The Gamma-Ray-Induced Crosslinking of Polyacrylamide

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Synopsis

The gamma-ray-induced crosslinking of polyacrylamide was carried out under various conditions. The molecular weight of the polymer before inrradiation was found to be the most important factor for crosslinking. When polymers have low molecular weights such as 80,000, the intensity of radiation, the external pressure applied, and the water content of the polymer powder became important for crosslinking. Although the polyacrylamide hydrogel can be obtained directly by irradiating the monomer, it was obtained more conveniently by the irradiation of monomer–polymer mixtures. The hydrogels obtained by the radiation with a dose of over 50 kgray, absorb water by 1000–1500 wt %.

INTRODUCTION

The effects of high energy radiation on macromolecules have been studied by many workers for the last 30 years, and the results have been edited in several monographs.[1] Polyacrylamide is a polymer which can be crosslinked by gamma irradiation, but its behavior toward the radiation was not well known before. In the past, polyacrylamides were assumed to be similar to those of other water soluble polymers such as polyvinyl pyrrolidone and polyvinylalcohol, which were studied in solutions by Alexander and Charlesby[2] in some detail. The present authors have studied the gamma-ray-induced crosslinking of polyacrylamide[3–5] in order to obtain basic data for the preparation of polyacrylamide hydrogel, which can be used as a water retainer in agricultural arid zones. They have found that the initial molecular weight of polymer is a very important factor for crosslinking and that, for the polymer with low molecular weight, the water content and the pressure applied to the solid polymer are important factors to increase the yield of crosslinking. In this paper, the crosslinking of polyacryalmide by gamma radiation under various conditions is described to provide information for obtaining hydrogel of polyacrylamide by the gamma radiation in air.

EXPERIMENTAL

Materials

The average number of molecular weights of various polyacrylamides (PAAm) were determined from the intrinsic viscosities measured at 30°C

Journal of Applied Polymer Science, Vol. 32, 3783–3789 (1986)
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in 0.1N aqueous solution of sodium nitrate, using the relationship[6]

$$[\eta] = 6.8 \times 10^4 M_n^{0.66}$$

The PAAms having molecular weights of 80,000, 1,600,000, and 2,200,000 were supplied by Monomer-Polymer and Dajac Laboratories, Inc., and those with 8000 and 148,000 were prepared in our laboratory by free radical polymerization. The PAAms with molecular weights of 4,000,000 and 15,000,000, which were not measured by viscosity, were supplied by American Cyanamid Co. The polymers were irradiated after purifying by reprecipitation from a water–methanol system, or without purification, but no appreciable difference in the crosslinking yields was observed.

IRRADIATION

The irradiation conditions were the same as reported previously[3–6] and it was carried out using a ^{60}Co Gamma Beam Type TR-317, with an activity of 15,400 Ci, in June 1984. A gamma cell was also used for the low intensity irradiation.

ANALYSIS

The amount of hydrogel formed was determined gravimetrically by extracting the sol with water. The values of incipient gel dose r_g, the dose when gelation starts, were determined graphically. In the case of irradiation in solid state, the Charlesby–Pinner relationship[7] was also used for estimating the r_g values.

RESULTS AND DISCUSSION

Effects of Molecular Weight

Little has been mentioned on the effects of molecular weight of the original polymer on the crosslinking. We reported previously that the initial molec-

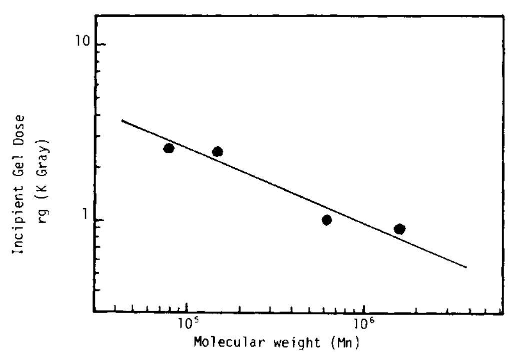

Fig. 1. Relationship between molecular weight of PAAm and incipient gel dose (r_g). Radiation intensity = 22 kgray/h. Concentration of PAAm = 3% in water.

ular weight is one of the most important factors for the crosslinking both in solution[3] and in solid state.[5] The greater the molecular weight of initial polymer, the faster the crosslinking, as can be seen in Figure 1. It seems that, in order to form gels, PAAm should have a certain size large enough to undergo crosslinking. As shown in Figure 2, this limit of molecular weight for crosslinking lies around 10^6 for solutions with a concentration of 3%. The dose less than r_g corresponds to the energy required to increase the molecular weight enough to undergo crosslinking. In the case of solid state irradiation, a similar trend was observed as shown in Table I, in which it can be seen that the r_g values become a constant independent of the molecular weight when it exceeds 1,600,000.

