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Grafting of Acrylonitrile onto Gelatin in Zinc Chloride Medium

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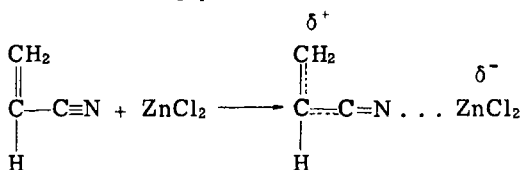
ABSTRACT

Grafting of gelatin with acrylonitrile in zinc chloride medium has been studied using potassium persulfate as the initiator. The rate of grafting, grafting efficiency, and percentage of grafting are calculated. The grafting results are discussed in the light of the rate of grafting. The enhanced activity of the monomer is due to the formation of AN . . . ZnCl₂ complexes.

INTRODUCTION

Significant progress has been made recently in the chemical modification of industrial proteinaceous materials to achieve improved physicochemical properties. Envisaging graft copolymerization as a means of modification, it was felt that it would be interesting to synthesize graft copolymers using gelatin as the backbone. Reaction in the presence of zinc chloride has been viewed as a conventional radical polymerization [1]. The interaction of polar monomers with zinc chloride is considered to result in the formation of a donor-acceptor complex, and that the effect of zinc chloride is to activate the monomer independent of its effect on gelatin. The free-radical-initiated polymerization of polar monomers containing pendant nitrile

and ester groups, e.g., acrylonitrile and methyl methacrylate in the presence of metal halides such as zinc chloride, is characterized by increased rates of polymerization, as well as the formation of polymers with considerably higher molecular weights than those formed in the absence of metal halides [2, 3]. This effect has been attributed to the formation of a complex between the polar group of the monomer and metal halides, resulting in an increase in reactivity of the complexed monomer [2].



The increased reactivity of the complexed monomer has been attributed to the delocalization of the electrons in the double bond of the polar electron acceptor monomer as a result of the complexation with the electron-accepting metal halide [4].

EXPERIMENTAL

Materials

Gelatin (Riedel, Germany) was used as such in all investigations. Acrylonitrile (AN) was washed with sodium hydroxide (5% solution) and ortho-phosphoric acid (3% solution) to remove inhibitors and basic impurities, respectively, washed with water, dried over calcium chloride, and then distilled in the presence of nitrogen under vacuum and stored at 5°C. Potassium persulfate (KPS) (Riedel, Germany) was used as obtained. Zinc chloride (BDH, G.R.) was used as such.

Grafting Procedure

The requisite amount of gelatin was dissolved in 60% aqueous zinc chloride. Grafting reactions were conducted in closed Corning glass ampules in nitrogen atmosphere. Specified amounts of gelatin, monomer, and KPS were added in zinc chloride medium to get a homogeneous phase, and the contents were stirred with a slow stream of nitrogen. The temperature was maintained at 60°C. Reactions were stopped by pouring the contents into excess cold acetone. The gross polymer was recovered by filtration, dried, and weighed.

Polymer Characterization

Isolation of Graft Copolymer

The gross polymer is a physical mixture of ungrafted gelatin, grafted gelatin, and free homopolymer. The isolation method of graft copolymerization by selective solvent-extraction is based on the differences in solubility between the graft copolymer and the ungrafted homopolymer. The unbound homopolymer was extracted with dimethylformamide (DMF). After 48 h, each sample was further extracted with fresh solvents till a constant value was obtained. The pure graft copolymer thus isolated was purified again and subjected to analysis. The amount of apparent graft formation was obtained from the difference in weight of extracted and original specimens, each of them weighed in a moisture-free state.

Hydrolysis of Gelatin Graft Copolymers

Samples of gelatin graft copolymers were hydrolyzed with 6 N HCl in a sealed boro-silicate glass tube. The contents were evacuated to minimize oxidation of methionine [5]. The temperature was maintained at 105-110°C for a period of 24 h. At the end of the hydrolysis period the hydrolysate was cooled. The side chain polyacrylonitrile samples were reprecipitated by dissolving in DMF and precipitated with methanol. The purified side chain grafts were used for viscosity measurements.

