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ORIGINAL CONTRIBUTION

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Grafting polyelectrolytes onto polyacrylamide for flocculation 1. Polymer synthesis and characterization

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Abstract Low-molecular-weight high-charge-density cationic diallyldimethylammonium chloride homopolymer (polyDADMAC) was grafted onto high-molecular-weight nonionic polyacrylamide (PAM) via a free radical mechanism using a gamma radiation technique. The graft copolymer systems were characterized in terms of viscosity, composition, gel content, degree of grafting and grafting efficiency. Degree of grafting was a strong function of radiation dose, dose rate and polyelectrolyte concentration. Gels were formed at high radiation doses and high PAM levels. Crosslinking between the electrolyte polymers was limited due to electrostatic repulsion. Gelation was mainly caused by coupling of PAM chains. High grafting efficiency was achieved: the lower the poly(DADMAC) concentration, the higher the grafting efficiency observed. The grafting mechanism and the effect of ion interactions on copolymer structural properties are also elucidated and discussed.

Key words Polymer flocculant – water-soluble polymer – polyelectrolyte – polyacrylamide – radiation grafting

Introduction

Cationic flocculants can be prepared by modifying polyacrylamide (PAM) or by copolymerizing acrylamide (AM), with comonomers including cationic charged groups [1–5]. During the last 30 years, the manufacture of AM homo- and copolymers has rapidly increased, partly due to their many applications (e.g., papermaking, wastewater treatment, and mineral processing [6–10]) and partly due to the important technical advances made in the controlled homo- and copolymerization of acrylamide [11–15]. PAM can also be modified by Mannich and Hofmann reactions [16–19] to give cationic flocculants with relatively high molecular weights [18–20]. The polymers are used for flocculation.

The synthesis methods usually involve free radical mechanisms and result in random copolymers. Ionic centers are inevitably distributed randomly along polymer backbones, which may not be the most effective arrangement for flocculation applications. Figure 1A gives a schematic presentation of a random copolymer chain of cationic type holding together two anionic particles. The cationic centers located on the bridging segments of the chain are simply wasted, while there are insufficient cationic centers at the adsorption sites to neutralize counter ions. In addition it is hard to control the charge density. Polymer chains with too few charges do not have enough adsorption, while too many charges make adsorbed loops too small, giving a flat configuration [21].

The ideal situation would be a comb-type polyelectrolyte chain as shown in Fig. 1B. The chain consists of a long backbone bearing short pendant cationic oligomers. These highly concentrated charge clusters can provide stronger adsorption points for the particles. The bridging portions are free of charges to save costs. This type of copolymer can be synthesized by grafting monomers from a polymer backbone or by

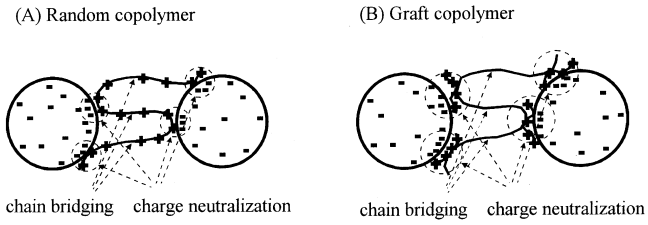


Fig. 1 Schematic presentation of flocculation effect of a polyelectrolyte chain: **A** random copolymer and **B** graft copolymer

grafting preformed polymer chains onto a polymer backbone.

Highly charged polymers, such as polyquats, polyimines and polyamines, are costly and it is very difficult to make high molecular weights because of their polymerization nature. In addition, homocationic polymers form a flattened adsorbed configuration when they become completely adsorbed, which does not favor chain bridging. PAM, however, is usually inexpensive with a very high molecular weight, but is nonionic.

In this work, we have investigated graft cationic copolymers with different charge densities synthesized via free radical mechanisms. The copolymers were prepared by grafting low-molecular-weight high-charge-density cationic polymers onto high-molecular-weight nonionic polymers. PAM was used as the backbone polymer and polyDADMAC as the graft polymer.

A γ-irradiation technique was employed; γ-radiation grafting occurs via a free radical mechanism. Free radical approaches usually result in varying amounts of homopolymers and gel. Too high a gel content is usually not useful for flocculation. Using high-energy γ-rays, the protons on the polymer backbones can be ejected, introducing backbone free radicals. In the case of PAM/polyDADMAC, there are two types of backbone radicals, which undergo termination. There are three possible types of radical combination, as shown in Fig. 2 polyDADMAC/polyDADMAC, polyDADMAC/PAM, and PAM/PAM. The second type is most desirable.

