tungsten-filament lamp passes through the liquid medium containing particles. The portable turbidimeter measures turbidity from 0.01 to 999 nephelometric turbidity units.

A preset amount of polymer from the stock solution (0.36 ml polymer stock solution for 1 mg polymer/g TiO_2 dose and 0.72 ml polymer stock solution for 2 mg polymer/g TiO2 dose) was added to 180 ml pH-stabilized TiO_2 suspension. The suspension was gently stirred at all times during the experiments (about 60 min). Turbidity measurements were made for flocculation times of 0, 5, 10, 15, 30, 45, and 60 min. The relative turbidity was calculated from T/T_o, where T is the turbidity of the polymer-induced flocculated suspension and T_o is the turbidity of a suspension without polymer (blank). It should be noted that the stirred dilute TiO_2 suspension was very stable. We observed only an 18% drop in the relative turbidity of the unstirred TiO_2 suspension after 24 h sedimentation.

Particle size distribution measurements

The particle size distributions (PSD) of TiO_2 suspension samples with and without polymer were measured using a disc centrifuge photosedimentometer (DCP, Brookhaven Instruments). This method is based on the principle of centrifugal sedimentation and it is used widely to obtain absolute PSD information for latexes, pigments, ceramics, clays, emulsions, and many other types of small particles. This method produces an apparent weight differential PSD directly and rapidly by continuously measuring the attenuation of light passing through a liquid medium as the particles pass through the light beam.

For this study, a disc speed of 3000 rpm was used. A preset amount of polymer from the stock solution (25 mg polymer/l H_2O) was quickly added to 100 ml pH-stabilized TiO_2 suspension and the mixture was stirred slowly. Then 15 ml of the mixture was injected into the DCP and the data were recorded for 15 min. Measurements were made for flocculation times of 0.5, 30, 60, and 90 min.

The particle size differential and the cumulative mass distribution for a TiO_2 colloid suspension without polymer are shown in Fig. 5. It can be seen that the PSD curve (differential mass distribution) is bimodal in nature with an average particle diameter of 0.235 μm. The first and larger peak has a maximum value at a diameter of about 0.1 μm, and the second and smaller peak has a maximum value at a diameter of about 0.4 μm. In order to evaluate the performance of the polymers as flocculants, we define a parameter f as the fraction of larger particles. This is the ratio of the area under the second peak over the total area. This is determined by the inflection point on the cumulative mass distribution curve. When flocculation occurs, the value of f increases as small particles agglomerate. The extent of flocculation is expressed as the relative fraction of larger particles, f_r, which is defined as follows: $f_r = f_p/f_o$, where f_p is the fraction of the area of the second peak of the TiO_2 suspension flocculated by the polymer and f_o is the fraction of the area of the second peak of the TiO_2 suspension without polymer. Therefore, as f_r increases, flocculation performance improves.

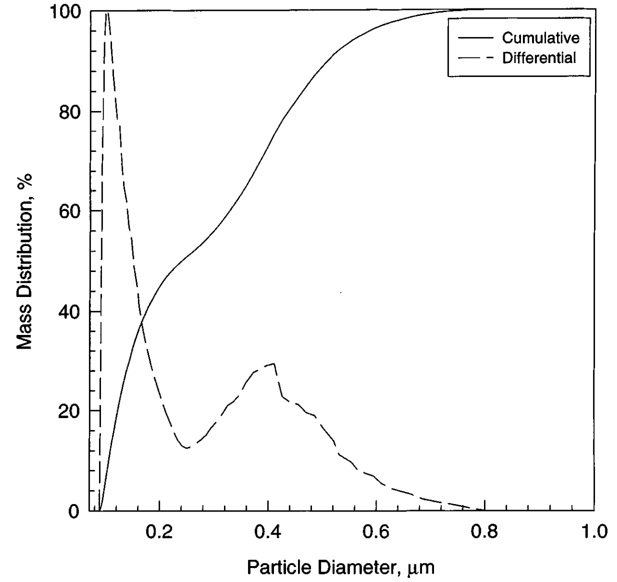


Fig. 5 Cumulative and differential mass distribution of TiO_2 particles without polymer

Results and discussion

The following nomenclature will be used to describe the polymers in this study:

