

The Accelerated Degradation of Aqueous Polyacrylamide at Low Temperature

JIANPING GAO, JIUGAO YU, WEI WANG, TONG LIN

Department of Chemistry, Tianjin University, People's Republic of China

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ABSTRACT: The accelerated degradation of aqueous polyacrylamide at low temperature was studied. The selected degradation agents included several peroxides, such as potassium persulfate ($K_2S_2O_8$), ammonium persulfate ($(NH_4)_2S_2O_8$), hydrogen peroxide (H_2O_2), and the potassium persulfate–sodium thiosulfate ($K_2S_2O_8$ – $Na_2S_2O_3$) redox system. The redox system showed the highest degradation rate at the first 2 hours, but its final degradation level was lower than that of potassium persulfate. The degradation temperature, concentration of potassium persulfate and polyacrylamide, and original molecular weight of polyacrylamide all affected the degradation rate and final degradation level. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 791–797, 1998

Key words: accelerated degradation; polyacrylamide; peroxides; low temperature

INTRODUCTION

Polyacrylamide (PAM) is one of the important water soluble polymers and has wide applications. High-molecular-weight PAM is mainly used as flocculant, while the medium-molecular-weight PAM is used in paper as dry fortifier, but low-molecular-weight PAM can be applied as disperser. So the molecular weight of PAM is the key factor to determine its application. In the production of PAM, it is not hard to get a high- and low-molecular-weight product, but it is difficult to obtain the medium one. Some researchers have tried to get a series of PAM with different medium molecular weights by chemical degradation. They found that this aim could be attained by adjusting the reaction parameters.^{1–3}

The use of PAM in alkaline–surfactant–polymer (ASP) flooding becomes wider and wider with the popularity of the second exploitation of the oil well because it can improve the exploiting efficiency.⁴ The main act of the polymer is to increase

the density of working liquid in ASP flooding, lower the oil–water mobility ratio, and adjust the osmosis section.⁵ But this technique may cause the accumulation of PAM remaining in the well. Numerical analogue computations indicated that the PAM holdup was about 25–53.6% of the PAM injected.⁶ PAM suffered shear degradation in the oil well.⁷ During injection, this degradation may lead to loss in viscosity, which affects the oil-displacing efficiency. But as for the produced liquid and the blockage section by PAM, the degradation can be helpful for the water purification, the reinjection of the working liquid, and the removing of blockage.^{8,9}

EXPERIMENTAL

Materials

Polyacrylamide A has a molecular weight of 12×10^6 and polyacrylamide B has a molecular weight of 15×10^6 . Potassium persulfate ($K_2S_2O_8$) and ammonia persulfate [$(NH_4)_2S_2O_4$] both came from Tianjin East Chemical Plant. Hydrogen peroxide (H_2O_2) was provided by Beijing Chemical Plant.

Correspondence to: J. Gao.

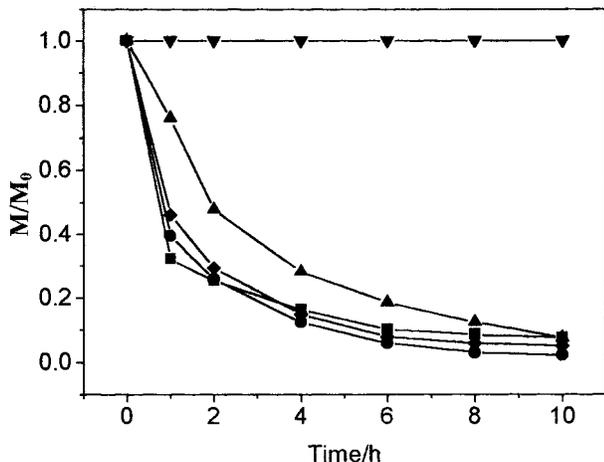


Figure 1 Molecular weight decrease of PAM under the action of peroxides: $M_0 = 12 \times 10^6$; $[\text{PAM}] = 0.6\%$ (wt %); $[\text{PO}] = 0.02962 \text{ mol/L}$; $[\text{Na}_2\text{S}_2\text{O}_3] = \frac{1}{2}[\text{PO}]$; Temperatures = 40°C . Peroxides are as follows: (\blacktriangle) H_2O_2 ; (\bullet) $\text{K}_2\text{S}_2\text{O}_8$; (\blacksquare) $\text{K}_2\text{S}_2\text{O}_8\text{-Na}_2\text{S}_2\text{O}_3$; (\blacklozenge) $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) was from Tianjin Second Chemical Reagent Plant.

