Synthesis of Nonionic Flocculants by Gamma Irradiation of Mixtures of Polyacrylamide and Poly(ethylene oxide)

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SYNOPSIS

The synthesis of polyacrylamide (PAM) graft poly(ethylene oxide) (PEO) has been investigated and the reaction conditions were varied by gamma irradiation to optimize polystyrene latex flocculation by the copolymers. The effects of the gamma ray dosage, the PEO chain length, the ratio of PEO to PAM, and the crosslinking degree of copolymer were studied. The most effective flocculant was obtained by exposing a mixture of 1.2 wt % PAM ($M_w = 5 \times 10^6$) and 0.94 wt % PEO ($M_w = 5000$) to 816 krad of gamma radiation. The resulting copolymer contained 24 wt % PEO. Crosslinking to give insoluble gels was an undesirable side reaction increased with γ-ray dose and decreased with PEO addition. The most effective flocculants contained more than 15 wt % PEO with little crosslinking. The grafting behavior of triblock copolymer, poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) ($E_m P_n E_m$, where m and n are oxyethylene and oxypropylene unit, respectively), onto PAM by gamma radiation was also studied; grafting occurred but effective flocculants were not obtained. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric flocculants are routinely used to enhance the deposition of colloidal particles onto wood pulp fibers in the paper-making process. Many types of flocculants have been used in paper manufacturing including high molecular weight cationic,[1-4] anionic,[5-8] and nonionic polymers.[9-12] Flocculation in mechanical pulps is more difficult because dissolved and colloidal wood polymers stabilize the colloids and sequester cationic flocculants. High molecular weight poly(ethylene oxide) (PEO), gives excellent flocculation in mechanical pulps, resulting in better paper properties.[10,13,14] The flocculation of mechanical pulp with PEO is usually enhanced by the presence of a phenol formaldehyde resin (PFR). Although the flocculation mechanism of this system has been argued and still is not clear, hydrogen bond complex formation between PEO and PFR is generally accepted to be an important part.[12,15]

Many studies[9-12,16] have shown that only very high molecular weight PEO is an effective flocculant. Molecular weights of less 1 million gave almost no flocculation, whereas molecular weights greater than 4 million produced good flocculation. Although very high molecular weight PEO is a good flocculant, it is an expensive and fragile polymer.[17,18]

The purpose of this study was to prepare, in an easy manner, effective flocculants with similar flocculation properties similar to those of high molecular weight PEO, but with higher shear and agitate stability. Potentially, graft copolymers based on a high molecular water soluble backbone and small PEO branched chains can serve this purpose. By carefully choosing the backbone, the copolymer can be inexpensive and free from degradation. High molecular weight polyacrylamide (PAM) is easy to prepare and is stable in aqueous solution. In this study, a series of graft copolymers with high molecular weight PAM and low molecular weight PEO was prepared using gamma radiation in polymer aqueous solution. Note, in this article we use the term PEO to refer to any molecular weight of the polyether homopolymer, whereas the lower molecular weight samples are usually called poly(ethylene glycol).

