
**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# Gamma Radiation-Induced Template Polymerization of Acrylic Acid in the Presence of Polyactrylamide

T. Siyam[a]; R. Ayoub[a]
[a] Nuclear Chemistry Department, Hot Labs. Centre Atomic Energy Authority, Cairo, Egypt

**To cite this Article** Siyam, T. and Ayoub, R.(1997) 'Gamma Radiation-Induced Template Polymerization of Acrylic Acid in the Presence of Polyactrylamide', Journal of Macromolecular Science, Part A, 34: 9, 1727 — 1735
**To link to this Article: DOI:** 10.1080/10601329708010038
**URL:** http://dx.doi.org/10.1080/10601329708010038

J.M.S.—PURE APPL. CHEM., A34(9), pp. 1727–1735 (1997)

# GAMMA RADIATION-INDUCED TEMPLATE POLYMERIZATION OF ACRYLIC ACID IN THE PRESENCE OF POLYACTRYLAMIDE

**T. Siyam and R. Ayoub**
Nuclear Chemistry Department
Hot Labs. Centre
Atomic Energy Authority
P. O. Code 13759, Cairo, Egypt



## ABSTRACT

Poly(acrylamide-acrylic acid) resin p(AM-AA) was prepared by gamma radiation-induced polymerization of acrylic acid in the presence of polyacrylamide as a template polymer. The polymerization was studied by a free radical mechanism at different experimental conditions such as: absorbed dose, monomer concentration, polymer/monomer molar ratio and the weight-average molecular weight or the swelling degree of added polymer. The resin was obtained at dose >10 KGy and there is no significant change in the swelling degree of the resin. The results showed that the capacity of the resin increases by increasing the monomer concentration, the weight-average molecular weight of the added polymer and decreases by increasing polymer/monomer molar ratio and the swelling degree of the added polymer. It was also found that the capacity of the resin depends on the radiation dose.

## INTRODUCTION

The polymerization of acrylic acid in the presence of a template polymer by a free radical mechanism exhibits, kinetically, characteristics of a template polymerization [1]. In such a process, complexes may be formed between two different type of polymers under suitable conditions [2-5]. It was reported that hydrogen bonds are the main factor for complex formation in the polymerization of *N*-vinyl-pyrolidone along polymethacrylic acid as a template [6] and also in the polymerization of acrylic or methacrylic acid along poly-4-vinylpyridine as templates [7-9].

In this work, the effect of γ-radiation dose, the monomer concentration the polymer/monomer molar ratio and the weight average molecular weight ( $\overline{Mw}$) or the swelling degree of added polymer was studied on the polymerization of acrylic acid "AA" in the presence of polymerylamide p(AM) were studied using a template polymerization technique for preparation of the resin. The capacity of the obtained resin was determined under different experimental conditions.

### Materials and Experimental Technique

Acrylic acid "AA" (Merck product) inhibited by hydroquinonemonoethylether was distilled under vacuum. Polyacrylamide p(AM) was prepared before by γ-radiation initiated polymerization of acrylamide monomer solution and the weight average molecular weight ($M_W$) was determined as described previously [10]. Acrylic acid was polymerized in the presence of p(AM) using a template polymerization technique as discussed previously [11].

The conversion percent was determined gravimeterically from the weight of the obtained copolymer and the original added polymer. The copolymer composition was also determined using the data of the conversion and the weight of added polymer.

The swelling degree of the polymer was calculated by the following equation:

$$\text{Swelling degree (S)} = (W_S - W)/W$$

where $W_S$ and W are the weight of the polymer after and before the polymer swelling, respectively.

The capacity of the resin tower Cu(II) was determined by the bath technique as described previously [12] at pH~7 using NaOH and copper sulfate concentration of 0.04 M/L at room temperature (25°C).

## RESULTS AND DISCUSSION

### Influence of Radiation Dose

The influence of radiation dose on the polymerization of AA in the presence of p(AM) was studied at the polymer/monomer molar ratio ~0.4. This molar ratio is