Chain Length Measurements

Chain lengths n of the purified grafted side chains were determined by viscometry. Distilled dimethylformamide was used as solvent. A 0.1% solution of the polymer was prepared and filtered through a glass filter to remove any dust particles. The dust-free polymer solution was taken in the Ubbelohde suspended level dilution viscometer with a flow time of 90 s for the solvent. The temperature of the thermostat was regulated to $\pm 0.05^\circ\text{C}$. Flow times for the polymer solutions and solvents were recorded at the temperature chosen. Intrinsic viscosities $[\eta]$ for the polymer solutions were determined. Chain lengths were computed from the $[\eta]$ values by using suitable Mark-Houwink equations relating $[\eta]$ with molecular weight $[M]$. For polyacrylonitrile [6]

$$[\eta] = 2.43 \times 10^{-4} M_n^{0.75} \text{ in DMF at } 25^\circ\text{C}$$

(a) Grafting Efficiency (G.E.). Grafting efficiency was computed gravimetrically from the weight of homopolymer formed and the total weight of graft and homopolymer:

$$\text{G.E.} = \frac{R_g}{R_p} = \frac{R_g}{R_g + R_h}$$

All weights are expressed in grams.

(b) Percent Grafting (P.G.).

$$\text{P.G.} = \frac{(\text{weight of graft copolymer} - \text{weight of gelatin})}{\text{weight of gelatin}} \times 100$$

(c) Rate of Graft Polymerization (R_g). The rate of graft polymerization was computed from the weight of polymer bound as grafts to the backbone. This is given by the amount of graft copolymer obtained after complete isolation of the free homopolymer:

$$R_g = R_p - R_h$$

In order to gain insight into the mechanism of the reaction, the effects of such variables as monomer concentration, initiator concentration, backbone concentration, reaction time, and temperature on graft copolymerization of acrylonitrile onto gelatin were studied.

Effect of Monomer Concentration

An increase in monomer concentration resulted in an increase of percent grafting, grafting efficiency, and rate of grafting as seen in Table 1. It was observed that the viscosity of the reaction medium increased with increasing monomer concentration, and this is attributed to the formation of a ZnCl_2 -AN complex. It seemed likely that the complex might exist in polymeric form in solution and hence gives rise to high viscosity. Thus the salt might complex with the propagating radicals in such a way as to increase their reactivity to acrylonitrile [7, 8]. It is also noteworthy that silk, which is a polyamide, promotes the polymerization of methyl methacrylate, presumably through monomer complexation [9].

The plot of R_g vs $[\text{AN}]^{1.0}$ was a straight line passing through the origin as shown in Fig. 1A. $\log R_g$ vs $\log [\text{AN}]$ gave a slope value of unity, showing the first-order dependence of rate on monomer concentration (Fig. 1B).

Effect of Initiator Concentration

Percent grafting, grafting efficiency, and rate of grafting were found to increase as the initiator concentration increases (Table 2). This may be due to the fact that an increase in persulfate concentration accelerates complex formation which results in a greater number of active centers.

TABLE 1. Potassium Persulfate-Acrylonitrile-Gelatin System in Aqueous Zinc Chloride Medium: Effect of Monomer on Grafting^a

AN $\times 10^1$ mol/L	$R_g \times 10^6$ mol/L·s	Grafting efficiency (%)	Percent grafting	Chain length n
3.06	29.01	74.30	41.48	150.47
4.59	42.12	78.41	60.23	215.66
6.11	58.34	80.34	83.48	290.60
7.65	72.17	84.44	103.28	360.25
9.16	88.26	89.17	126.30	440.40
10.70	105.32	89.54	150.72	475.34

^aKPS = 10×10^{-3} mol/L; gelatin = 3.33×10^{-4} mol/L; total volume = 50 mL; temperature = 60°C; time = 90 min.

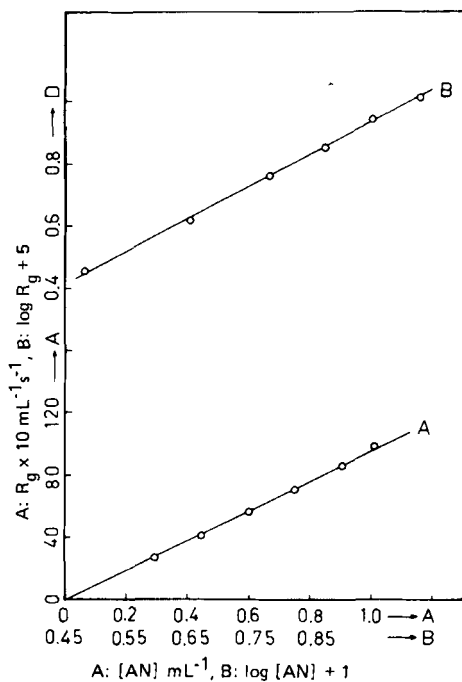


FIG. 1. Effect of [monomer] on rate of grafting. A: R_g vs [AN]. B: $\log R_g$ vs $\log [AN]$.