Gamma irradiation is potentially a useful approach to the preparation of high molecular weight graft copolymer. Crosslinking of poly(ethylene oxide)[19-21] and polyacrylamide[22,25] using gamma radiation were studied previously. It is well known that high molecular weight polyacrylamide becomes insoluble under γ-ray radiation because of intermolecular crosslinking. It should be noted that the chemical structure of crosslinked polymer is complicated because the polymer radicals can form on both α and β carbons of acrylamide resulting in different crosslinking types. Ishigaki et al.[22-24] proposed that the crosslinking of polyacrylamide was attributed to imidation of two amide groups (reaction 1) and to the recombination of backbone polymer radicals (reaction 2). Ishigaki et al.[22-24] found that the addition of an alcohol could suppress the recombination of polymer radicals so that a water-soluble polymer could be obtained by γ-ray radiation-induced polymerization of acrylamide.
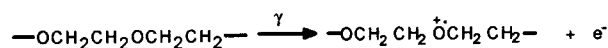
Reaction 1: imidation of amide groups
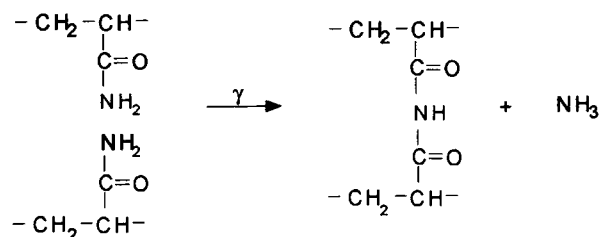
Reaction 2: recombination of polymer radicals
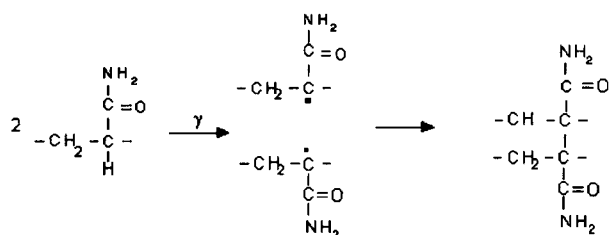
The gamma radiation of PEO in aqueous solution also has been studied.[20,21] The ESR spectra presented by Ferlori et al.[20] indicates that, under γ-ray radiation, the positive charges are first localized on the PEO oxygen atoms:

The positive polymer radicals then undergo α and β scissions resulting in three types of radicals:[20]
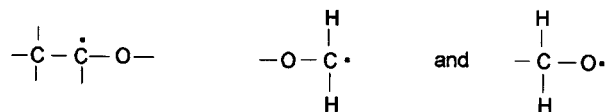
Free radicals combination gives a crosslinking structure of PEO molecules.

In this work, we report the first synthesis of high molecular weight graft copolymer by gamma radiation of mixtures of low molecular weight PEO and high molecular weight PAM. Results for the flocculation of polystyrene latex by copolymer in the presence of cellulose fiber and phenol formaldehyde resin are reported. In a related project in our laboratory, comb copolymers of acrylamide having short pendent PEO chains were prepared by free radical copolymerization.[31] The minimum pendent PEO degree of polymerization for effective flocculation was 10, whereas, total copolymer molecular weights greater than 1 million were required for flocculation comparable to that obtained using very high molecular weight PEO homopolymer.

EXPERIMENTAL

Materials

Poly(ethylene oxide) (Aldrich, M_w = 300,000), poly(ethylene glycol) (Aldrich, M_w = 8000, 2000), poly(ethylene glycol) methyl ether (Aldrich, M_w = 5000, 750), polyacrylamide (Aldrich, M_w = 5 $\times 10^6$) and Pluronic F127, F108, F88, and F68 [triblock copolymers of poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide)], were used without further purification. The molecular weight and PEO ratio of Pluronics that were used in this study are given in Table III. Poly(ethylene oxide), poly(ethylene glycol), and poly(ethylene glycol) methyl ether are referred to as PEO in this study except when particular identification is needed. Milli Q water was used for all experiments.

Polystyrene latex (PSL) was prepared by the method of surfactant-free emulsion polymerization. Dynamic light scattering gave a z-average hydrodynamic diameter of 725 nm for PSL.

Water-soluble low molecular weight phenol formaldehyde resin (PFR) (Cascophen C27, Borden Chemical Diversion) was used without further purification.

Forty grams of dried bleached softwood kraft pulp (Noranda Forest Co.) was soaked in 4 L deionized water for $\sim$ 24 h and then was dispersed in water

by a blender at high speed. The bleached pulp suspension was stored at $\sim 4°C$.