The effect of dose rate, i.e., intensity, is also important. As can be seen in Figure 2, the greater the dose rate the faster the crosslinking and the less does is required.

EFFECTS OF WATER

In the case of irradiation in solutions, there exists an optimum concentration for crosslinking, as reported previously for PAAm[3] and for polyvinylpyrrolidone.[2] In the case of irradiation in solid state, when the molecular weight is small, such as 80,000, and irradiated in powder form, little crosslinking took place, and an addition of water to the powder remarkably

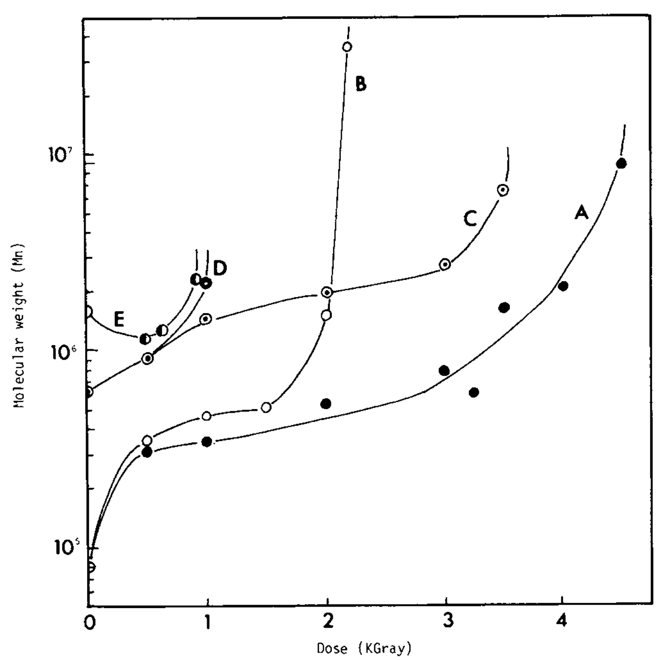

Fig. 2. Effects of molecular weight and of radiation intensity on crosslinking in aqueous solution: concentration = 3%; (A) initial M_n = 80,000; intensity = 1 kgray/h; (B) initial M_n = 80,000; intensity = 18 kgray/h; (C) initial M_n = 636,000; intensity = 1 kgray/h; (D) initial M_n = 636,000; intensity = 18 kgray/h; (E) initial M_n = 1,600,000; intensity = 18 kgray/h.

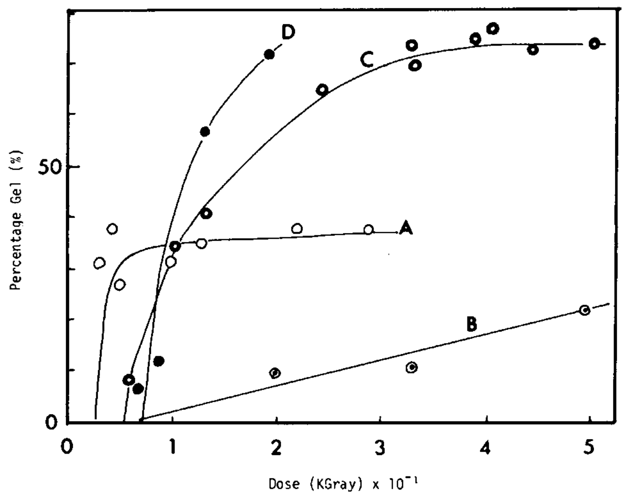

Fig. 3. Effects of water on crosslinking of PAAm: M_n of PAAm = 148,000; (A) 3% aqueous solution; intensity 1.5 kgray/h; (B) powder with 10% water; intensity 1.5 kgray/h; (C) powder with 20% water; intensity 1.5 kgray/h; (D) powder with 10% water; intensity 26.5 kgray/h.

increased the crosslinking.[5] Figure 3 shows relationships between crosslinking, dose, dose rate, and water content. Both the addition of water and increase in dose rate increased crosslinking yield. Further addition of water beyond 20% does not increase crosslinking any further. It can be concluded from the results of Figure 3 and those of previous work[5] that up to 20% of water is necessary to crosslink PAAm in powder form by the irradiation in air. However, the effect of water is less prominent when the molecular weight of PAAm is higher.