Degradation Procedure

The degradation of polyacrylamide (PAM) was carried out in a D-8401 microbe cultivating case. First, a certain amount of PAM and peroxide were weighed out and put into two beakers, respectively, and then distilled water was poured into the beakers to form solutions. The two solutions were poured into and mixed in a volumetric flask, which was consequently and immediately placed on a rotation bed in the cultivating case to allow PAM to undergo degradation at a certain temperature. After a period of time of degradation, the samples were taken out to determine the rotation viscosity of PAM solution and the molecular weight of PAM samples.

The viscosity $[\eta]$ of PAM was tested with a Ubbelohde viscometer at the temperature of 30°C , and then the molecular weight was calculated according to the following equation:

$$[\eta] = KM^\alpha$$

where $K = 6.31 \times 10^{-3}$ and $\alpha = 0.90$.

The rotation viscosity of PAM solution was determined with a NXS-II rotation viscometer.

RESULTS AND DISCUSSION

Degradation Agents

The chemical degradation of PAM was carried out at 40°C in a microbe cultivation case, and the chosen degradation agents are all water-soluble peroxides. If the molecular weight of the original PAM was taken as a standard and defined as M_0 , and the molecular weight of the degraded PAM was tested as M , the ratio of M to M_0 (M/M_0) can be used to represent the degradation level of the PAM during the reaction. Figures 1 and 2 are the changes of molecular weight (M/M_0) and rotation viscosity (η/η_0) of PAM during the degradation under the action of four different chemicals, including curves on the top that represent the M/M_0 and η/η_0 values of a sample without addition of chemicals, under the same reaction conditions. The aqueous PAM without chemicals almost did not undergo degradation at 40°C , while the same sample showed a drastic degradation, if it was added with degradation agents. Especially at the beginning, the molecular weight and rotation viscosity fell significantly. Two hours later, the decreasing trends of M and η subsided; and 8 h later, the change in molecular weight of PAM was slight, and M almost reached a constant. In the initiating stage of the reaction, peroxides decomposed and formed numerous free radicals, which induced the degradation of polyacrylamide and led to the rapid decrease of molecular weight and rotation viscosity of aqueous PAM. Meanwhile, the free radicals could react with each other to reduce the concentration of free radicals in the aqueous PAM and cause the termination of the

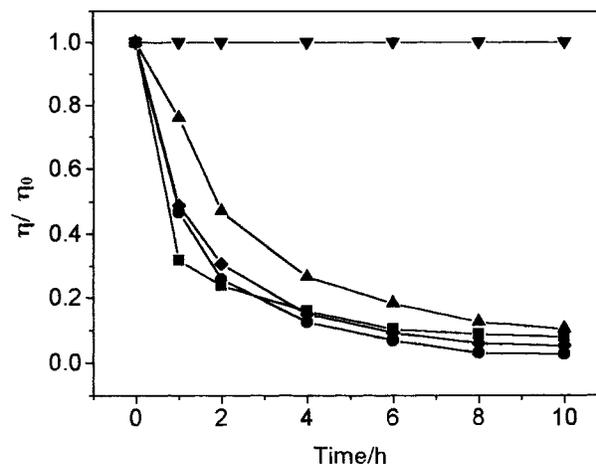


Figure 2 Viscosity decrease of PAM aqueous solution.