Polymer Preparation

The required amount of PAM and PEO was dissolved in Milli Q water in 20 mL glass bottles or a 30 mL polyethylene bottles. The aqueous solution was exposed to γ-radiation from a ^{60}Co source at a dose rate of 34 krad h^{-1} at room temperature. After irradiation, the product was precipitated by the addition of acetone, leaving PEO homopolymer in solution. The copolymer was dissolved in water, reprecipitated by acetone, and dried at 60°C. Control experiments confirmed that PEO homopolymers did not precipitate in this procedure.

Polymer Characterization

Molecular weight distributions of some copolymers were estimated by GPC. The system comprised three TSK gel columns (PW2000, PW4000, and PW6000 length 30 cm, internal diameter 7.5 mm) and a differential refractometer. The eluant was Milli Q water at 45°C (controlled by means of a block thermostat) and a flow rate of 1 cm^3 min^{-1} was employed. The system was calibrated with poly(ethylene oxide) standards of known molecular weight.

^{1}H NMR spectra were obtained using a Bruker Spectrospin AC200 Fourier Transform Spectrometer operating at 200 MHz. Samples were dissolved in D_2O (~ 0.01 g cm^3). The copolymer compositions were calculated from the relative intensities of the protons in the PEO backbone ($\delta = 3.5$ ppm) and the protons of —CH_2— in the PAM backbone ($\delta = 1.45$ ppm) which were obtained with a pulse interval of 3.4 s.

The reduced viscosities, η_{sp}/c, of the copolymer in the concentration range 1.2 to 3.79 g/dL were measured at 18°C using a #75 Cannon Ubbelohde viscometer.

The flocculation ability of copolymers was determined as follows. One mililitter 0.025% (w/v) PSL, 0.1 mL 1N NaCl, 0.1 mL 0.02N HCl, 10 mL 0.5% (w/w) fiber, and 0.4 mL 0.025 wt % PFR were added to a 80 mL test tube that contained 40 Milli Q water. The suspension was shaken approximately 10 s. The required amount of copolymer solution (less 0.5 mL in volume) was added and the mixture was immediately shaken for another 10 s. The mixture was allowed to stand for 1 h at room temperature and the turbidity of the solution was measured with an HP 8452 Diode Array UV/VIS spectrophotometer

(Hewlett Packard) at a wavelength of 500 nm. Milli Q water was used as a reference (transmittance = 100%) and the same suspension system without copolymer of PAM-g-PEO was used as a control solution. The relative turbidity, τ/τ_0, was used to determine the flocculation ability of the copolymer, where τ and τ_0 are the turbidities of the solution with and without copolymer (control solution), respectively. Error in the relative turbidity values was estimated to be ±5% of mean.

RESULTS

Copolymerization

The properties of copolymers prepared by γ-irradiation are summarized in Tables I and II. In the absence of PEO the intra- and intermolecular recombination of high molecular weight PAM radicals, produced by γ-ray irradiation, resulted in gel formation. At the same radiation dose and PAM concentration, the higher the PEO concentration, the less was the degree of gelation of the final product.

The results shown in Table II indicate that higher PEO molecular weight gives higher crosslinking degree with all other parameters constant. It was also found that the system having the PEO molecular weight of 300,000 formed a gel at very low doses (170 krad), but the system with a PEO molecular weight of 750 did not form a hard gel even at doses of up to 1190 krad.

The molecular properties of the copolymers were examined by GPC and viscometry. The samples that were prepared at low PEO contents or high gamma ray dosages could not be examined by GPC due to clogging of the filter (pore size 0.85 μm). Typical GPC results are given in Figure 1. Curve A shows the sample that has the same composition as A-25-2 but before exposure to gamma radiation. The peak at the eluant volume 26.2 cm^3 indicates PEO homopolymer ($M_w = 5000$) and the peak at the eluant volume 18.6 cm^3 represents homopolymer PAM ($M_w = 5 \times 10^6$). Curve B shows the results for sample A-25-2. It is interesting that the peak of the homopolymer PEO ($M_w = 5000$) is split into two separated peaks: one has lower eluant volume (24.0 cm^3) and the other has a higher eluant volume (28.5 cm^3) compared with the original PEO peak. This indicates that there is significant chain cleavage and recombination of PEO. Chain scission lowers the molecular weight, whereas chain recombination increases the molecular weight. It has been noted that there was almost no eluant volume shift for PAM in curve