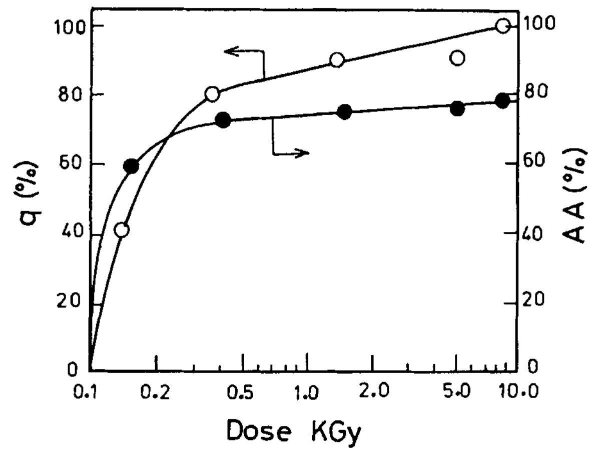
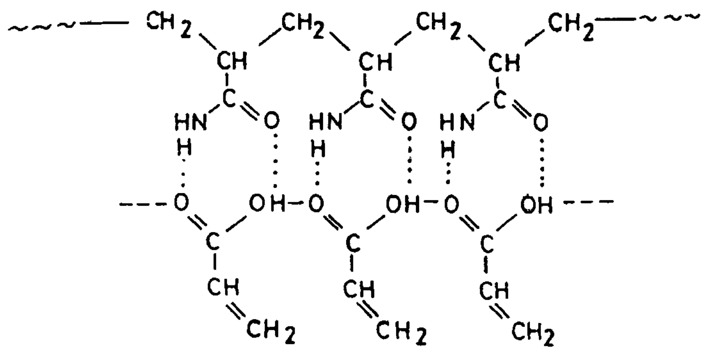



**Figure 1.** Influence of the radiation dose on the polymerization of AA in the presence of PAM, ○. The conversion percent (q%) and ● . The percent of AA in the copolymer.



the obtimum condition for the template polymerization of AA in the presence of poly(diallylethyylamine-hydrochloride) [11] which corresponded to the molar ratio of polymer/monomer of 0.5 in the polymerization of methacrylyic acid on poly(4-vinylpyridine-co-acrylamide) [8]. The results of polymerization are shown in Figure 1 which shows that, at the onset of the polymerization the conversion percent (q%) increases fast then increases slowly before complete conversion. The great increase in the conversion can be attributed to the increase of propagation reactions in the presence of the gel-effect [13,14]of such systems and also increasing the association between the monomer and the added polymer [15-19]. It was assumed that in a polar solvent such as water, acrylic acid is associated via hydrogen bonds and forms "plurimolecular aggregates or molecular association (linear oligomers) [15,19] with itself and with many solvents. Such oligomers may also associate with the added polymer via hydrogen bonds as represented in Structure 1. During the polymerization process the swelling of polymer favors the monomer diffusion to a large monomer-polymer association. This increases the conversion percent.

The conversion percent increases slowly at high doses, and may be due to a monomer depletion and chaining propagation reactions into diffusion-controlled [20,21]. This is in agreement with the previous finding in the polymerization of AA in the presence of poly(diallylethylamine-hydrochloric) [11] and poly(amido-amines) [22].



**Structure 1.** Monomer-polymer association.

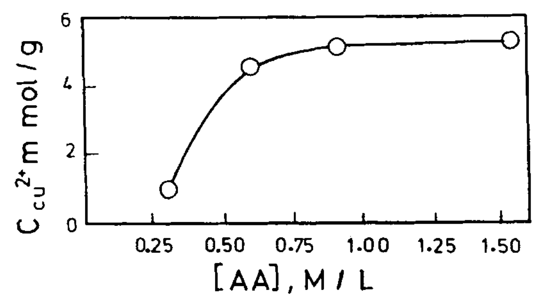



**Figure 2.** Influence of the monomer concentration on the capacity of the resin.



The composition of the formed polymer complex is shown also in Figure 1 which shows that the percent of AA in the copolymer increases by increasing the dose. This is due to increasing the conversion percent.

Also, propagation reactions may occur by the action of the free radicals on the monomer, the complex of the monomer with the added polymer or with the formed polymer. The propagation process was discussed previously in the polymerization of AA along p(DAEA-HCl) as a template polymer [11].

### Influence of Monomer Concentration

The influence of the monomer concentration on the capacity of the obtained resin was studied at a radiation dose of 50.4 KGy and p(AM) concentration of 0.4M/L. The results are shown in Figure 2, which shows that the capacity increases by increasing the monomer concentration. On increasing the monomer concen-

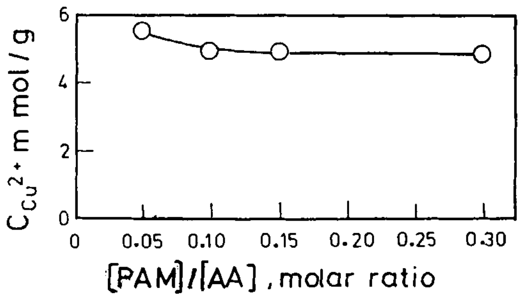



**Figure 3.** Influence of the polymer/monomer molar ratio on the capacity of the resin.



tration, the probability of the association between the monomer and the added polymer increases which then increases the degree of crosslinking (permanent trapped entanglements) between polymer chains of the resin [23,24]. In addition, the number of the carboxylic groups increases by increasing the monomer concentration. These increase the capacity of the obtained resin.