Table I Activation Energies

	$K_2S_2O_8-Na_2S_2O_3$	$K_2S_2O_8$	H_2O_2
E_d (kJ/mol ⁻¹)	41.9	140	220

degradation. The changes in molecular weight and rotation viscosity of PAM in four peroxide solutions showed the similar trends, though the rate of degradation and degradation level were different.

The starting degradation rates of PAM in four peroxide aqueous solution are in the following order:



This is just opposite to the sequence of their decomposing activation energies (Table I). $K_2S_2O_8-Na_2S_2O_3$ is a redox system, and the rate of breakdown is the fastest, so the degradation rate initiated by the free radicals is also the fastest. On the other hand, the chance of termination among free radicals is also the highest because of the higher free radical concentration, leading to a slow degradation rate 2 h later and a lower final degradation level than that of $K_2S_2O_8$, though the starting degradation rate of the latter was lower than that of $K_2S_2O_8-Na_2S_2O_3$.

By comparing the curves in Figure 1 and in Figure 2, we could find that the tendency of molecular weight of PAM and rotation viscosity of aqueous PAM were very similar for each of the four degrading agents.

Effect of Temperature on the Degradation of PAM

Temperature is one of the key factors that affect the degradation of PAM. We studied the degrading reaction of PAM in 0.0296 mol/L $K_2S_2O_8$ solution at the temperatures of 30, 40, 50, and 60°C, respectively, and the results are shown in Figures 3 and 4. The degradation rate and final degradation level of PAM both increased as the temperature rose from 30 to 50°C because the decomposing rate of $K_2S_2O_8$ grew. But further increase of temperature from 50 to 60°C brought about no evident change in the degradation of PAM. When temperature rose, the decomposing rate of the $K_2S_2O_8$ increased, so a larger amount of free radicals were formed which caused the growth in degradation of PAM and interaction between free radicals. The two actions counteracted each other

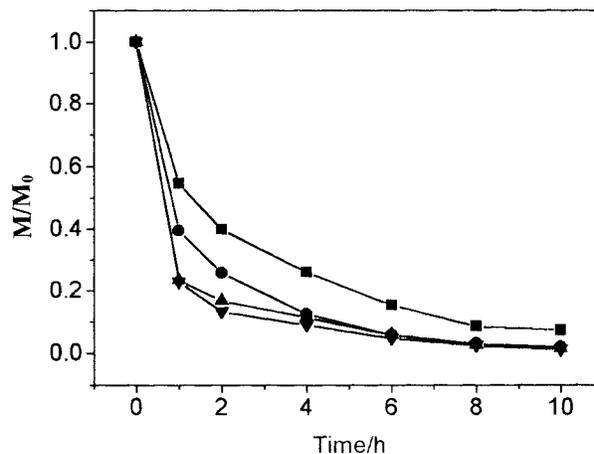


Figure 3 Effect of temperature on the molecular weight of PAM: $M_o = 12 \times 10^6$; [PAM] = 0.6% (wt %); [$K_2S_2O_8$] = 0.02962 mol/L. Temperatures are as follows: (■) 30°C; (●) 40°C; (▲) 50°C; (▼) 60°C.

and showed the above changes. The decomposing rate and $t_{1/2}$ of $K_2S_2O_8$ at different temperatures were calculated according to the following equation, and the results are listed in Table II:

$$k_{d2}/k_{d1} = (E_d/2.30R)(1/T_1 - 1/T_2),$$

$$E_d = 140 \text{ kJ/mol}, \quad R = 8.25 \text{ J/mol} \cdot K$$

Effect of $K_2S_2O_8$ Concentration

At the temperature of 40°C, we studied the effect of $K_2S_2O_8$ concentration in the range of 0.0089–0.05962 mol/L on the viscosity of 0.6% PAM solution and molecular weight of PAM. Figures 5 and 6 are the molecular weight and viscosity changes