Table I   Summary of Radiation Grafting Polymerization of PAM and PEO; PAM: $M_w = 5 \times 10^6$, Concentration: 1.1 wt % Dose Rate: 24 krad/h; Room Temperature

Designation	M_w of PEO	PEO Conc. wt %	Dose (krad)	Physical State	Physical Stability of Storage	PEO Content of Copolymer (wt %)
A-18-12	5000	0	816	hard gel	shrinking gel	*
B-3-12	5000	0.46	816	hard gel	shrinking gel	19.3
F-11-1	5000	1.35	816	hard gel	shrinking gel	*
B-18-12	5000	0.94	816	soft gel	stable	24.0
E-3-12	5000	1.68	816	hard gel	stable	*
A-3-12	5000	2.30	816	soft gel	stable	36.1
D-4-1	5000	5.45	816	soft gel	stable	*
C-18-12	5000	6.26	816	liquid	stable	33.0
D-18-12	5000	no PAM	816	liquid	stable	*
K-17-3	no PEO	0	510	hard gel	shrinking gel	*
D-17-3	8000	0.54	510	soft gel	slowly shrinking gel	*
C-17-3	8000	1.35	510	liquid	stable	17.3
B-17-3	8000	2.70	510	liquid	stable	23.6
A-25-2	5000	1.35	170	liquid	stable	*
C-25-2	5000	2.70	170	liquid	stable	*
I-25-2	5000	3.50	170	liquid	stable	*

* Not measured.

B (18.5 cm^3). This is perhaps because the sensitivity of the GPC was not high enough for very large molecules. The PAM used in this study has a molecular weight of 5×10^6, which is close to the upper limit of column (the upper limit of the PW6000 column is 8×10^6). It is also interesting that a peak at the eluant volume 22 cm^3 was present in curve B but was not in curve A. This peak corresponds to a molecular weight of 8×10^4 based on the PEO calibration samples. It probably resulted from cleavage of PAM homopolymer and from PAM-PEO copolymer chains but not from homopolymer PEO because there was no peak found at an eluant volume between 19.5 to 21.5 cm^3 for sample I-25-2, which was prepared by homopolymer PEO (no PAM in the system) at the same conditions.

Multiple peaks were also found for sample C-25-2 (see Fig. 1, Curve C). The PEO peaks at the eluant volume 24.0 and 28.4 cm^3 were the same as shown in curve B. A broad polymer signal between 19.5 to 22 cm^3 was also present.

Figure 2 shows the relationship between the η_{sp}/c of the polymer mixture and gamma radiation energy. It is interesting that the η_{sp}/c is almost constant when low gamma ray energy was used (< 510 krad for the system with 2.70 wt % PEO and < 280 krad for the system with 1.35 wt % PEO). We propose that chain scission and intramolecular crosslinking, both of which lower viscosity, balanced the intermolecular crosslinking, which increases viscosity. A similar phenomenon has been reported by Minkova et al.[26] and Charlesby et al.[27] who found

Table II   Effect of PEO Molecular Weight on the Physical State of Graft Copolymer

Samples	M_w of PEO	PEO Conc. (wt %)	Dose (krad)	Physical State
G-8-3	300,000	2.70	340	hard gel
A-8-3	8000	2.70	340	viscous liquid
C-11-3	5000	2.70	340	viscous liquid
D-11-3	2000	2.70	340	liquid
E-11-3	750	2.70	340	liquid