DADMAC-1:	PolyDADMAC ($M_W = 1 \times 10^5$ g/mol)
DADMAC-2:	PolyDADMAC ($M_W = 2.4 \times 10^5$ g/mol)
Graft-1:	Graft copolymer microgels of DADMAC-1 and PAM
Graft-2:	Graft copolymer microgels of DADMAC-2 and PAM
Blend-1:	Blend of DADMAC-1 and PAM (DADMAC content = 30 wt% by weight)
Blend-2:	Blend of DADMAC-2 and PAM (DADMAC content = 30 wt% by weight)
Random L:	Linear random copolymer of DADMAC and AM (DADMAC content = 30 wt% by weight)
Random M:	Microgels obtained by irradiating random L (DADMAC content = 30 wt% by weight)

Effect of DADMAC dose on the surface charge of TiO_2 particles

The effect of the polyDADMAC (DADMAC-1) dose on the electrophoretic mobility (surface charge) of TiO_2 particles at room temperature in a 10^{-3} M NaCl solution with a pH of 8 is shown in Fig. 6. At first, the surface charge of the particles is negative. With the addition of polyDADMAC, the positive charge of the polymer begins to neutralize some of the negative charge on the particle surface. The isoelectric point of the particles was observed at a polyDADMAC dose of about 2.5 mg/g TiO_2. At levels of polyDADMAC over 2.5 mg/g TiO_2, the particle surface shows a positive charge and the particle surface charge finally levels off at a dose of 20 mg/g TiO_2. This indicates that the particles are completely covered by the polymer. Overdosing with polyDADMAC results in the reversal of particle charge (from negative to positive) due to the adsorption of excess polyDADMAC molecules, and it is difficult for the particles to form flocs because of electronic repulsion of the adsorbed polyDADMAC. This phenomenon of overdosing has been demonstrated in many colloidal flocculation systems [28, 29]. Optimum flocculation occurs when the electrophoretic mobility of the particles has been reduced to nearly zero. The point of zero charge determined by colloid titration appears to correlate well with the optimum dose required to flocculate turbid water [30]. For this study, polymer doses of 1 and 2 mg polymer/g TiO_2 were used for the flocculation experiments. The choice of these doses for the flocculation testing was also based on the results of our previous studies [27, 30].

Flocculation performance of linear homopolymers and their blends, the linear random copolymer, graft copolymer microgels, and random copolymer microgels

Turbidity

The flocculation performance of irradiated and nonirradiated linear homopolymers and their blends, the linear random copolymer and its microgels, and graft copolymer microgels containing different amounts of DADMAC were studied by measuring the turbidity of TiO_2 colloid suspension for doses of 1 and 2 mg polymer/g TiO_2 and flocculation times of 0, 5, 10, 15, 30, 45, and 60 min. The flocculation performance and the kinetics for graft copolymer microgels containing 40% DADMAC-1 and a dose of 2 mg/g of TiO_2 are shown in Fig. 7. Similar measurements were made for all polymers used in this study. The TiO_2 suspension was constantly stirred at a slow speed throughout the experiment. This was done to promote better mixing between the injected polymer and the TiO_2 particles in the suspension. From Fig. 7, it can be seen that stirring promoted better mixing between the flocculant and the colloidal particles at lower flocculation times, thereby decreasing the turbidity of the suspension; however, as the flocculation time increased, there was an increase in the turbidity of the flocculated suspension. This increase in turbidity could be attributed to the breakup of flocs due to stirring. Therefore, the relative turbidity of each flocculated suspension went through a minimum. In general, all polymers used in this study reached their lowest relative turbidity value within 30 min after addition to the TiO_2 suspension.