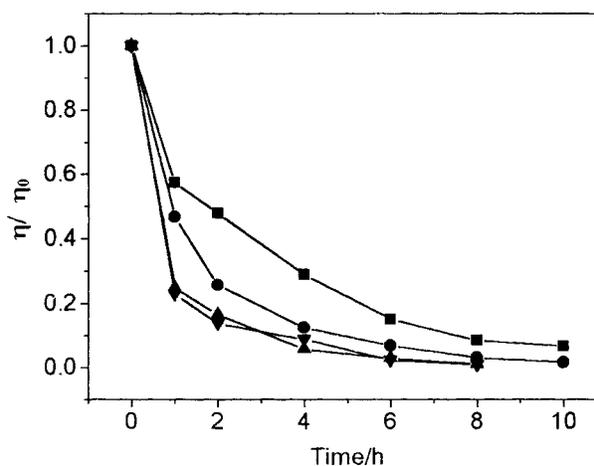


Figure 4 Effect of temperature on the viscosity of PAM aqueous solution.

Table II k_d and $t_{1/2}$ of Peroxides at Different Temperatures

Temperature (°C)	30	40	50	60
$k_d \times 10^7$ (s ⁻¹)	0.297	1.780	9.50	31.6
$t_{1/2}$ (h)	6481	1081	202	60
$k_{d(t+10)} : k_{d(t)}$		6	5.34	3.37
$k_{d(30)} : k_{d(40)} : k_{d(50)} : k_{d(60)} = 1 : 3.37 : 18 : 108$				

during the degradation of PAM. The trends of both molecular weight and viscosity were similar at any $K_2S_2O_8$ concentrations. At the first 2 h, the molecular weight and viscosity of PAM fell drastically, and then their changes gradually leveled off at any $K_2S_2O_8$ concentrations. But in the same reaction period, the molecular weight of PAM and viscosity of PAM solution became much lower if $K_2S_2O_8$ concentration was high because of the growth in the degradation rate and degradation level.

Effect of Original Molecular Weight of PAM

From discussion above, we can see that when molecular weight of PAM is comparatively small, the degrading rate is also lower, which suggests that molecular weight affects the degradation of PAM. Figures 7 and 8 are the degradation results of PAM having different original molecular weights. This indicates that original molecular weight of PAM had some effect on the degradation of PAM. As far as degrading proportion is concerned, original molecular weight makes little difference in

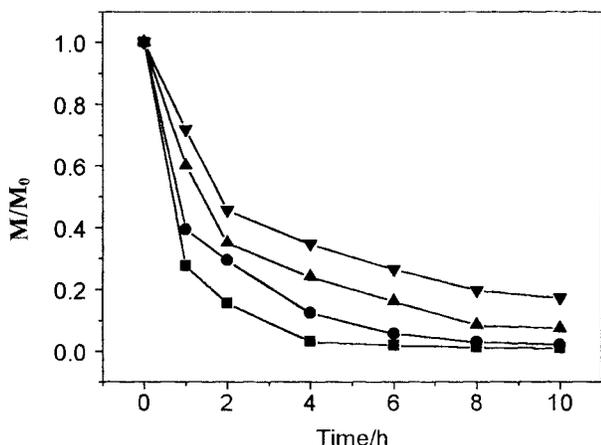


Figure 5 Effect of $[K_2S_2O_8]$ on the molecular weight of PAM: $M_0 = 12 \times 10^6$; $[PAM] = 0.6\%$ (wt %); temperature = 40°C. $[K_2S_2O_8]$: (▼) 0.0089; (▲) 0.01481; (●) 0.02962; (■) 0.05962 mol/L.

the degradation of PAM (Fig. 7), but when we consider molecular difference ($\Delta M = M_0 - M$) between original molecular weight (M_0) and degraded molecular weight (M), we found that the ΔM difference between two different original molecular weight PAM gradually increased as the reaction went (Fig. 9).