PAM: $M_w = 5 \times 10^6$, concentration 1.16 wt %; dose rate: 34 krad/h; room temperature.
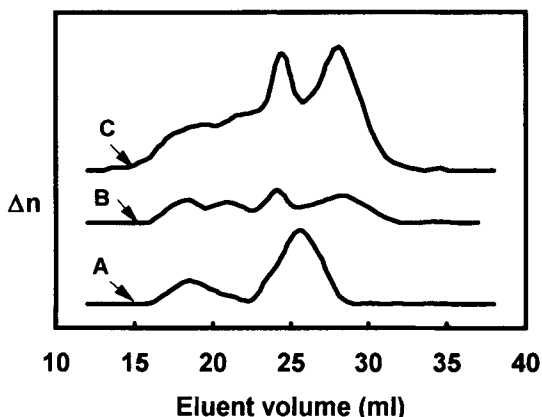
Figure 1 GPC curves of (a), sample A-25-2 before γ-ray radiation; (b), sample A-25-2 after γ-ray radiation and (c), sample C-25-2.

that during gamma irradiation of high molecular weight PEO aqueous solution, the viscosity of the solution decreased initially, followed by an increase that continued until the gelation radiation dose (520 krad for 2 wt % solution, PEO molecular weight M_w > 10^6) had been reached.

Without PEO, the viscosity of PAM increased at a very low radiation dose (30 krad) to reach a gelation dose ($\sim$ 102 krad, not indicated in Fig. 2), as evidenced by the presence of a hard and insoluble PAM gel. As the PEO content was increased, the break points in the curves in Figure 2 increased to 280 krad for 1.35 wt % PEO and 510 krad for 2.70 wt % PEO. It can be concluded that at the same PAM concentration the radiation dose at which the solution viscosity suddenly increased was PEO concentration dependent. That is, the higher the total PEO content in the system, the higher the radiation dose for viscosity increase. Comparing viscosity measurements and visual observations, it can be
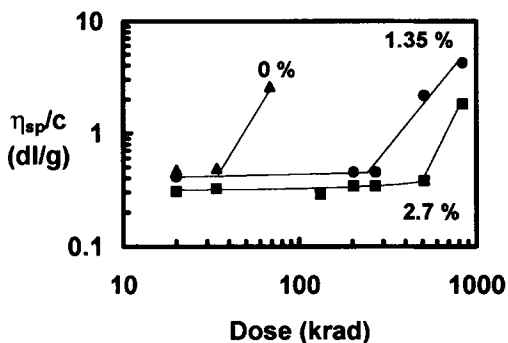

Figure 2 The influence of PEO concentration on η_{sp}/c vs. γ-ray dose. PAM: $M_w = 5 \times 10^6$, $c = 1.1$ wt %; PEO: $M_w = 8000$, dose rate: 34 krad/h.

concluded that the gelation or crosslinking of PAM is suppressed by the addition of low molecular weight PEO.

The content of grafted PEO on the PAM backbone was determined by ^{1}H NMR spectrum and results are given in Figure 3. It was found that the content of grafted PEO increased with the γ-ray radiation dose when the PEO molecular weight and concentration were fixed. The higher the PEO molecular weight, the higher the PEO content in the copolymer. For example, at the same polymer concentrations of PAM (1.1 wt %) and PEO (1.35 wt %), the PEO content in the copolymer after 170 krad was 53 wt % for the PEO with a molecular weight of 300,000, but only 11 wt % for the PEO with a molecular weight of 8000. The results in Figure 3 show that the content of grafted PEO was not greatly affected by the PEO concentration, e.g., the system with 2.70 wt % PEO gave only a little higher content of grafted PEO than the system with 1.35 wt % PEO.