**Influence of the Polymer/Monomer Molar Ratio**

The influence of the added polymer on the resin capacity was studied at a radiation dose of 50.4 KGy and different polymer/monomer molar ratio. The results are shown in Figure 3, which shows that the resin capacity decreases by increasing the concentration of the added polymer. On increasing the amount of the added polymer, the association between the monomer and the added polymer increases which leads to higher increase in the extent of crosslinking between polymer chains of the resin. The higher increase in the extent of crosslinking decreases the resin capacity.

**Influence of Weight-Average Molecular Weight ($M_w$) and Swelling Degree of the Added p(AM):**

The influence of $M_W$ and the swelling degree of the added p(AM) on the capacity of the resin was studied at different polymer molecular weight and constant polymer/monomer molar ratio of 0.4 at different doses. The results are shown in Table 1 which shows that the capacity increases by increasing $M_W$ of the added p(AM). The higher $M_W$ of the added polymer the higher is the capacity of the resin. On increasing $M_W$ the chain length of the added polymer increases and the propability for crosslinking formation increases which then increases the capacity of the resin.

TABLE 1: Influence of Weight-Average Molecular Weight ($M_w$) of the Added Soluble p(AM) on the Capacity of the Resin

| Dose, KGy | C, m mol /g | | |
|---|---|---|---|
| | $\overline{Mw} = 0.6x10^5$ | $\overline{Mw} = 1.0x10^5$ | $\overline{Mw} = 3.0x10^5$ |
| 11.76 | 2.81 | 3.9 | 4.8 |
| 30.24 | 3.0 | 3.75 | 5.4 |
| 42.0 | 3.2 | 5.1 | 3.9 |
| 57.0 | 3.75 | 2.7 | 4.2 |
| 84.0 | 2.5 | 2.4 | 4.35 |

TABLE 2: Influence of the Swelling Degree(s) on the Capacity of the Resin

| Dose, KGy | C, m mol /gm | |
|---|---|---|
| | S = 4 | S = 550 |
| 11.76 | 6.3 | 3.15 |
| 30.24 | 5.1 | 5.25 |
| 42.0 | 7.5 | 3.45 |
| 57.0 | 6.15 | -- |
| 84.0 | 5.48 | 3.60 |

The influence of radiation dose on the capacity of the obtained resin is shown in Table 1 which shows that the capacity increases then decreases by increasing the radiation dose. The increase in the capacity may be attributed to the increase in the degree of crosslinking between polymer chains of the resin [13, 25, 26]. The decrease in the capacity may be attributed to higher increase in the extent of crosslinking and decreasing the number of carboxylic groups [27, 28]. In addition, the number of amide groups decreases due to imidation of amide groups [25, 29] This

TABLE 3: Influence of Radiation Dose on Swelling Degree of the Resin at Different $M_W$

| Dose, KGy | Swelling degree of the resin | | |
|---|---|---|---|
| | $\overline{Mw} = 0.6x10^5$ | $\overline{Mw} = 1.0x10^5$ | $\overline{Mw} = 3.0x10^5$ |
| 11.76 | 6.4 | 4.2 | 3.81 |
| 30.24 | 6.5 | 3.4 | 3.4 |
| 42.0 | 8.2 | 7.3 | 6.12 |
| 57.12 | 5.6 | 2.6 | 3.75 |
| 84.0 | 4.0 | 1.9 | 4.5 |



agrees with the previous findings [12, 22] in preparation of cationic and amphoteric resins.

The influence of the swelling degree on the capacity of the resin was studied for different p(AM) gels at constant polymer/monomer molar ratio of 0.4 at different doses. The results are shown in Table 2 which shows that the capacity of the resin decreases by increasing the swelling degree of the added p(AM) gel. On increasing the swelling degree of the added p(AM) gel the degree of crosslinking and the association for the added gel decreases which decreases the degree of crosslinkings in the formed resin. Consequently, the capacity of the resin decreases.

The data of Tables 1 and 2 shows that the capacity of the resin which is prepared in p(AM) gel is higher than that of soluble p(AM). This may be attributed to higher degree of crosslinking for p(AM) gel relative to soluble ones.