Effect of PAM Concentration

Like $K_2S_2O_8$ concentration, PAM concentration also affects the degradation. Figures 10 and 11 are the results of PAM at three different concentrations. Both the degrading rate and degradation level increased as the PAM concentration rose. When PAM concentration is higher, the decomposed free radicals have more chance to react with PAM molecules and cause the break down of PAM macromolecules. But the degradation difference between the PAM concentration of 0.6 and 0.8% ($M_{(0.6\%)} - M_{(0.8\%)}$) is lower than that between PAM concentration of 0.4 and 0.6% ($M_{(0.4\%)} - M_{(0.6\%)}$), or 0.4 and 0.8% ($M_{(0.4\%)} - M_{(0.8\%)}$) (Fig. 12), and the difference reaches a maximum after 2 h reaction.

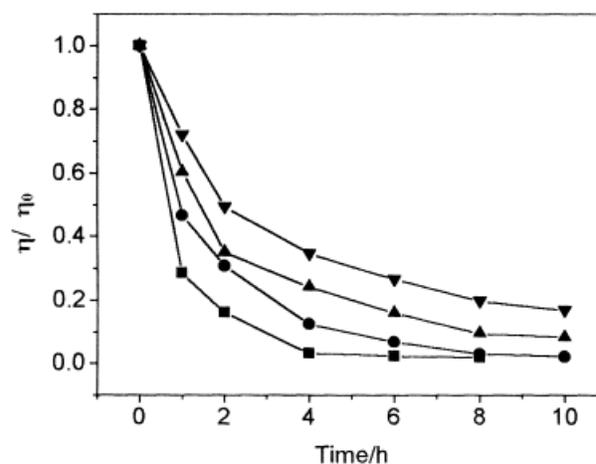


Figure 6 Effect of $[K_2S_2O_8]$ on the viscosity of PAM aqueous solution.

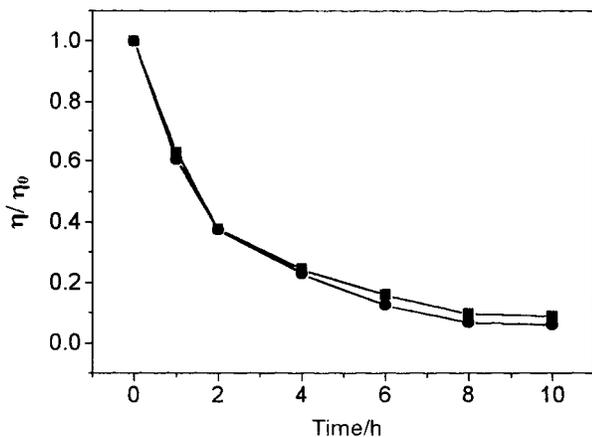


Figure 7 Effect of M_0 on degradation: [PAM] = 0.6% (wt %); $[K_2S_2O_8]$ = 0.02962 mol/L; temperature = 40°C. PAM: (■) $M_0 = 12 \times 10^6$; (●) $M_0 = 15 \times 10^6$.

Degradation Degree of PAM in Different Chemicals

Number-average molecular weight (M_n) and weight-average molecular weight (M_w) have a functional relationship with the degradation degree (P), which is represented in the equation below, as follows:

$$M_{n(p)} = \frac{\sum n_{i(p)} M_{ni}}{\sum n_{i(p)}}, \quad M_{w(p)} = \frac{\sum n_{i(p)} M_{ni}^2}{\sum n_{i(p)} M_{ni}}$$

As for the random degradation of macromolecules with higher initiating molecular weight, the distribution of the molecular weight during degradation immediately trends to index distribution,