It is well known that hydrogen atoms attached to tertiary carbon atoms are more easily abstracted than those attached to secondary and primary carbon atoms.[28] A series of $E_m P_n E_m$ triblock copolymers was used instead of PEO homopolymer because the tertiary propylene hydrogen was predicted to give higher copolymer yield without crosslinking. The PEO contents of copolymers prepared by $E_m P_n E_m$ and PAM are given in Table III. The results indicated that there was no significant improvement in the grafted amount of PEO on PAM. For example, with all other parameters constant, the grafted amounts of PEO for F127 (M_w = 11300, 70 wt %
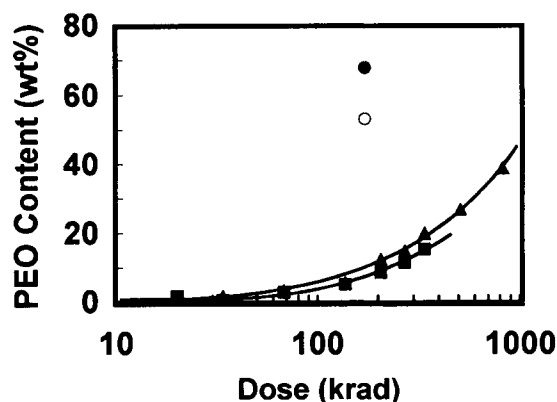

Figure 3 Grafted amount of PEO vs. γ-ray radiation dose. Dose rate: 34 krad/h; PAM molecular weight: 5 × 10^6, concentration $c = 1.1$ wt %; PEO molecular weight and concentration in mixture: ▲, M = 8000, c = 2.37 wt %; ■, M = 8000, c = 1.35 wt %; ●, M = 300,000, c = 2.70 wt %; ○, M = 300,000, c = 1.35 wt %.

Table III **Preparation Conditions and PEO Content of PAM-g-$E_mP_nE_m$ and PEO-g-PAM**

Sample	Polymer Type	Polymer Molecular Weight	PEO Content in $E_mP_nE_m$ (wt %)	Polymer Conc. (wt %)	PEO Content of Copolymer (wt %)
C-31-3	F108	16250	80	1.35	10.0
A-31-3	F127	11300	70	1.35	9.67
G-31-3	F88	11250	80	1.35	8.68
E-31-3	F68	8750	80	1.35	9.3
L-31-3	PEO	3400	100	1.35	6.6
I-31-3	PEO	8000	100	1.35	11.1
D-31-3	F108	16250	80	2.80	13.1
B-31-3	F127	11300	70	2.70	10.3
F-31-3	F68	8750	80	2.70	16.1
M-31-3	PEO	3400	100	2.70	6.1
K-31-3	PEO	8000	100	2.70	14.9

PAM: $M_w = 5 \times 10^6$, concentration 1.16 wt %; dose rate: 34 krad/h; total dose: 272 krad; room temperature. None of the PAM-g-$E_mP_nE_m$ samples formed gel.

PEO) was 9.67 wt % and for PEO-8000 was 11.1 wt %, respectively, although the former had a higher molecular weight than the later. It was also found that none of the PAM-g-$E_mP_nE_m$ formed gel. This was perhaps because the PAM radicals were easier to transfer to the PPO than to the PEO, resulting in a decrease of crosslinking between PAM molecules.

Polystyrene Latex Flocculation

The flocculation of polystyrene latex (PSL) by the copolymers was investigated. It has been reported[10,11,29,30] that the flocculation of wood pulp fines or PSL by very high molecular weight PEO can be enhanced by the addition of phenol formaldehyde resin (PFR) and cellulose fibers.

The graft copolymers prepared in this study were evaluated as flocculants. Of the copolymers prepared in this study, purified C-18-12 and B-18-12 were found to be the most effective flocculants. The relative turbidity fell to 0.37 for C-18-12 at a copolymer concentration of 4 ppm, indicating that approximately 63% PSL was flocculated by the copolymer. Further increasing the copolymer concentration caused a small increase in the relative turbidity. A similar phenomenon was reported for high molecular weight PEO for cellulosic fines[9,10] and for polystyrene latex.[29,32] The results summarized in Figure 4 indicate that the flocculation efficiencies of certain copolymers prepared in this study are comparable

to those of high molecular weight PEO homopolymer. Other significant observations based on the data in Table 4 are:

1. Crosslinked copolymer gel with low swelling (hard gel) gave no effective flocculation of PSL in the copolymer concentration range studied (0 to 60 mg/L).
2. All of the copolymers in which the PEO content was less than 15 wt % gave weak flocculation. For example, the relative turbidity of the system after addition of copolymer was greater than 85 wt %.
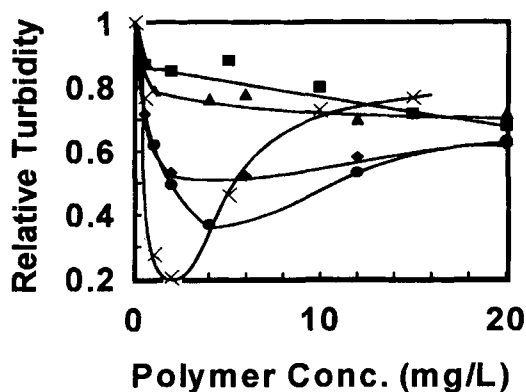

Figure 4 Effect of copolymer concentration on the flocculation of PSL. ▲, original C-18-12; ●, purified C-18-12; ■, original B-18-12; ♦, purified B-18-12; ×, PEO-309. For the unpurified mixtures, the concentrations are based on the copolymer weight rather than the total weights of PAM and PEO in the system.

Table IV   The Flocculation of Polystyrene Latex by Copolymers

Sample	Physical State	PEO Content of Copolymer (wt %)	Polymer Concentration Range (mg/L)	Lowest Relative Turbidity
A-18-2	hard gel	†	0.5–100	0.92
B-3-2*	hard gel	19.3	0.5–60	0.87
B-18-12	soft gel	24.0	0.5–100	0.83
B-18-12*	soft gel	24.0	0.5–70	0.52
A-3-12	soft gel	36.1	0.5–40	0.86
B-17-3	soft gel	23.6	0.5–80	0.53
A-16-4	liquid	1.86	0.5–65	0.93
G-16-4	liquid	3.5	0.5–70	0.93
J-16-4	liquid	12.6	0.5–80	0.68
C-17-3*	liquid	17.3	0.5–45	0.51
C-18-12*	liquid	33.0	0.5–40	0.37

* Purified copolymer.
† Not measured.

3. The flocculation was enhanced by removing ungrafted PEO (see Fig. 4).

The flocculation ability of copolymers made by gamma radiation of Pluronic, $E_m P_n E_m$, and PAM in aqueous solution was also investigated. The results are shown in Figure 5. The Pluronic copolymers were less capable of flocculating latex particles compared with C-18–12 and B-18–12, which were prepared by PEO homopolymer and PAM. It should be noted that C-18–12 and B-18–12 have a higher PEO content than the copolymers that were used in Figure 5. It is not clear whether the flocculation ability can be improved by increasing the PEO content in PAM-g-$E_m P_n E_m$ copolymers.

DISCUSSION

The goal of this work was to prepare PAM-g-PEO copolymer flocculants from recombination of γ-ray–induced backbone radicals on PAM with those on PEO. Too much branch formation produced insoluble macroscopic gels that were not effective flocculants. Gel formation appeared to be a more serious problem than chain scission. Thus much of the emphasis of this work was to maximize copolymer formation while avoiding gelation.

Scheme I of Figure 6 shows schematically the desired reaction. Undesirable gel formation could occur when PAM radicals combine with other PAM radicals (Scheme II), or when more than one backbone radical is produced on the PEO chains (Scheme III). In the absence of quantitative information about

the relative rates of formation of PAM and PEO backbone radicals in γ-rays, it is assumed in the following discussion that the rates are equal. Furthermore, it seems reasonable to assume that rates of backbone radical formation are independent of molecular weight.

