# Grafting of Polyelectrolytes onto Polyacrylamide by Reactive Processing

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**ABSTRACT:** Low-molecular-weight high-charge-density cationic poly diallydimethyl ammonium chloride (polyDADMAC) was grafted onto nonionic polyacrylamide (PAM) using organic peroxide initiators in the molten state carried out in a batch mixer. The graft copolymer can be used as a high performance flocculant. Glycerol was selected as a plasticizer. The grafting reaction was characterized in terms of composition, temperature, degree of grafting, and grafting efficiency. It was found that free radicals on polymer chains were induced by the decomposition of the initiator. Grafting was produced by free radical recombination termination. The degree of grafting increases with an increase of the polyDADMAC/PAM feed ratio. However, the grafting efficiency was lower than 10 wt % in this highly viscous polymer melt system. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1412–1416, 1999

**Key words:** reactive polymer processing; polymer flocculants; water-soluble polymer; polyelectrolyte; polyacrylamide

## INTRODUCTION

During the last 30 years, the production of polymeric flocculants has increased rapidly. Many applications have been found in paper making, wastewater treatment, and mineral processing industries.[1–3] Highly charged cationic polymers such as polyquats, polyimines, and polyamines are costly. As a flocculant, homo-cationic polymers often have a flattened absorbed configuration on the surface of particles,[4] which is not beneficial for particle aggregation by chain bridging. Cationic flocculants can also be prepared by modifying PAM or copolymerization of acrylamide (AM) with comonomers having cationic charged groups[5–8] where ionic centers are inevitably randomly distributed along polymer chains.

Recently, a new scheme of grafting cationic polymers onto nonionic PAM was proposed to combine the chain bridging and charge neutralization flocculation mechanisms into one molecule.[9,10] As an example, polyDADMAC was grafted onto high-molecular-weight PAM by $\gamma$-ray initiation. The highly charged grafts provide strong adsorption to particle surfaces while the charge free backbone bridges the particles together. The copolymer was tested for its flocculation and sludge dewatering abilities. The graft copolymers showed an improvement over either PAM or polyDADMAC homo-polymers and their dual polymer blends in both aspects. However, synthesis by $\gamma$-radiation requires a relatively lower polymer concentration (0.8% wt) in a water solution.[10] In addition, the generation of free radicals by $\gamma$-ray is less selective and uncontrollable in comparison to chemical initiation.

The polymer grafting reaction can be carried out by reactive processing in polymer melts rather than in a large amount of solvent. Because of concerns of the environmental impact of or-

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ganic solvents, more and more reactions involving polymers have been run solventless.[11] Bulk polymerization, graft reactions,[12] functionalization of polyolefin,[13–15] and controlled molecular-weight degradation[16] have all been realized with reactive processing using chemical initiators. In this work, organic peroxide initiators were used to prepare graft copolymers in polymer-plasticizer melts. The reaction was carried out in a batch mixer. PAM was selected as the backbone polymer and polyDADMAC as the graft polymer.

## EXPERIMENTAL

### Materials

Two PAM samples were used in this work. One sample (PAM1) had a $5 \times 10^6$ weight-average molecular weight in granular form. The other sample (PAM2) had a $10^4$ molecular weight dried from a 40 wt % water solution. Both were supplied by Aldrich Canada Ltd. (Oakville, ON). PolyDADMAC was supplied in solution by Nalco Canada Ltd. (Burlington, ON). The polyDADMAC has a weight-average molecular weight of $2.3 \times 10^5$, dried from solution under vacuum at room temperature. Lupersol 130 and Lupersol 101 were selected as peroxide initiators, supplied by Aldrich Canada Ltd. Glycerol ($C_3H_8O_3$, 99.6%), supplied by Fisher Scientific (Whitby, ON) were selected as a plasticizer. All commercial materials were used without further purification.

### Sample Preparation for Grafting Reaction

PAM and polyDADMAC polymer powders were dry blended. The polymer blend was purged with a calculated amount of initiator acetone solution. Blending continued until the acetone was completely evaporated at room temperature. A preweighed amount of glycerol was added and blended thoroughly. The sample was allowed to swell for 24 h at room temperature. Immediately before the reaction, the sample was put in an oven at 80°C for 2 h to reach ultimate swelling balance. The sample size was about 2.5 g swelled polymer (20 – 80 wt %) in glycerol for each reaction run.