The aim of this work was to synthesize graft copolymers for flocculation applications. The copolymers were tested as flocculants for a titanium dioxide suspension and as a conditioner for paper mill sludges. The experimental results are reported in the next paper of this series [22].

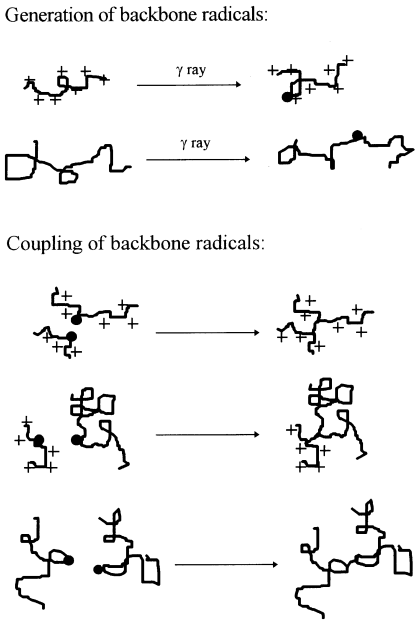


Fig. 2 Schematic presentation of generation and termination of polyDADMAC and polyacrylamide (PAM) backbone radicals

Experimental

Materials

PAM was supplied in granular form by Aldrich; it has a weight-average molecular weight of 5×10^6. PolyDADMAC was supplied in solution by Allied Colloids; it has a weight-average molecular weight of 10^5. The solid content of polyDADMAC was 0.411 g/ml, determined by drying samples of polymer solution under vacuum at room temperature. The charge density of polyDADMAC was 3.14 mEq/g; determined by titration. All commercial materials were used without further purification. Experiments were carried out at room temperature. Deionized water was used in the preparation of all solutions. PAM is prone to stick to glass walls; therefore, to avoid polymer loss, polyethylene bottles were used. All bottles were washed using an ultrasonic device and rinsed with deionized water.

Crosslinking tends to occur at high polymer concentrations, forming water-insoluble copolymers during irradiation. Therefore, grafting was carried out using a relatively low polymer concentration, to minimize gel content. In this study, the term dual polymers refers to two polymers that are physically mixed but not linked by chemical bonds. A series of dual polymer solutions with a total concentration of 0.8 wt% was prepared. The polyDADMAC contents were 0, 10, 20, 30 and 100 wt% of the total polymer mixture. These samples were exposed to γ-irradiation from a ^{60}Co source for 1, 2, 3, 4 and 5 h at a dose rate of 100 krad/h.

Viscosity measurement

The viscosity behavior of the copolymers was measured at 25 $\pm$ 0.1 °C using a no. 75 Cannon Ubbelohde semi-

micro dilution viscometer. The viscosity data provide a general guide to the change in molecular weight during modification.

Gel extraction

The gel fractions of the graft copolymers were measured by filtering dilute graft copolymers under vacuum with excessive deionized water. The metal screen used for filtration had a pore size of 20 mm. The gel was then dried under vacuum at room temperature.

Copolymer separation

Graft copolymers need to be purified prior to characterization. Acetone was chosen as a nonsolvent for PAM and polyDADMAC. In the samples with polyDADMAC levels of 10, 20 and 30 wt%, the amount of polyDADMAC was 0.08, 0.16 and 0.24 g per 100 ml solution, respectively. A series of polyDADMAC solutions was prepared with concentrations of 0.08, 0.16, 0.24, 0.32, 0.4, 0.64 and 0.8 g in 100 ml deionized water. The samples were treated with acetone to determine the nonsolvent to solvent ratio for precipitation. The volume of acetone at the point at which solution started to become turbid is its critical volume. When the volume ratio of acetone over polymer solution is higher than the critical ratio, polyDADMAC precipitates out.

The critical ratios for the seven polyDADMAC solutions are listed in Table 1. Higher concentrations of polyDADMAC need less acetone. When the concentration was below 0.24 g/100 ml, no turbid point was observed even with the aid of turbidity measurements (HP 8452 Diode Array UV/VIS spectrophotometer). Experiments were carried out with the ratio range 0.5–15; the transmittance of the solution stayed above 99% no matter how much acetone was added.