Without PEO, recombination of PAM backbone radicals (Scheme II) gave insoluble gel in agreement with published results.[22-24] Increasing the concentration of PEO increased the importance of Scheme I relative to Scheme II. If the above assumptions are correct, PEO inhibited gel formation simply because its molecular weight was low. In other words, for a given radical production rate, the probability of two backbone radicals being produced simultaneously or sequentially on the same PEO chain decreases with PEO molecular weight.
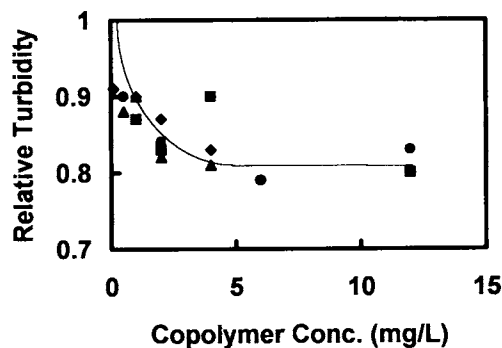

Figure 5 Relative turbidity vs. copolymer (PAM-g-Pluronic) concentration. ●, A-31–3; ▲, C-31–3; ◆, E-31–3; ■, G-31–3. All copolymers were purified by precipitation with acetone.
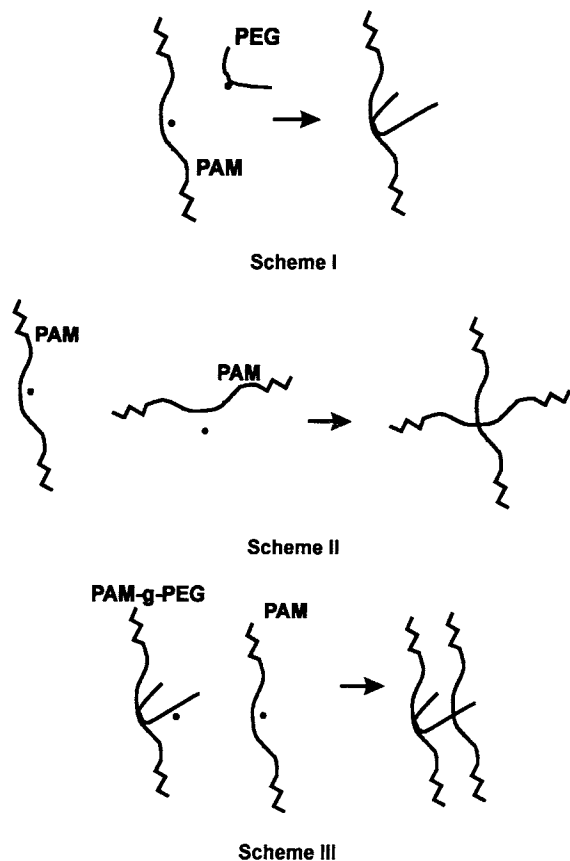
Scheme I

Scheme II

Scheme III

Figure 6 Possible radical recombination reactions. Scheme I shows desired route to copolymer, whereas Scheme II and Scheme III show routes to undesirable gel.

Chain transfer from PAM to PEO perhaps is another factor that can reduce the PAM radical concentration when PEO is added. Fukuzaki et al.[24] and Ishigaki et al.[25] have reported that the addition of alcohol during the radiation-induced polymerization of acrylamide could effectively inhibit intra- and intermolecular crosslinking of PAM giving water soluble polymer.

CONCLUSIONS

The main conclusions from this work are:

1. Graft copolymers can be prepared by gamma irradiation of aqueous solutions of low molecular weight PEO and high molecular weight PAM.
2. Copolymers containing more than 15 wt % PEO are effective latex flocculants when used with phenol formaldehyde resin and cellulose

fibers. Best results are achieved with purified copolymer.
3. Gel formation is an undesirable side effect of too much irradiation. Gel formation is inhibited by the presence of low molecular weight PEO.
4. Copolymers are also formed from irradiation of Pluronic PEO-PPO-PEO triblock polymers in the presence of PAM.

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