### Device

All grafting tests were performed in an Atlas LMM Laboratory Mixing Molder (Rexdale, ON), or mini-mixer. The mixer has a cylindrical mixing chamber with a sample capacity of 3–4 g. Mixing is provided by a piston that moves vertically and rotates in the mixing chamber.

### Graft Copolymer Separation

After the reaction, all the samples were dissolved in water to form an ≈30% wt solution. If no gel was found in the sample, the solution was dropped into methanol with vigorous agitation. The ungrafted polyDADMAC in solution dissolved while PAM and graft copolymer precipitated. The precipitates were collected and dried under vacuum at room temperature. If there was gel found in the sample, the gel portion was collected by centrifugation and then washed with a large amount of water. The remaining gel contains only crosslinked PAM and grafted polyDADMAC.

### Degree of Grafting and Grafting Efficiency

The degree of grafting and grafting efficiency of graft copolymer were defined and experimentally determined to describe the grafting reaction.

$$\text{degree of grafting} = \text{DG} = \frac{\text{polyDADMAC}_{\text{grafted}}\,(\text{wt})}{\text{PAM}_0\,(\text{wt})} \quad (1)$$

$$\text{grafting efficiency} = \text{GE} = \frac{\text{polyDADMAC}_{\text{grafted}}\,(\text{wt})}{\text{polyDADMAC}_0\,(\text{wt})} \quad (2)$$

The mol contents of PolyDADMAC and PAM in the copolymer samples were determined by H-NMR and then reported as weight fractions in eqs. (1) and (2). $\text{PolyDADMAC}_{\text{grafted}}$ is the amount of polyDADMAC that has been grafted onto PAM; $\text{polyDADMAC}_0$ and $\text{PAM}_0$ are the initial feed amount of polyDADMAC and PAM, respectively.

## RESULTS AND DISCUSSION

### Generation of PAM and polyDADMAC Chain Radicals

The scheme of grafting in this study is to first generate radicals on both PAM and polyDADMAC polymer chains. The termination of a polyDADMAC and a PAM chain radical by recombination will form a graft. The recombination of homopolymer will have no contribution to grafting. Experiments

**Table I Gel Fraction (wt % of Initial PAM) after Reaction (0.5 wt % Initiator)**

| Conditions | Lupersol 101 | Lupersol 130 |
|---|---|---|
| 140°C, 60 min | 33.6 | 66.2 |
| 160°C, 10 min | 38.3 | 67.2 |

were first conducted to generate PAM and polyDADMAC chain radicals individually.

PAM1 was mixed with Lupersol 101 or 130, heated to a prescribed temperature (140–180°C) and kept for a period of time under nitrogen atmosphere. Different initiator levels were used, 0.5 wt %, 1 wt %, and 2 wt %. Gel was found in every sample. Parallel tests for PAM without initiator showed no gel under same conditions. Gel formation suggests the generation and termination of PAM chain radicals. To quantify the gel fraction, reacted samples were put in water to wash out sol PAM. The remaining gel content was dried for 48 h under vacuum at room temperature and weighed. The gel fraction results are listed in Table I. The results show that Lupersol 130 is more effective in generating PAM chain radicals.

Similar tests were performed with polyDADMAC and Lupersol 101 or 130. No gel was found under the same reaction temperatures and time as used for PAM1. Lack of gel may be due to one of the following reasons: 1. the chain structure is stable to proton abstraction by peroxides, 2. chain scission is predominant, or 3. there may be chain coupling, with an increase in molecular weight, but not enough crosslinking to form gel. Previous research showed evidence of polyDADMAC chain scission under $\gamma$-radiation by measuring the intrinsic viscosity.[17] This suggested that chain scission is favored for polyDADMAC under the attack of a high energy moiety. The intrinsic viscosity of polyDADMAC samples after reaction with Lupersol 101 and 130 were measured.

The measurement procedures followed those of Ma.[17] The results are presented in Table II. The intrinsic viscosity of the initial polyDADMAC sample is 0.45.

From the results in Table II, only at a reaction temperature from 160–180°C using Lupersol 130 as an initiator did the sample show a significant intrinsic viscosity decrease compared with unreacted polyDADMAC. Thus, under selected conditions, the initiator can induce a radical chain scission mechanism rather than crosslinking. The measurement also confirmed the ability of Lupersol 130 to generate polyDADMAC chain radicals. Lupersol 101 is obviously unable to react with polyDADMAC at tested conditions. In addition, Lupersol 101 will decompose before the reaction if the temperature exceeds 160°C. Therefore, Lupersol 130 was selected for further grafting reaction tests.