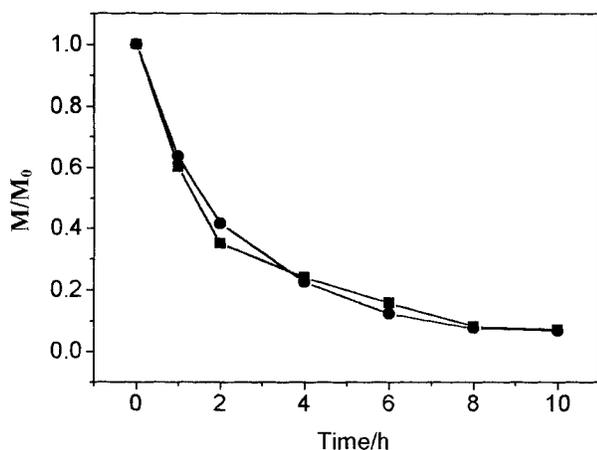


Figure 8 Effect of M_0 on degradation: [PAM] = 0.6% (wt %); $[K_2S_2O_8]$ = 0.02962 mol/L; temperature = 40°C.

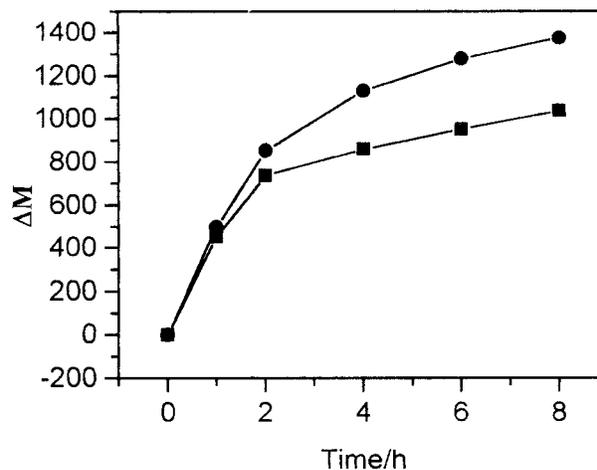


Figure 9 ΔM of two different original molecular weight PAM: [PAM] = 0.6% (wt %); $[K_2S_2O_8]$ = 0.02962 mol/L; temperature = 40°C. PAM: (■) $M_0 = 12 \times 10^6$; (●) $M_0 = 15 \times 10^6$.

based on which of the following relationships between M_n , M_w , and M_v exist.

$$M_w : M_v : M_n = 2 : [(1 + \alpha)\Gamma(1 + \alpha)]^{1/\alpha} : 1 \quad (1)$$

where α is the index in Mark–Houwink equation, and the value of 0.9 is chosen in our experiment.

Again, if the molecular weight accords to index distribution, the degradation rate is represented below, as follows:

$$R = \frac{dp}{dt} = -\frac{1}{\phi(p)} \cdot \frac{1}{M_{w(p)}^2} - \frac{dM_{w(p)}}{dt} \quad (2)$$

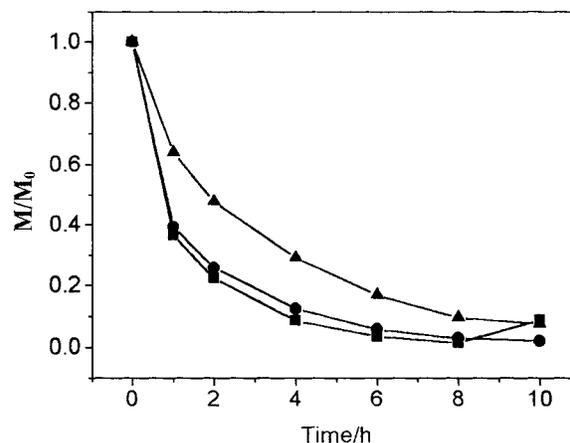


Figure 10 Effect of [PAM] on the molecular weight decrease of PAM: $M_0 = 12 \times 10^6$; $[K_2S_2O_8]$ = 0.02962 mol/L; temperature = 40°C. [PAM]: (▲) 0.4%; (●) 0.6%; (■) 0.8%.