TABLE 2. Potassium Persulfate-Acrylonitrile-Gelatin System in Aqueous Zinc Chloride Medium: Effect of Initiator on Grafting^a

KPS $\times 10^3$ mol/L	$R_g \times 10^6$ mol/L's	Grafting efficiency (%)	Percent grafting	Chain length n
6	16.24	84.32	23.24	398.12
10	26.42	85.12	37.81	350.24
16	40.04	86.16	57.30	201.81
20	51.83	88.21	74.16	165.54
24	62.17	88.46	88.97	135.46
30	76.28	88.94	109.16	100.72

^aAN = 6.11×10^{-1} mol/L; gelatin = 3.33×10^{-4} mol/L; total volume = 50 mL; temperature = 60°C; time = 90 min.

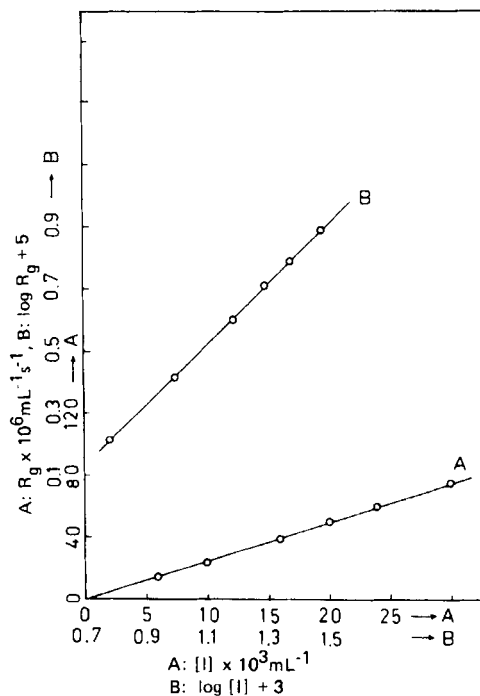


FIG. 2. Effect of [initiator] on rate of grafting. A: R_g vs $[I]$. B: $\log R_g$ vs $\log [I]$.

A plot of $\log R_g$ vs $\log [I]$ gave a slope of unity and a plot of R_g vs $[I]$ gave a straight line passing through the origin (Fig. 2A and B). This may be attributed to the fact that the initiator forms a redox system with the functional groups of gelatin, which results in the observed change in the kinetic order.

Effect of Backbone Concentration

From the tables it can be seen that as the concentration of gelatin increases, grafting efficiency and rate of grafting increase (Table 3). Percent grafting was found to pass through a maximum. This may be due to the fact that the relative increment of side chain grafted is less, comparatively, than that of the backbone.

A plot of $\log R_g$ vs $\log [\text{gelatin}]$ gave a slope value of unity, and R_g vs $[\text{gelatin}]$ was a straight line passing through the origin (Fig. 3A and B). This observation indicates that rate of grafting is first-order dependent on the gelatin concentration.

Effect of Temperature

Percent grafting, grafting efficiency, and rate of grafting were found to increase with increasing temperature (Table 4). The increase in temperature enhanced decomposition of the initiator and also activated the backbone, and hence the observed increase in percent grafting, grafting efficiency, and rate of grafting. This is a characteristic behavior of homogeneous free radical polymerizations in contrast to that of polymerizations involving precipitation of the

TABLE 3. Potassium Persulfate-Acrylonitrile-Gelatin System in Aqueous Zinc Chloride Medium: Effect of Gelatin Concentration on Grafting^a

Gelatin $\times 10^4$ mol/L	$R_g \times 10^6$ mol/L·s	Grafting efficiency (%)	Percent grafting	Chain length n
2.2	26.24	64.32	53.64	325.12
2.5	30.12	72.46	53.88	298.18
3.2	38.88	78.53	55.64	265.36
3.8	45.51	78.97	54.27	235.52
4.8	56.17	79.32	53.59	194.38
6.3	70.24	80.29	50.26	133.24

^aKPS = 10×10^{-3} mol/L; AN = 6.11×10^{-1} mol/L; total volume = 50 mL; temperature = 60°C; time = 90 min.

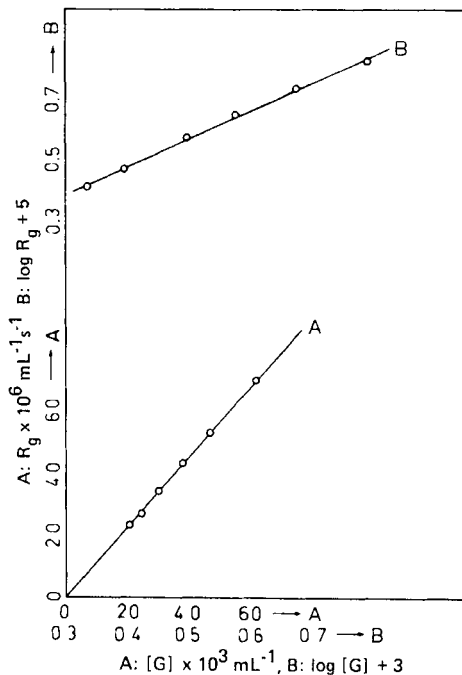


FIG. 3. Effect of [gelatin] on rate of grafting. A: R_g vs $[G]$. B: $\log R_g$ vs $\log [G]$.