## Grafting of polyDADMAC onto PAM2

The reason for using low-molecular-weight PAM (PAM2) is to minimize the diffusion effect by high molecular weight on grafting reaction so that the chemical feasibility of grafting can be proven.

The grafting reaction was conducted in the mini-mixer using Lupersol 130 as the initiator. The total polymer content in the sample was about 80 wt %. The initiator concentration was calculated based on the total weight of dry polymers. After the reaction, no gel was found in any of the samples. The graft copolymer was separated and measured according to the procedure described previously.

Figure 1 shows the degree of grafting of polyDADMAC plotted against the initiator concentration at 160 and 180°C with a reaction time of 10 min. The initial feed ratio of polyDADMAC/PAM is 1:1. Therefore, the degree of grafting is equal to the grafting efficiency of polyDADMAC. Both increase with increasing initial concentration of initiator. If the initial ratio of polyDADMAC is increased, more grafting is expected to be found. The degree of grafting and grafting efficiency as a function of initial polymer feeding ratios are plotted in Figure 2(a,b). It was found that the degree of grafting can be as high as 30% with a 4:1 polyDADMAC/PAM ratio. However, the grafting efficiency was not remarkably affected by changing the PAM/polyDADMAC feed ratio, and remained less than 10%.

**Table II Intrinsic Viscosity of polyDADMAC after Reaction (2.0 wt % Initiator)**

| Initiator | Reaction Time (min) | Temperature (°C) | Intrinsic Viscosity |
|---|---|---|---|
| Lupersol 101 | 30 | 160 | 0.40 |
| | 60 | 140 | 0.35 |
| Lupersol 130 | 10 | 180 | 0.05 |
| | 30 | 160 | 0.29 |
| | 60 | 140 | 0.40 |

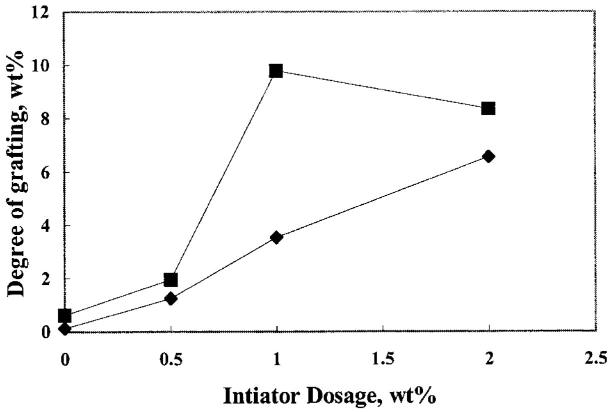

**Figure 1** Degree of grafting of polyDADMAC at different initiator concentrations. ■, 180°C; ◆, 160°C.

## Grafting of polyDADMAC onto PAM1

After the grafting of polyDADMAC onto low-molecular PAM (PAM2) was confirmed, grafting tests with high-molecular-weight ($M_w = 5 \times 10^6$) PAM (PAM1) were conducted. Due to the very high molecular weight of PAM1, a large amount of glycerol was used to facilitate the polymer chain mobility during the reaction. Three samples are listed in Table III. Soft gel was found in every sample after reaction.

During the reaction period, there are two types of chain radical recombination reactions. One is the recombination termination between PAM chain radicals which eventually leads to gelation. The other is between PAM and polyDADMAC chain radicals which contributes to grafting. PolyDADMAC can only undergo chain scission under current conditions. When the reaction begins, these termination reactions proceed in parallel. If polyDADMAC can be found grafted in gel, it must be grafted in sol as well.

After the reaction, the samples were put in water. A large portion of the sample now becomes gel. The gel was collected and then washed with a large amount of deionized water. Glycerol, sol PAM, polyDADMAC, and their sol copolymers were removed by washing. The gel remaining is a network of PAM with polyDADMAC attached to it.