EFFECTS OF PRESSURE

The low molecular weight PAAm does not give gel when irradiated in air in the form of a dry powder, but when the powder is compressed into a disk, the crosslinking takes place.[5,7] In the case of compressed disks, no water is

TABLE I
Relationships between Incipient Gel Dose (r_g) and the Molecular Weight of PAAm[a]

M_n	r_q (kgray)	Irradiation conditions
80,000	2.5	3% aqueous solution
80,000	15.2	Powder
148,000	7.5	Powder
1,600,000	2.1	Powder
2,200,000	2.1	Powder
4,000,000	2.1	Powder

[a] Irradiation intensity = 22.1 kgray/h.

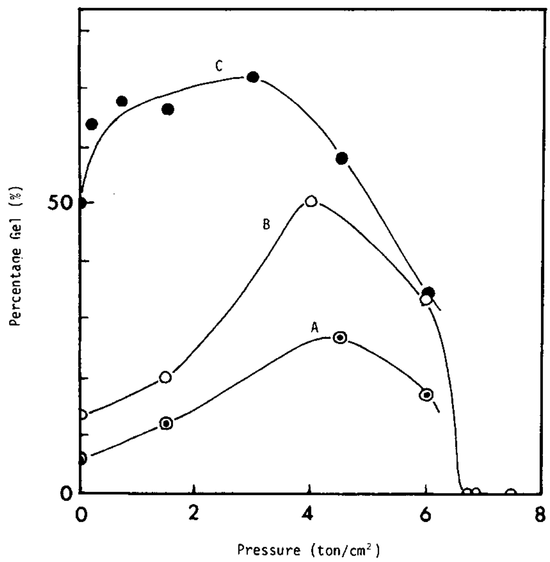

Fig. 4. Effects of pressure on crosslinking of PAAm; total dose = 50 kgray; (A) M_n = 80,000; intensity = 1 kgray/h; (B) M_n = 80,000; intensity = 24.8 kgray/h; (C) M_n = 2,200,000; intensity = 1 kgray/h.

necessary. The increase in pressure increases the crosslinking, but it decreases with further increase in pressure, as can be seen from Figure 4. The effects of pressure were more enhanced for lower molecular weight PAAm irradiated with low dose rates. For the high molecular weight PAAm, i.e., over 1,000,000, the effect of pressure was small. These observations suggest that the crosslinking reaction is rather independent of the pressure, and the applied pressure only accelerates the formation of molecules large enough to undergo crosslinking.

IRRADIATION OF MONOMER–POLYMER MIXED SYSTEMS

In order to obtain crosslinked PAAm by the irradiation directly from the monomer, 50 g of pure monomer were irradiated at room temperature with a dose rate of 20 kgray/h. The heat, due to the exothermic polymerization, caused violent sublimation of monomer. Subsequently, the monomer was diluted by the polymer and some of the mixed systems were studied, and the results are shown in Table II. For the low molecular weight PAAm, the higher the monomer content the higher the gelation yield, the addition of monomer increasing the crosslinking yield. In the case of high molecular weight PAAm, the gelation yields were higher than those for the low molecular weight PAAm. These yields indicated that the molecular weight is the most important factor for gelation. It can be seen from the table that the effect of irradiation intensity is not important in the polymer–monomer mixed systems. This is rather unusual since it was always observed for the irradiation of PAAm that the higher the intensity the higher the crosslinking yield.