**Swelling Behavior**

The swelling degree of the resin are shown in Table 3. The results show that the swelling degree varies from 2 to 6 and that there is a little change. The swelling degree increases then decreases by increasing the radiation dose. This may be due to the increase of crosslinking by increasing the radiation dose which hinders the swelling of the formed copolymer.

## REFERENCES

[1] J. Freguson and S. A. D. Shah, *Eur. Polym. J., 4*, 344 (1968).

[2] J. Gons, E. J. Vorenkamp, and G. Challa, *J. Polym. Sci. A-1, 13*, 1699 (1975).

[3] Y. Sakaguchi, K. Tamaki, T. Shimizu, and Nishino Kohunshi Kagaku, *Chem. Abst. 73*, 88202 h (1970).

[4] N. Shavit and J. Gohen, Polymerization Organized Systems, Midland Macromol. Monogr, H. G. Elias, Ed., Gordon & Breach, Vol. 3, pp. 213-228, N.Y. (1977).

[5] R. Buter, Y. Y. Tan, and G. Challa, *J. Polym. Sci. A-1, 10*, 1031 (1972).

[6] T. Bartels, Y. Y. Tan, and G. Challa., *J. Polym. Sci. A-1, 15*, 341 (1977).

[7] K. Fujmori, G. T. Trainor, and M. J. Costigan, *J. Polym. Sci., A-1*, 22, 2479 (1984).

[8] K. Fujimori, *Polym. Bull., 8*, 207-210 (1982).

[9] K. Fujimori and G. T. Trainor, *Polym. Bull., 9*, 204 (1983).

[10] T. Siyam, *Studies on Gamma Radiation-Induced Copolymerization of Acrylamide- Sodium Acrylate as Flocculant*, Faculty of Science, Cairo Univ. (1981).

[11] T. Siyam, *J. Macromolecular. Sci. Pure. Appl. Chem., A31*, 383 (1994).

[12] T. Siyam, M. M. Abdel-Hamid, and I. M. El-Naggar, *Macromolecular Reports., A32, 5&6,* 871 (1995).

[13] A. Chapiro, *Radiation Chemistry of Polymeric Systems,* Interscience Publishers, New York., Ch. IV, p. 131 (1962).

[14] G. Odian, *Principles of Polymerization,* McGraw Hill Inc., N.Y., I, Ch. 3, p. 165 (1970).

[15] A. Chapiro and J. Dulieu, *Eur. Polym. J., 13*, 563 (1977).

[16] A. Chapiro and L. Perec, *ibid*, *7*, 1335 (1971).

[17] V. F. Gromov, P. M. Homikosh, A. K. Abkin, and A. K. Vysokomolek, *Soedin Ser., B 12*, 767 (1970).

[18] V. F. Kuenkov and V. A. Myagchenkov, *Eur. Polym. J., 16*, 1229 (1980).

[19] A. Chapiro, *Pure Appl. Chem., 643* (1981).

[20] A. K. Ghaudri and S. R. Palit, *Trans. Farad. Soc., 53*, 476 (1957).

[21] A. M. North and G. A. Reed, *J. Polym. Sci., A-11*, 1311 (1963).

[22] T. Siyam, I. M. El-Naggar, and H. F. Aly, *International Topical Meeting on Nuclear and Hazardous Waste Management Spectrum '96*, p. 66, Aug. 18-23, Seattle, Washinghton (1996).

[23] D. W. Koetsier, Y. Y. Tan, and G. Challa, *J. Polym. Sci. A-1, 18,* 1933 (1980).

[24] S. Candau, J. Bastide, and M. Delsanti, *Structural, Elastic, and Dynamic Properties of Swollen Polymer Networks*, in: Advances in Polymer Science (Polymer Networks) p. 27, Springer-Verlag Berlin Heidelberg, N.Y. (1982).

[25] T. Okada, I. Shiqaki, T. Suwa, and S. Machi, *J. Appl. Polym. Sci., 24,* 1713 (1979).

[26] H. J. Ji, W. X. Zhang, Z. W. Sun, J. J. Che, and Z. H. Li, *Radiat. Phys. Chem., 42(1-3),* 81 (1993).

[27] E. V. Egorov and P. D. Novikov, *Action of Ionizing Radiation on Ion-Exchange Materials*, Atomizdat, Moscow (1965).

[28] A. M. Semushin and I. A. Kusin, *Zhur Priki. Khim*, *33*, 2323 (1960).

[29] T. Wada, H. Sekiya, and S. Machi, *J. Appl. Polym. Sci.*, *20*, 3233 (1976).