The molecular weight of PAM is 50 times higher than that of polyDADMAC. PAM solutions with equal concentrations of polyDADMAC require less acetone to precipitate out the polymer. If a volume ratio of nonsolvent to solvent is chosen carefully, the graft copolymers and homo-PAM precipitate while ungrafted polyDADMAC remains in the solution. This facilitates the separation of polyDADMAC from the mixture.

Figure 3 shows that when the ratio of acetone/water is above 4, over 94% of PAM is precipitated out. For the copolymer systems with a polyDADMAC concentration of 10, 20 and 30 wt%, the amount of polyDADMAC is equivalent to 0.08, 0.16 and 0.24 g/100 ml (Figures listed in the last three rows in Table 1). It was found that at these polyDADMAC concentrations, polyDADMAC would not precipitate, even when the nonsolvent/solvent ratio was above 15. Therefore the ratio of 4 was chosen to separate ungrafted polyDADMAC from polymer mixture in this work.

Table 1 Critical ratios of acetone/water for polyDADMAC solutions

Concentration of polyDADMAC (g/100 ml)	Volume ratio of acetone/water when solution becomes turbid
0.8	2.14
0.64	2.19
0.48	2.34
0.40	2.64
0.32	2.95
0.24	>15
0.16	>15
0.08	>15

Infrared spectra

Fourier transform infrared spectroscopy (FTIR) was used for qualitative analysis of the copolymer structures. Dried polymer samples were ground with potassium bromide powder. The samples were pressed into pellets and analyzed at room temperature using a FTS-40 IR spectrophotometer.

Grafting efficiency and degree of grafting

The grafting efficiency (g.e.) and the degree of grafting (d.g.) are defined as follows:

$$\text{g.e.} = \frac{\text{polyDADMAC}_{\text{grafted}}}{\text{polyDADMAC}_0}$$

$$\text{d.g.} = \frac{\text{polyDADMAC}_{\text{grafted}}}{\text{PAM}_0}$$

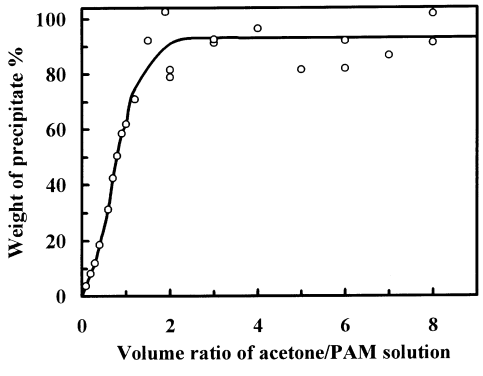


Fig. 3 Weight percentage of precipitates for PAM solution by adding acetone

where polyDADMAC$_{grafted}$ is the amount of polyDADMAC grafted onto PAM, and PAM_0 and polyDADMAC$_0$ are the initial amounts of PAM and of polyDADMAC, respectively. The amount of polyDADMAC grafted can also be determined by titrating the residual polyDADMAC after irradiation.

Results and discussion

Change in viscosity during irradiation

Figure 4 shows the experimental intrinsic viscosity [η] of polyDADMAC as a function of irradiation time. A slight decrease in [η] was observed with increasing irradiation. This suggests that polyDADMAC experiences some chain scission under γ-irradiation. Because the cationic charges repel each other, polyDADMAC backbone radicals are not readily terminated by coupling. As shown in Fig. 2, there may be three types of termination; these experimental results exclude the first type, i.e., the termination between polyDADMAC radicals.

Crosslinking is realized by bimolecular combination of macroradicals. This consists of three steps [23–25]: two radicals migrate together via translational diffusion; the radical centers reorient by segmental diffusion; they overcome the chemical activation barrier and react. The activation energies for radical reactions are often very low, so the termination reaction is likely to be diffusion controlled. In dilute solutions, due to the low viscosity of the solvent, the translational diffusion of polymer chains is relatively quick. The rate-determining step is therefore the segmental orientation. This is particularly true when the reactants are polyelectrolyte species such as polyDADMAC.