TABLE 4. Potassium Persulfate-Acrylonitrile-Gelatin System in Aqueous Zinc Chloride Medium: Effect of Temperature on Grafting^a

Temperature (°C)	$R_g \times 10^6$ mol/L·s	Grafting efficiency (%)	Percent grafting	Chain length n
30	11.96	84.20	17.11	275.32
40	17.73	87.32	25.37	242.16
50	23.37	88.47	33.44	238.29
60	28.81	89.24	41.23	200.12
70	45.19	93.30	64.67	196.52
80	62.45	94.28	89.36	190.31

^aAN = 6.11×10^{-1} mol/L; gelatin = 3.33×10^{-4} mol/L; KPS = 10×10^3 mol/L; total volume = 50 mL; time = 90 min.

polymer formed. This trend has also been observed by other workers in the graft copolymerization of acrylic acid to poly(vinyl alcohol) [9] and methyl cellulose [10].

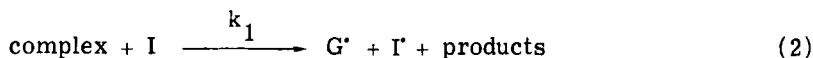
Chain Length

The chain length was found to increase with monomer concentration and decrease with an increase in initiator concentration.

Mechanism and Rate Laws

From the foregoing discussions it follows that the rate of grafting is proportional to acrylonitrile concentration, persulfate concentration, and gelatin concentration. It is also found that chain length is proportional to acrylonitrile concentration. The above observations lead to the following mechanism for the graft copolymerization reaction. The elementary reactions taking place during graft copolymerization are outlined.

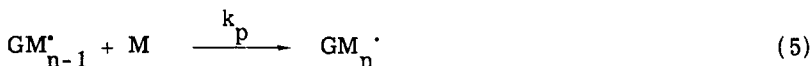
- 1) Production of gelatin radicals $[G^*]$:



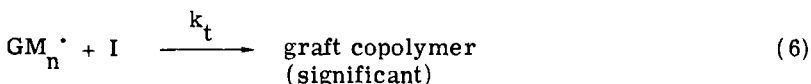
- 2) Initiation with monomer:



- 3) Propagation:



- 4) Chain transfer to initiator:



- 5) Rate law and chain length: Assuming steady-state conditions,

$$k_2 [G^*] [M] = k_t [GM_n^*] [I] \quad (7)$$

$$[GM_n^*] = \frac{k_2[G^*][M]}{k_t[I]} \quad (8)$$

$$\frac{d[G^*]}{dt} = Kk_1[I]^2[G] = k_2[M][G^*] = 0 \quad (9)$$

i. e.,

$$[G^*] = \frac{Kk_1[I]^2[G]}{k_2[M]} \quad (10)$$

substituting the value of $[G^*]$ in Eq. (8), we get

$$[GM_n^*] = \frac{k_1K[G][I]}{k_t} \quad (11)$$

$$R_g = k_p[GM_n^*][M] \quad (12)$$

Substituting the value of $[GM_n^*]$ from Eq. (11) into Eq. (12), we get

$$R_g = \frac{k_p k_1 K [G] [I] [M]}{k_t} \quad (13)$$

$$R_g = \frac{k_g [G] [I] [M]}{k_t} \quad (14)$$

where $k_g = k_p k_1 K / k_t$, and G^* , GM_n^* , M^* , and I^* refer to gelatin radical, gelatin graft radical, monomer radical, and initiator radical, respectively.

$$\text{chain length } n = \frac{k_p [GM_n^*][M]}{k_t [GM_n^*][I]} \quad (15)$$

$$n = \frac{k_p [M]}{k_t [I]} \quad (16)$$

TABLE 5. Potassium Persulfate-Acrylonitrile System in Aqueous Zinc Chloride Medium: Effect of [Monomer] on Grafting

[AN] $\times 10$ mol/L	$R_h \times 10^6$ mol/L·s	Chain length n
3.06	23.53	125.21
4.59	32.32	180.31
6.11	43.61	235.12
7.65	56.18	300.52
9.16	67.29	360.02
10.70	75.14	399.18

^a[KPS] = 10×10^{-3} mol/L; zinc chloride = 60%; total volume = 50 mL; temperature = 60°C; time = 90 min.