The lowest relative turbidity values after a flocculation time of 30 min for graft copolymers containing 10, 20, 30, 40, and 50% DADMAC by weight as a function of irradiation time and doses of 1 and 2 mg polymer/g TiO_2 are shown in Figs. 8–11 (two polymer doses and two different molecular weight polyDADMACs) and are compared with those of the homopolymers (PAM, DADMAC-1 and DADMAC-2) and their blends (blend-1 and blend-2), the linear random copolymer

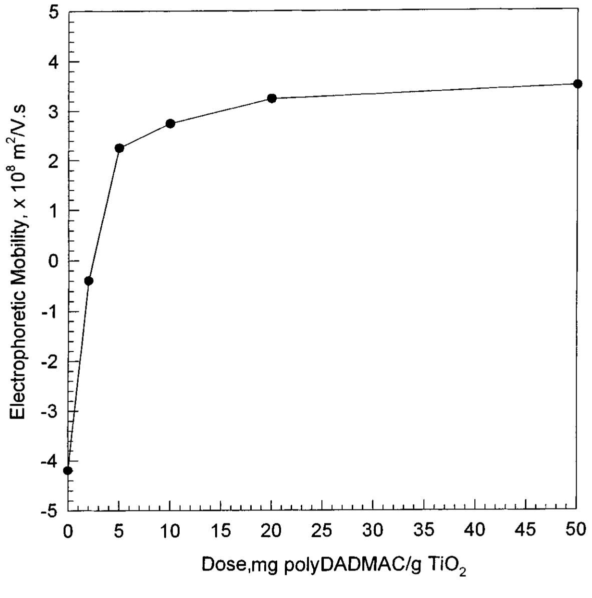


Fig. 6 Electrophoretic mobility of TiO_2 particles as a function of polyDADMAC ($M_w = 1 \times 10^5$ g/mol) dose in a 10^{-3} M NaCl solution at pH 8 and $T = 25$ °C

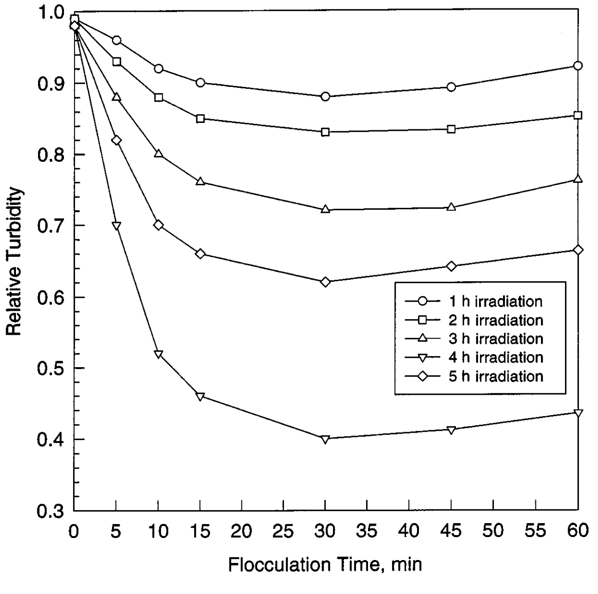


Fig. 7 Relative turbidity of 40% DADMAC-1 graft copolymers as a function of flocculation time for a polymer dose of 2 mg/g TiO_2

(random L) and the random microgel (random M). From these figures it can be seen that graft copolymers (graft-1 and graft-2) containing 30 wt% DADMAC synthesized after 3 h of irradiation showed the maximum reduction in relative turbidity of the colloidal suspensions.

The flocculation performance of graft copolymers containing 30 wt% DADMAC was then compared to that of the commercial linear random copolymer with the same DADMAC charge content and its microgels obtained by irradiation (Figs. 8–11). From Figs. 8–11 it can be seen that the graft copolymers always performed better than their corresponding linear random copolymer and microgel counterparts. The random microgels produced after an irradiation time of 3 h performed slightly better than the linear random copolymer.

The irradiation time plays a key role in determining polymer molecular structure and in turn flocculation performance. Overirradiation leads to the formation of macrogels which are insoluble in water giving poor flocculation performance. From these figures we can see that, as the amount of polyDADMAC increases, the irradiation time required to have the optimum flocculation performance increases, i.e., the time required to crosslink (gel) the linear random copolymer or graft the homopolymer blends increases. This indicates that gelation occurs mainly due to PAM.