On polyDADMAC chains, the quaternary center is located in the vicinity of the backbone radical, preventing the chain segment from approaching other radicals with the same configuration because of the repulsion force. As a result, the radical combination and, in turn, the gel formation are restricted. The gelability of polyelectrolyte solutions depends on two competing factors [26]: the distance between radical and neighboring ions on the polymer backbone and the thickness of the double layer (the Debye-Hückel length) around the ionic centers. When the latter is much smaller than the former, the repulsion potential should not affect radical termination. For polyDADMAC solution systems the Debye-Hückel length can be regulated using salt concentration. However, since every monomer unit on a polyDADMAC chain is ionized, the neighboring quaternary centers are very close. PolyDADMAC chains are therefore either grafted onto PAM or remain ungrafted in the mixture.

On the other hand, PAM radicals are prone to combining with each other. Gelation occurs at a certain stage during irradiation. It was observed that with increasing irradiation time, the mixture first became a sticky mobile liquid, then a soft gel, and finally an immobile hard gel. There was some gelation in the PAM solutions even after 1 h of γ-irradiation. The [η] of pure PAM without radiation is 0.93 l/g. The [η] data of dual polymer solutions and homopolymers are shown in Fig. 5. After addition of polyDADMAC, the viscosity first decreases to 0.4 l/g for 10% polyDADMAC. The viscosity for 100% polyDADMAC is 0.62 l/g. The experimental result of viscosity exhibits a minimum point. The viscosity then increases with increasing percentage of polyDADMAC; after reaching a maximum, it drops slightly and finally reaches the value of pure polyDADMAC.

Compared with homo-PAM, the viscosity of a dual polymer system with 10% polyDADMAC decreases significantly. The reasons for this are twofold. First, PAM is much more viscous than polyDADMAC of the same concentration. In the dual system, 10% of the PAM is replaced by the same weight of polyDADMAC

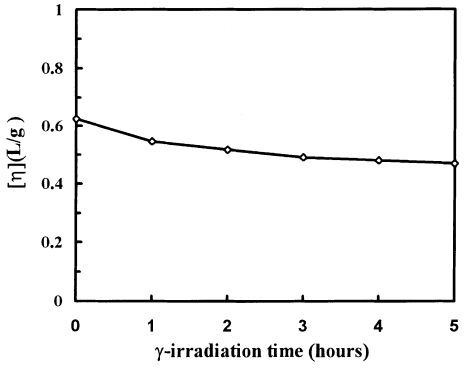


Fig. 4 Intrinsic viscosity of polyDADMAC versus γ-irradiation time

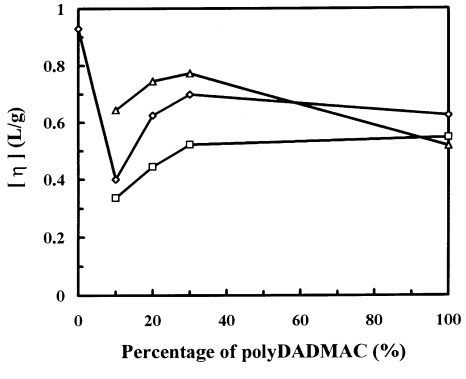


Fig. 5 Intrinsic viscosity versus percentage of polyDADMAC: ◇ without irradiation, □ 1 h irradiation, △ 2 h irradiation

maintaining the total concentration of polymer. The viscosity of the 10% dual system is no longer as high as that of homo-PAM of the same concentration. Secondly, when we calculated [η], we plotted η_{sp}/C versus concentration of total polymers for both systems. PAM amounts in the two systems are different. PAM dominates viscosity behavior over 10% polyDADMAC. For the same concentration of polymer, in dual systems the amount of PAM is always less than that in the homo-PAM. The percentage of PAM is one of the important factors which affect the [η].

Although the percentage of PAM decreased further for 20% and 30% polyDADMAC solutions, the charged groups on polyDADMAC reach a concentration level at which they repel each other, causing the polyDADMAC chains to stretch out. Thus the polymer chains expand the coil dimension more than nonionic PAM. Therefore, with increasing polyDADMAC fraction [η] increases, which overcomes the effect caused by the reduction of PAM. This is an electroviscous effect. In the 10% solution, polyDADMAC chains are separated from each other so that the effect is minor.