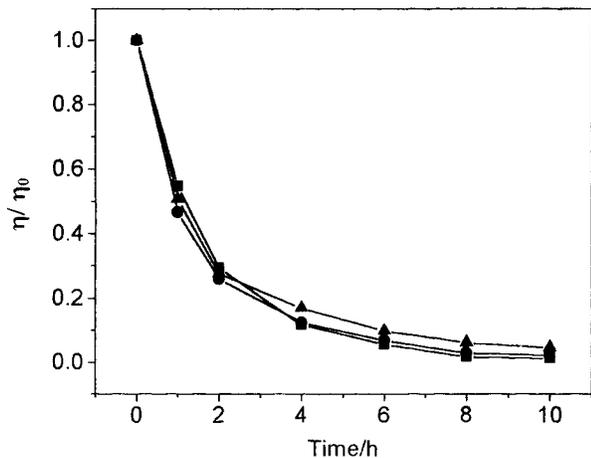


Figure 11 Effect of [PAM] on the viscosity of PAM aqueous solution.

When eq. (2) is integrated, the following equations can be obtained:

$$\frac{1}{M_{w(p)}} = \frac{1}{M_{w(0)}} + \frac{1}{2}p \quad (3)$$

or,

$$\frac{1}{M_{n(p)}} = \frac{1}{M_{n(0)}} + \frac{1}{2}p \quad (4)$$

where $M_{w(0)}$ and $M_{n(0)}$ represent the corresponding original molecular weight. So the following degradation degree is derived:

$$P = \frac{1}{M_{n(p)}} - \frac{1}{M_{n(0)}} \quad (5)$$

According to eq. (1), the $M_{n(p)}$ and $M_{n(0)}$ can

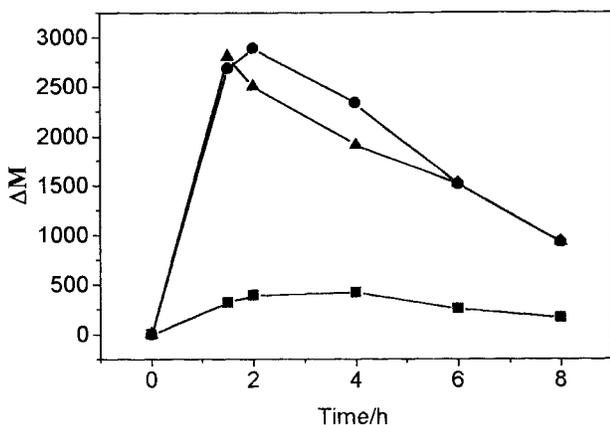


Figure 12 Molecular weight difference between three [PAM]: (■) $M_{(0.6\%)} - M_{(0.8\%)}$; (●) $M_{(0.4\%)} - M_{(0.8\%)}$; (▲) $M_{(0.4\%)} - M_{(0.6\%)}$.

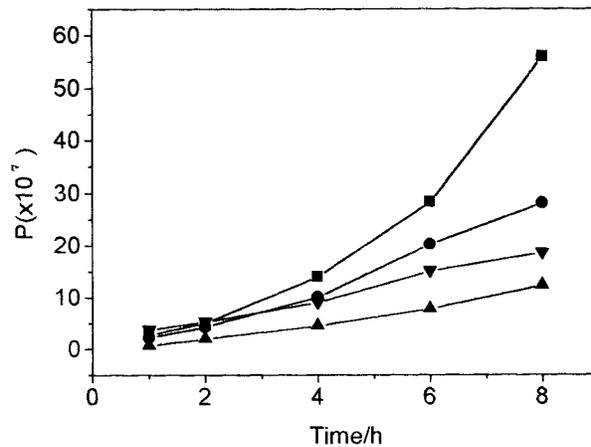


Figure 13 Degradation degree of PAM: (▲) H_2O_2 ; (●) $K_2S_2O_8-Na_2S_2O_3$; (■) $K_2S_2O_8$; (▼) $(NH_4)_2S_2O_8$.