TABLE II
Crosslinking of PAAm–AAm Mixed Systems

PAAm/AAm (w/w %)	Intensity (kgray/h)	Total dose (kgray)	M_n	Pressure (ton/cm^2)	Water (%)	Gel %
100/0	1.03	30	80,000	1.5	0	22
100/0	1.03	30	80,000	1.5	10	11
70/30	1.03	30	80,000	1.5	0	33
70/30	1.03	30	80,000	1.5	10	33
50/50	1.03	30	80,000	1.5	0	49
50/50	1.03	30	80,000	1.5	10	42
100/0	1.2	32	2,200,000	1.5	0	69
70/30	1.2	32	2,200,000	1.5	9	68
50/50	1.2	32	2,200,000	0	10	38
50/50	1.2	32	2,200,000	1.5	10	65
30/70	1.2	32	2,200,000	1.5	9	62
0/100	1.2	32	—	0	10	85
70/30	25	12.5	80,000	1.5	0	4.5
70/30	25	25	80,000	1.5	0	20
70/30	25	37.5	80,000	1.5	0	26
70/30	25	50	80,000	1.5	0	38
70/30	25	50	80,000	7.5	0	38
70/30	25	50	80,000	7.5	10	10
70/30	25	100	80,000	1.5	0	53

WATER RETAINING OF HYDROGEL

Table III shows an example case of swelling of polyAAm. The swelling reached a constant independent of the intensity, after a dose of about 50 kgray.

TABLE III
Relationships between Irradiation Conditions and Swelling of Hydrogel Obtained[a]

Radiation intensity (kgray/h)	Dose (kgray)	Gelation yield (%)	Swelling (%)[b]
1.5	21	50	5100
1.5	27	58	3300
1.5	36	68	2400
1.5	43	64	2900
1.5	45	77	1700
1.5	51	72	1500
1.5	60	90	1500
1.5	50	70	1500
12.0	50	73	1500
26.5	50	87	1000

[a] M_n of PAAm = 148,000; water content = 20%
[b] Amount of water taken up by hydrogel at room temperature with respect to the weight of hydrogel.

CONCLUSION

From the experimental results of this work and those of previous work,[3-5,8] the following conclusions were made on the gamma-ray induced crosslinking of PAAm in air:

1. It is desirable for PAAm to have an average molecular weight greater than about 1,500,000.

2. The greater the intensity of radiation, the higher the crosslinking yield, except in the case of the monomer–polymer mixed system where the intensity was not an important factor.

3. When the molecular weight of PAAm is small, an addition of 10–20% of water accelerates the crosslinking in powder form. However, if the polymer powder is compressed to a disk, no water is necessary, and water, in this case, behaves as an inhibitor.

4. There exists a certain molecular weight above which crosslinking takes place. When PAAm has a low molecular weight, the incipient gel dose r_g corresponds to the energy required to build up high molecular weight species. This stage seems to be accelerated by the external pressure (compression) applied to the solid polymer.

5. Irradiation of a large amount of the monomer to obtain directly a crosslinked PAAm, causes a violent sublimation of monomer unless the polymerization vessel is efficiently cooled. This can be avoided by mixing the monomer with the polymer.

The authors wish to express their gratitude to the Consejo Nacional de Investigacion Cientifica y Tecnologia (CONACYT), who partially supported this work under Grant No. PCAFBNA-001805.

References

1. A. Charlesby, *Atomic Radiation of Polymers*, Pergamon, London, 1960; A. Chapiro, *Radiation Chemistry of Polymeric Systems*, Wiley-Interscience, New York, 1960; F. A. Makhlis, *Radiation Physics and Chemistry of Polymers*, Wiley, New York, 1975.
2. P. Alexander and A. Charlesby, *J. Polym. Sci.*, **23**, 355 (1957).
3. G. Burillo and T. Ogawa, *Macromol. Chem., Rapid Commun.*, **1**, 545 (1980).
4. G. Burillo and T. Ogawa, *Radiat. Phys. Chem.*, **18** (5–6), 1143 (1981).
5. G. Burillo and T. Ogawa, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 615 (1983).
6. E. Collinson, F. S. Dainton, and G. S. McNaughton, *Trans. Faraday Soc.*, **53**, 489 (1957).
7. A. Charlesby and S. H. Pinner, *Proc. Roy Soc. (London)*, **A249**, 367 (1959).
8. G. Burillo and T. Ogawa, *Radiat. Phys. Chem.*, **25**, (1–3) 383 (1985).

Received November 11, 1985
Accepted