After 3 h of irradiation, the gel level was too high; it reached the limit of viscosity measurement where only the linear and slightly branched polymer could be measured. Therefore, the viscosity was measured only for 1 and 2 h of irradiation. Compared with nonirradiated samples (0 h), the viscosity of copolymers decreased after 1 h of irradiation. This implies that after 1 h of irradiation, the polymer chains experienced some chain scission, resulting in lower [η]. Although the [η] of polymers cannot be measured after 3 h of irradiation, we can still clearly observe that molecular weight tends to increase, which is shown by a sharp increase of viscosity at 2 h of irradiation. This suggests that the molecular weight constantly increases, resulting in gel formation. The viscosity decreases after 1 h of irradiation, then rises after 2 h, so the polymer chains must first break up and then re-react to become branched, gradually forming a gel network.

It was found that pure PAM samples produced gel when exposed to γ-irradiation for even 1 h, but when polyDADMAC was added, gelation was delayed. PolyDADMAC limits PAM intermolecular crosslinking. This explains why with polyDADMAC the [η] of copolymers drops dramatically. The viscosity of pure PAM after 1 and 2 h of irradiation was very high and could not be measured.

However, higher fractions of polyDADMAC may not result in lower [η]. In fact, the [η] of 30% polyDADMAC is higher than that of 10% polyDADMAC. For dual systems (refer to Fig. 5), we concluded that it was due to the electroviscous effect. The same effect was observed for irradiated samples. The [η] profiles for irradiated polymers also have maximum points and finally reach the [η] of irradiated 100% polyDADMAC.

Gel formation during grafting

It was observed that with increasing irradiation time, the polymer mixture started as a sticky mobile liquid, becoming a soft gel and finally turning to an immobile hard gel, which could be broken into small pieces. The soft gel, unlike the hard gel, could not be broken into pieces. The soft gel swells; it contains a lot of water but does not flow freely like a liquid. Gel formation is a function of both radiation dosage and polymer composition. With higher percentages of polyDADMAC less gel network is produced and these gels are mainly soft. PolyDADMAC helps to inhibit the intermolecular crosslinking, and limits therefore the gel formation.

Gel content results are shown in Fig. 6. The gel fraction increases with increasing irradiation time. After 1 and 2 h of irradiation very little gel is produced, especially at 1 h of irradiation. This result agrees with previous viscosity measurements. The amount of gel increases gradually with irradiation time and finally levels off. As the percentage of polyDADMAC increases, the gel fraction decreases. Homo-PAM has the highest level of gel; for pure polyDADMAC, even if it had undergone 5 h of irradiation, no gelation was observed.

As stated above, gel formation in the polymer systems is mainly attributed to PAM. Reddy et al. [27] studied γ-irradiated PAM through electron spin resonance (ESR) at room temperature. They found that under irradiation, PAM may generate two types of free radicals: (I) a radical on the tertiary carbon atom and (II) a radical on the oxygen atom. Cleavage of the C—H bond results in configuration I. It has been reported that the hydrogen atom bound to the tertiary carbon atom can easily be rejected as compared with those bound to the secondary and primary carbon atoms [28]. Configuration II is an interconvertible form of configuration I. PAM polymer chains are branched by the coupling of

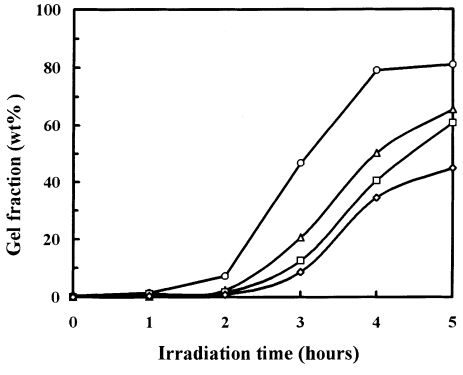
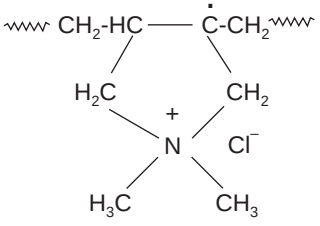


Fig. 6 Gel fraction versus irradiation time using 20 mm pore size metal screen: ○ PAM, △ 10% polyDADMAC, □ 20% polyDADMAC, and ◇ 30% polyDADMAC

radicals onto tertiary carbon and oxygen atoms. They easily form water-insoluble intermolecular crosslinkages. Therefore the domain of water-soluble polymers increases as the weight fraction of PAM decreases.