be displaced by $M_{v(p)}$ and $M_{v(0)}$ respectively, as follows:

$$M_{n(p)} = \frac{M_{v(p)}}{[(1 + \alpha)\Gamma(1 + \alpha)]^{1/\alpha}},$$

$$M_{n(0)} = \frac{M_{v(0)}}{[(1 + \alpha)\Gamma(1 + \alpha)]^{1/\alpha}}$$

$$P = \frac{1}{M_{n(p)}} - \frac{1}{M_{n(0)}} = \left[\frac{1}{M_{v(p)}} - \frac{1}{M_{v(0)}} \right] \times [(1 + \alpha)\Gamma(1 + \alpha)]^{1/\alpha} \quad (6)$$

Since α is 0.9, $\Gamma(1 + \alpha)$ becomes 0.9618 in the following:

$$P = \left[\frac{1}{M_{v(p)}} - \frac{1}{M_{v(0)}} \right] \times 1.954 \quad (7)$$

Therefore, the degradation degree p can be calculated from measured M_v according to eq. (7). Figure 13 shows the degradation degree of PAM in different peroxides in water. The P of PAM in $K_2S_2O_8$ was the greatest, and H_2O_2 was the lowest. The $P-t$ curves in Figure 13 were almost linear, except $K_2S_2O_8$. The P value in $K_2S_2O_8$ increased abruptly at 4 h. Meanwhile, the degradation rate could be obtained from the slopes of fitted $P-t$ diagrams and is listed in Table III.

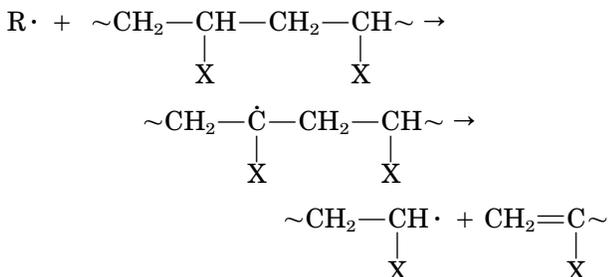
Degradation Mechanism

The degradation of PAM may be carried out in the following scheme.

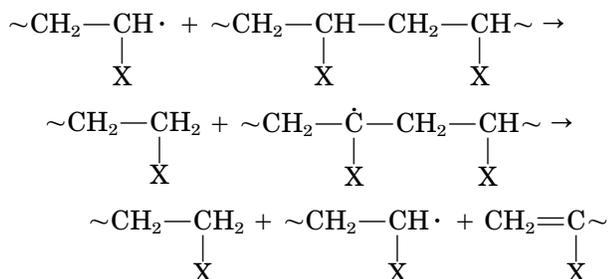
Table III Degradation Rate of PAM in Peroxides

	K ₂ S ₂ O ₈	(NH ₄) ₂ S ₂ O ₈	K ₂ S ₂ O ₈ -Na ₂ S ₂ O ₃	H ₂ O ₂
R (×10 ⁷)	5.8025	3.7943	2.1916	1.6321

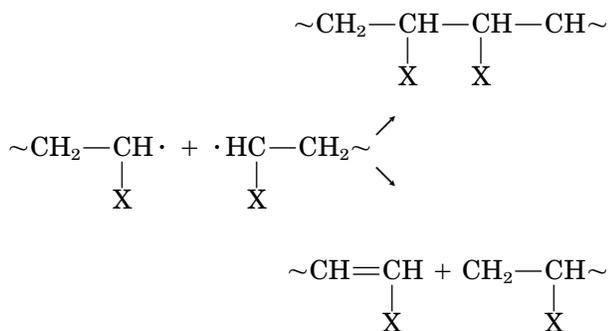
Initiation:



Transferring:



Termination:


 where X is the group of —CONH₂.

CONCLUSION

1. The efficiency of four peroxides in the degradation of PAM is K₂S₂O₈, (NH₄)₂S₂O₈ > K₂S₂O₈-Na₂S₂O₃ > H₂O₂
2. The higher the PAM concentration is, the faster the degrading rate and the higher the degrading level.
3. The original molecular weight of PAM has no effect on the degrading proportion but has obvious influence on the absolute molecular weight of the degraded PAM.
4. High temperature can cause intensive degradation of PAM.

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