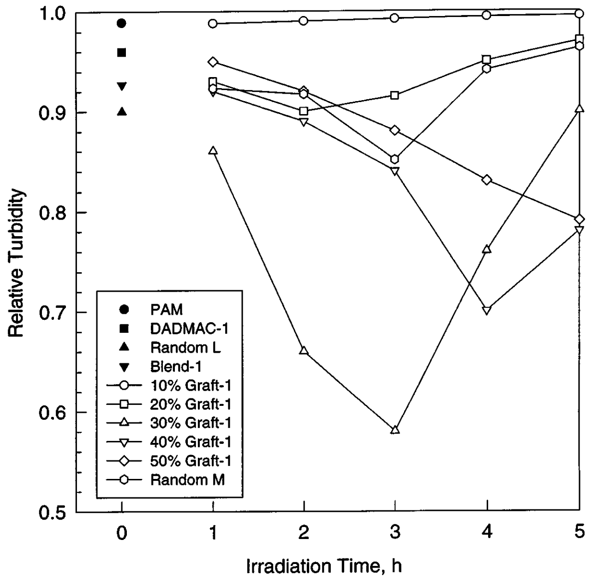


Fig. 8 Relative turbidity of homopolymers and their blend, random copolymers (linear and microgel), and DADMAC-1 graft copolymers as a function of irradiation time (flocculation time = 30 min, polymer dose = 1 mg/g TiO_2)

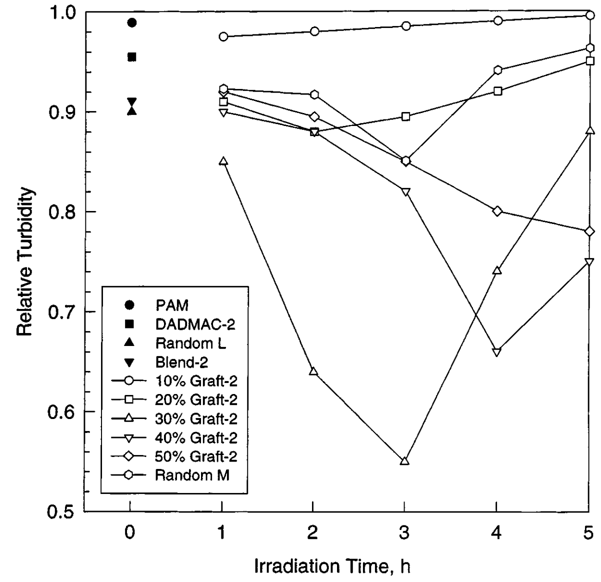


Fig. 9 Relative turbidity of homopolymers and their blend, random copolymers (linear and microgel), and DADMAC-2 graft copolymers as a function of irradiation time (flocculation time = 30 min, polymer dose = 1 mg/g TiO_2)

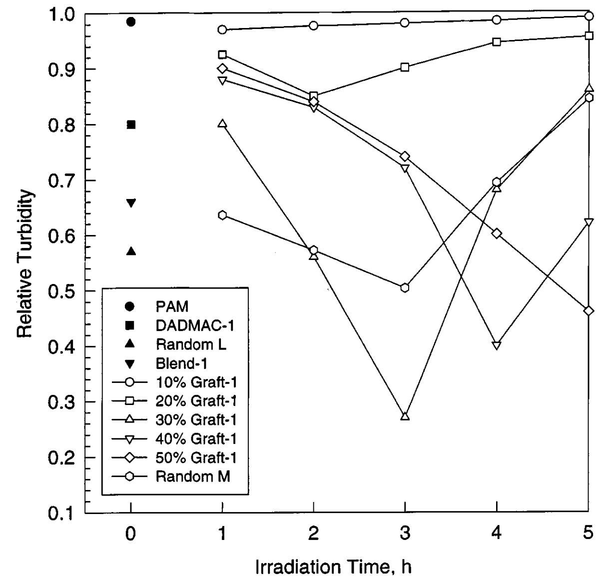


Fig. 10 Relative turbidity of homopolymers and their blend, random copolymers (linear and microgel), and DADMAC-1 graft copolymers as a function of irradiation time (flocculation time = 30 min, polymer dose = 2 mg/g TiO_2)

Floc size distribution

The cumulative and differential PSDs of flocculated TiO_2 suspensions with various polymers containing 30 wt% DADMAC were obtained for doses of 1 and 2 mg polymer/g TiO_2 and flocculation times of 0.5, 30, 60, and 90 min using a disc centrifuge photosedimentometer. All graft and random microgel copolymers were synthesized after 3 h of irradiation. The differential mass distributions of the suspension without polymer (TiO_2 blank) and those with polymer after 30 min for a dose of