The nitrogen atom in polyDADMAC carries a positive charge. It is relatively electron withdrawing, and the adjacent carbon atoms are relatively electron starved. Therefore the protons on the nitrogen-adjacent carbon atoms are less likely to be abstracted. PolyDADMAC is more likely to generate radicals on the tertiary carbon atoms,



PolyDADMAC radicals would be more likely to combine with the PAM radicals of configuration I. Crosslinking is the combination of two polymer backbone radicals.

Graft efficiency and degree of grafting

Figure 7 shows representative IR spectra of PAM, polyDADMAC and their graft copolymers. Comparison of the three spectra reveals that polyDADMAC has a weak characteristic doublet at a wavenumber of about 971.3 cm^{-1}, which is presumably attributed to the C—N stretching vibration [29]. This doublet is absent in the PAM spectrum. After γ-irradiation, there were three types of polymers in the solution. The mixture was purified by removing the ungrafted polyDADMAC, so that only the graft copolymers and homo-PAM remained. Comparing the spectra of the two homopolymers with that of the purified mixture shows that after γ-irradiation, the spectrum of the graft copolymer contains not only the peaks attributable to PAM but also the unique doublet attributable to polyDADMAC. This indicates that some polyDADMAC has been grafted onto the PAM backbone. The peaks at a wavenumber of 2100 cm^{-1} also indicate that polyDADMAC is one of the components in the copolymer. However, it is impossible to carry out a quantitative analysis at this wavenumber due to its weak intensity and the possible complexation with water.

The graft efficiency and the degree of grafting results are presented in Figs. 8 and 9 and are shown to be strong functions of irradiation time and polyDADMAC concentration. They both increase with increasing γ-irradiation time, and a high percentage of polyDADMAC results in lower graft efficiency with a higher degree of grafting. More energy is provided with longer irradiation times proton abstraction and free radical coupling are more active. As a result, polyDADMAC has a better chance of being grafted onto the PAM backbone. The experimental results show that over 90% of the polyDADMAC is grafted onto PAM in the sample with 10% polyDADMAC. With increasing polyDADMAC levels, more cationic groups are grafted onto PAM; however, the percentage of grafted polyDADMAC versus initial polyDADMAC decreases. As more and more polyDADMAC molecules are grafted onto PAM, the grafting reaction becomes more difficult. The grafted polyDADMAC chains may prevent other polyDADMAC chains from approaching, and therefore reduce the possibility of further grafting.

The graft frequency (g.f.) is the number of repeat units between neighboring graft points. It is expressed as:

$$\text{g.f.} = \frac{\text{total number of PAM repeat units}}{\text{total number of grafted polyDADMAC molecules}}$$

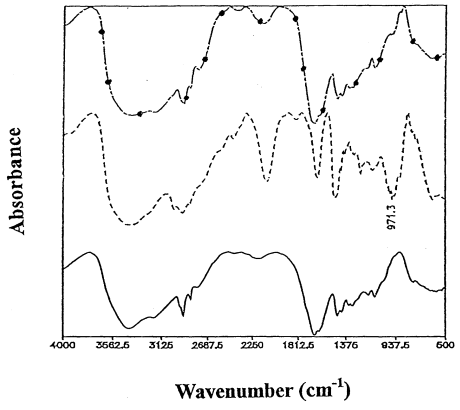


Fig. 7 Infrared spectra of PAM, polyDADMAC and their graft copolymers: — PAM, - - - - polyDADMAC, –●– graft copolymer

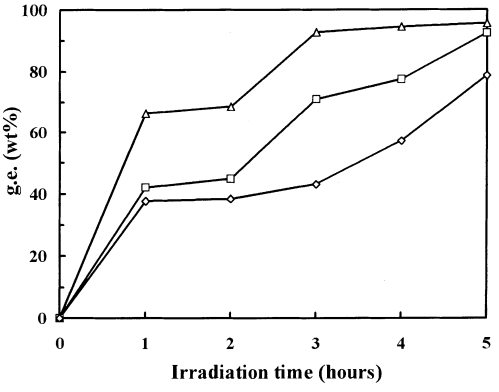


Fig. 8 Graft efficiency versus irradiation time: Δ 10% polyDADMAC, □ 20% polyDADMAC, and ◇ 30% polyDADMAC