As shown in Table III, a maximum of 10 wt % polyDADMAC was found in gel. Further increase of the initial polyDADMAC/PAM ratio beyond 2:1

**Table III Grafting Test with High-Molecular-Weight PAM (2.0 wt % Lupersol 130)**

| PAM/PolyDADMAC/Glycerol (wt ratio) | PolyDADMAC Content in Gel (wt %) |
|---|---|
| 1 : 1 : 8 | 10.6 |
| 1 : 0.5 : 6 | 3.9 |
| 1 : 2 : 9 | 5.0 |

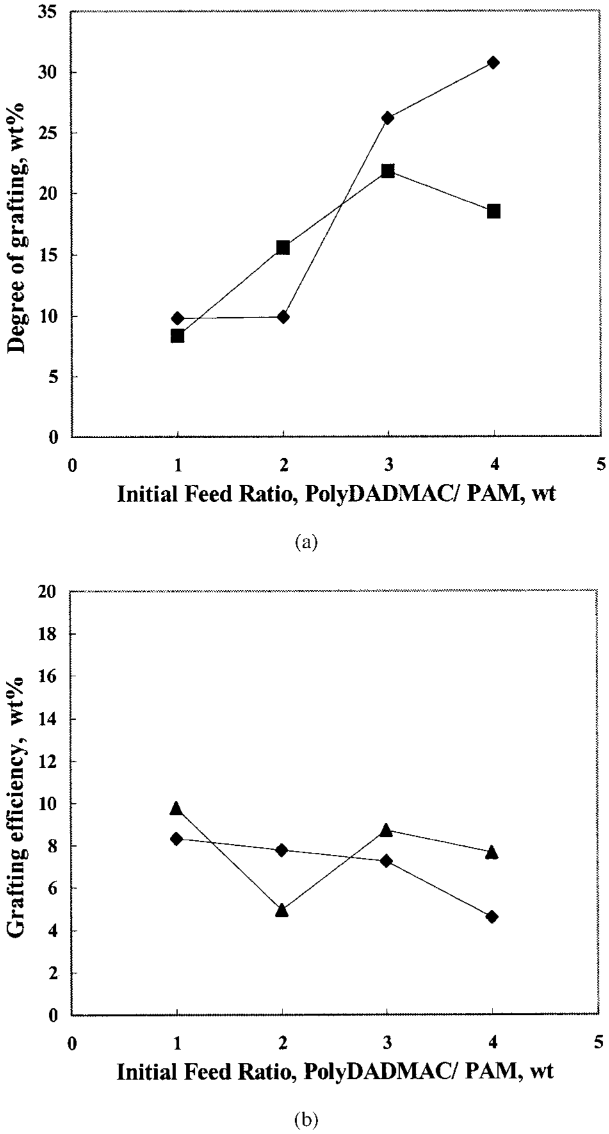

**Figure 2** (a) Degree of grafting of polyDADMAC onto PAM at different feeding ratios after reaction at 180°C for 10 min. ◆, degree of grafting, 1.0 wt % initiator; ■, degree of grafting, 2.0 wt % initiator. (b) Grafting efficiency of polyDADMAC onto PAM at different feeding ratios after reaction at 180°C for 10 min. ▲, grafting efficiency, 1.0 wt % initiator; ◆, grafting efficiency, 2.0 wt % initiator.

prevents the mixing of the two polymers because of phase separation. The radical mechanism of grafting was confirmed with high-molecular-weight PAM. The grafting of high-molecular-weight PAM is important for flocculation applications. However, with the increase of PAM molecular weight, severe gelation problems emerge from the reaction. The PAM chain radicals favor termination with PAM radicals rather than polyDADMAC chain radicals. This in turn reduces the chance of grafting causing low yield and degree of grafting. In addition, the polymer gel is not useful for the purpose of flocculation in comparison with the grafted material in the sol. Future studies will focus on reducing the gel content.

## CONCLUSIONS

A cationic polymer polyDADMAC was grafted onto PAM by a chemical initiator via free radical mechanism. PAM radicals are found to be in favor of crosslinking while chain scission for polyDADMAC radicals. The grafting reactions were performed in a mini-mixer in the state of polymer melts. PolyDADMAC was grafted onto both low-molecular-weight ($10^4$) and high-molecular-weight ($5 \times 10^6$) PAM samples. With low-molecular-weight PAM, the degree of grafting can be as high as 30 wt %. However, the grafting efficiency was always less than 10 wt %. With high-molecular-weight PAM, grafting was also found but gelation problems occurred.

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