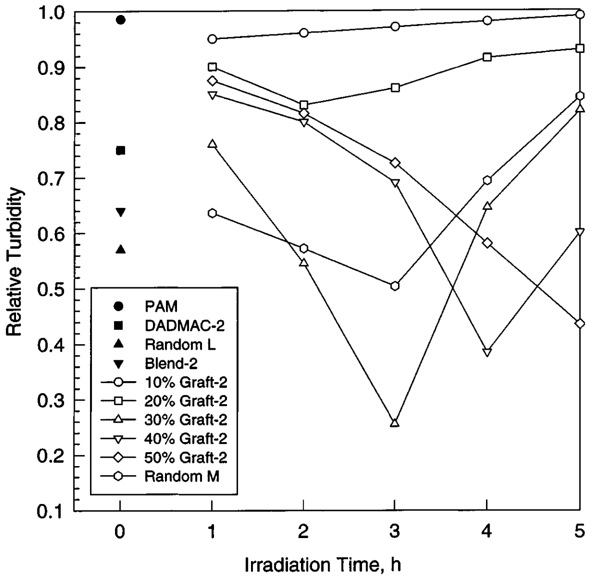


Fig. 11 Relative turbidity of homopolymers and their blend, random copolymers (linear and microgel), and DADMAC-2 graft copolymers as a function of irradiation time (flocculation time = 30 min, polymer dose = 2 mg/g TiO_2)

1 mg polymer/g TiO_2 are shown in Fig. 12. It can be seen that the addition of polymers caused the area under the second peak to become larger, indicating the onset of flocculation.

The relative fraction (f_r) of the larger peak due to flocculation as a function of flocculation time for doses of 1 and 2 mg polymer/g TiO_2 is shown in Figs. 13–14. There is a significant increase in the relative fraction of TiO_2 particles due to flocculation induced by the graft copolymers. This effect is more pronounced after 30 min of flocculation, and it does not change significantly thereafter. The homopolymer blends (blend-1 and blend-2) showed a very small increase in f_r (about 5% for a 1 mg polymer/g TiO_2 dose and 10–14% for a 2 mg polymer/g TiO_2 dose), whereas the two grafted copolymers showed a remarkable improvement in f_r (about 45% increase for a dose of 1 mg polymer/g TiO_2 and 60–66% increase for a dose of 2 mg polymer/g TiO_2). Also, the linear random copolymer and its microgel showed higher f_r values than the homopolymer blends, but they were not as good as the graft copolymers. We also found the flocculation performance (from turbidity and particle size measurements) of graft-2 copolymer to be better than that of graft-1 copolymer. This is probably because DADMAC-2 has longer teeth that enable it to absorb preferentially onto the particle surface compared to DADMAC-1, which has a lower molecular weight.

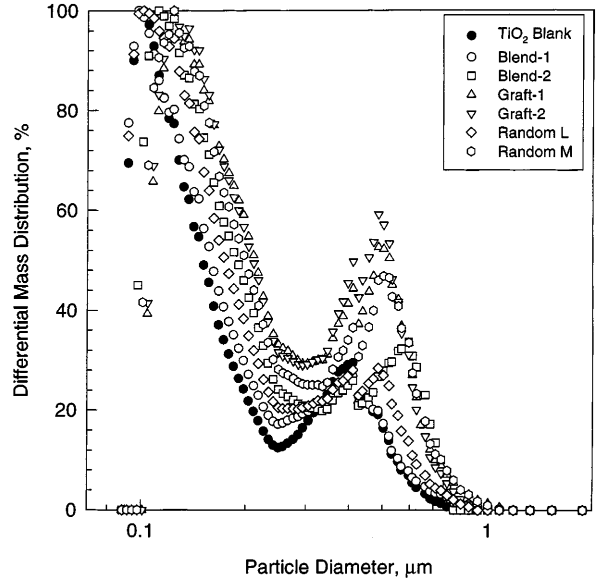


Fig. 12 Differential mass distribution versus particle diameter after 30 min of flocculation for a polymer dose of 1 mg/g TiO_2 (DADMAC content = 30 wt%, irradiation time = 3 h)