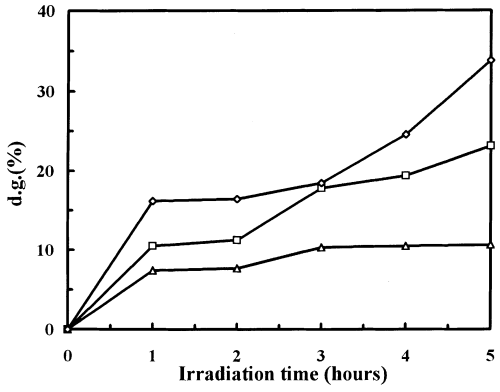


Fig. 9 Degree of grafting versus irradiation time: △ 10% polyDADMAC, □ 20% polyDADMAC, ◇ 30% polyDADMAC

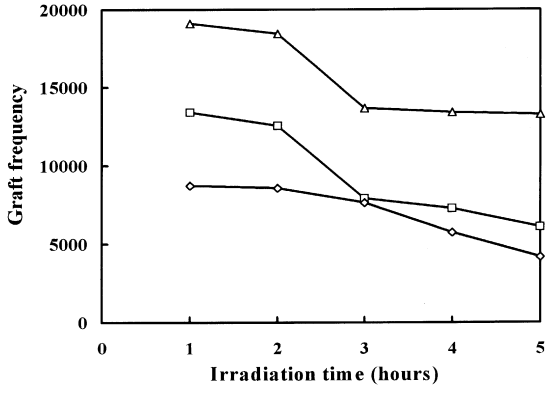


Fig. 10 Graft frequency versus irradiation time: Δ 10% polyDADMAC, □ 20% polyDADMAC, ◇ 30% polyDADMAC

In this work, we use an in situ graft frequency, due to intermolecular crosslinking. As the molecular weight of polyDADMAC did not change much during irradiation, we calculated the graft frequency using the initial molecular weight of polyDADMAC, which was 10^5. Figure 10 shows that with increasing irradiation time, the graft frequency decreases; a higher percentage of polyDADMAC results in a lower graft frequency.

We assumed that the PAM radicals of gel and sol molecules would have the same probability of coupling with polyDADMAC radicals. Based on this assumption, one can also calculate the average number of grafted polyDADMAC chains that each PAM molecule would contain, using the initial molecular weight of PAM. The calculated number of grafted polyDADMAC molecules is 4–6 for 10% polyDADMAC samples; 6–12 for 20% polyDADMAC; and 8–17 for 30% polyDADMAC. The numbers of grafted polyDADMAC molecules on each PAM molecule increased with increasing irradiation time, as shown in Fig. 11.

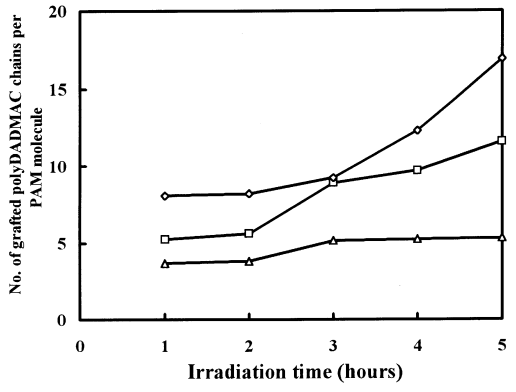


Fig. 11 Average number of grafted polyDADMAC per PAM molecule as a function of irradiation time: △ 10% polyDADMAC, □ 20% polyDADMAC, ◇ 30% polyDADMAC

Conclusions

High-charge-density low-molecular-weight polyDADMAC has been successfully grafted onto nonionic high-molecular-weight PAM using γ-irradiation via a free radical mechanism. PAM radicals were found to play an important role in gel formation, while crosslinking between cationic chains was limited. PolyDADMAC is either grafted onto the PAM backbone or remains ungrafted in the solution.

The viscosity behavior and gel fraction of the graft copolymers were found to be a strong function of irradiation time and polymer composition. A water-soluble copolymer of various molecular weights and cationic density can be synthesized by selecting suitable reaction conditions. The graft efficiency and degree of grafting also depend on irradiation time and polymer fraction: the lower the weight fraction of polyDADMAC, the lower the degree of grafting and the higher the graft efficiency.

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