Another set of experiments was carried out in the absence of gelatin. The effect of monomer concentration and effect of initiator concentration on the rate of homopolymerization were studied.

Effect of Monomer Concentration

The rate of homopolymerization was found to increase with increasing monomer concentration (Table 5). This could be due to the formation of a coordination complex $ZnCl_2$ -AN. The enhancement of the reactivity of the complex formation is ascribed to increased conjugation resulting from the complex formation. The complex might exist in polymeric form in solution and thus give rise to high viscosity. This could result in a lower rate of termination, thus increasing the rate of homopolymerization. Similar results were obtained during the polymerization of methyl methacrylate in zinc chloride medium [5].

A plot of R_h vs [AN] was a straight line passing through the origin, and $\log R_h$ vs $\log [AN]$ plot gave a slope value of unity which showed that R_h was proportional to the first power of [AN] (Fig. 4A and B).

Effect of Initiator Concentration

Rate of homopolymerization was found to increase when the concentration of initiator was increased (Table 6).

A plot of $\log R_h$ vs $\log [I]$ gave a slope value of 0.5 and R_h vs $[I]^{0.5}$ was a straight line passing through the origin (Fig. 4C and D). These observations imply that R_h is proportional to the half power of initiator concentration.

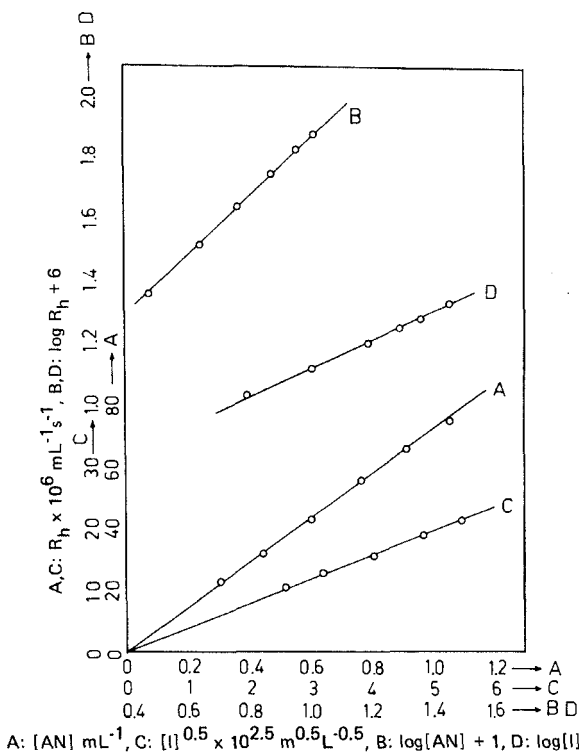


FIG. 4. Effect of [monomer] and [initiator] on rate of homopolymerization. A: R_h vs $[\text{AN}]$. B: $\log R_h$ vs $\log [\text{AN}] + 1$. C: R_h vs $[\text{I}]^{0.5}$. D: $\log R_h$ vs $\log [\text{I}] + 3$.

TABLE 6. Potassium Persulfate-Acrylonitrile System in Aqueous Zinc Chloride Medium: Effect of Initiator on Grafting

$[\text{KPS}] \times 10^3 \text{ mol/L}$	$R_h \times 10^6 \text{ mol/L} \cdot \text{s}$	Chain length n
6	18.50	212.24
10	24.24	198.31
16	32.31	160.27
20	36.19	151.46
24	39.65	138.57
30	43.34	110.61

$[\text{AN}] = 3.1 \times 10^{-1} \text{ mol/L}$; zinc chloride = 60%; temperature = 60°C ; time = 90 min; total volume = 50 mL.

The above observations indicate that the rate of homopolymerization is proportional to the first power of monomer concentration and to the half power of initiator concentration. By comparing the two systems, it is seen that the reaction in the presence of gelatin proceeds much more rapidly than that in the absence of gelatin. The conversion of monomer to polymer is much higher in the presence than in the absence of gelatin. The molecular weights of the grafted polymers are found to be higher than those of homopolymers. The possible explanation may be as follows.

The AN . . . ZnCl₂ complexes are arrayed in the form of a matrix. In the presence of gelatin the matrix complexes may be absorbed or anchored on the gelatin, resulting in the formation of a stable matrix. As a result, the monomer conversion and molecular weight of graft copolymers are higher than in ordinary homopolymers.

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