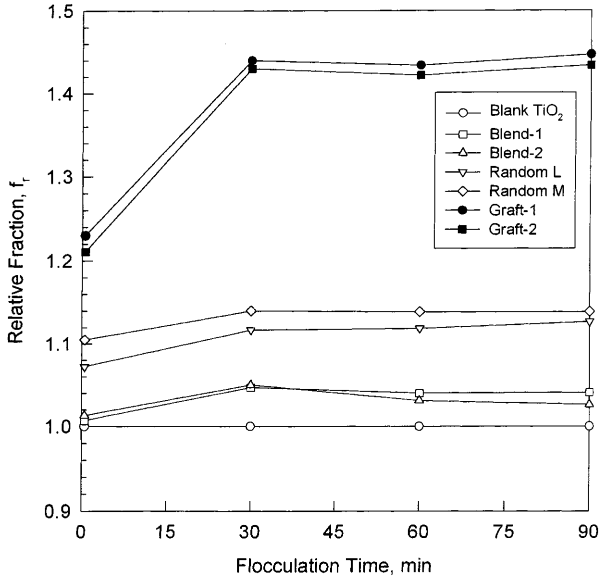


Fig. 13 Relative fraction of larger TiO_2 particles as a function of flocculation time for a polymer dose of 1 mg/g TiO_2 (DADMAC content = 30 wt%, irradiation time = 3 h)

It should be noted that no matter what type of adsorption mechanism prevails, the amount of polymer added should not exceed greatly the amount required to adsorb. The adsorption of polymer molecules on the particle surface often determines the stability of the particles. If the particles are completely coated by the polymer, it becomes impossible for them to approach each other and flocculate. Eventually, this introduces restabilization of the particles. This is known as surface-charge reversal (ionic polymer) and/or steric stabilization (nonionic polymer). An optimum dose for flocculation usually occurs when half the adsorption sites on the particles are taken up by the polymers [28].

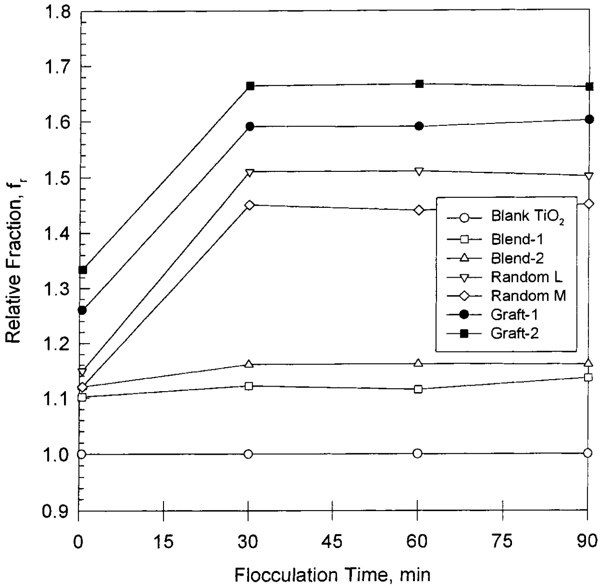


Fig. 14 Relative fraction of larger TiO_2 particles as a function of flocculation time for a polymer dose of 2 mg/g TiO_2 (DADMAC content = 30 wt%, irradiation time = 3 h)

Conclusions

The grafting of two low-molecular-weight, high-charge-density polyDADMACs onto the backbone of a high-molecular-weight, nonionic PAM and microgelation of a linear random copolymer of DADMAC and AM were accomplished via a free-radical mechanism using a γ-radiation technique. The polymers were tested as flocculants for a model TiO_2 suspension. The measurements included turbidity and PSDs. There appeared to be an optimum irradiation time for superior flocculation performance. Overirradiation led to the formation of insoluble macrogels giving poor flocculation results. The optimum irradiation time increased with the polyDADMAC content indicating that PAM was mainly responsible for crosslinking. At the optimum conditions, the graft copolymer microgels gave better flocculation performance than their random copolymer counterparts. The random copolymer microgels were better than the linear random copolymer which, in turn, was better than the linear homopolymer blends. The graft copolymer microgels containing 30 wt% polyDADMAC which were produced after 3 h of irradiation exhibited the largest reduction in the relative turbidity and the most significant increase in the fraction of larger flocculated TiO_2 particles.

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