

# KINETICS AND MECHANISM OF GRAFT POLYMERIZATION OF ACRYLONITRILE ONTO STARCH INITIATED WITH POTASSIUM PERSULFATE

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## Abstract

A new potassium persulfate redox system has been investigated for the graft polymerization of vinyl monomers. In this study potassium persulfate system was used for initiation the polymerization. Graft polymerization of acrylonitrile (AN) onto starch (Sta) was carried out in aqueous solution using potassium persulfate (I) redox system. It was found that the percentage of grafting and rate of grafting were all dependent to some extent, on the concentration of the I, AN, Sta and Sta/water as well as reaction time and temperature. The kinetics of the graft polymerization of AN onto Sta in aqueous solution was studied by Kjeldahl method (quantity and qualitative determination nitrogen content), and the kinetics of AN homopolymerization in the same system was studied by bromometry titration (residue monomer determination). The following rate expression (rate of graft polymerization and rate of homopolymerization)  $R_g = k \cdot [AN]^{1.185} \cdot [I]^{0.499} \cdot [Sta]^{0.497}$  and  $R_h = k \cdot [AN]^{1.359} \cdot [I]^{0.436}$  were obtained and a suitable mechanism was suggested. The graft copolymer was investigated with an infrared spectroscope. The overall activation energy was found to be 56.95 kJ/mol within the temperature range of 40-65°C.

## Introduction

Graft copolymerization of starch can be initiated by transition metal ions [3,4] of which  $Co^{+3}$ ,  $V^{+3}$  and especially  $Ce^{+4}$  were widely used in the graft modification of cellulose [5] and starch [6]. Since Mino put forward for the first time the ceric ions could form

copolymerization of starch grafting ethylene monomers initiated by ceric salts. The high price of ceric initiators limited the wide use of this product. In order to find an inexpensive and efficient initiator, in this study we used an initiator system  $K_2S_2O_8$ . Potassium persulfate system was found to be an efficient redox initiator in this specific system in aqueous medium. This method is one of the most interesting methods of graft vinyl monomers on polymer presenting oxidizable functional groups, in which free radicals are formed on a trunk polymer. Grafting has been utilized as an important technique for modifying physical and chemical properties of a poly-

**Keywords:** Kinetics; Starch; Acrylonitrile; Graft polymerization; Potassium persulfate very efficient redox systems in the presence of organic reductors [7]. Many specialists have studied the

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mer. Vinyl graft copolymerization onto starch represents useful way to elucidate the kinetics and mechanism of copolymerization reaction as well as to obtain information required for the improvement of starch with respect to enlarging the range of its utilization. The objective the present work was to graft polymerize AN onto starch in aqueous media by  $K_2S_2O_8$  redox system.

## Experimental Section

### Materials

Starch, AN and  $K_2S_2O_8$  were all supplied by Merck and used without further purification. AN was freshly distilled under reduced pressure before use.

### Procedure

Starch ( $w_0$ ) was slurrified in 25 ml distilled water in a neck flask which was equipped with a stirrer and a condenser and funnel. The starch slurry was preheated at  $85^\circ\text{C}$  for about half an hour under the atmosphere of nitrogen gas and cooled to the reaction temperature desired ( $60^\circ\text{C}$ ). After that, initiator was added first, followed by monomer ( $w_3$ ) after 30 min [8]. The above reaction mixture was stirred and reacted for 2-3 hours and then was terminated by pouring the product into ethanol to precipitate it. Then it was washed thoroughly with alcohol, dried and weighed ( $w_1$ ) [9].

The starch-grafted-polyacrylonitrile (S-G-PAN) copolymers were treated with three DMF washes to remove homopolymer [10]. Then dried and weighed ( $w_2$ ). Thus

$$\text{graft (\%)} = ((w_2 - w_0)/w_0) \times 100$$

and

$$\text{convert (\%)} = ((w_2 - w_0)/w_3) \times 100, [11,12].$$

The optimum conditions for synthesis S-g-PAN were obtained:

$[I] = 0.009 \text{ M}$ ,  $[AN] = 1.88 \text{ M}$ ,  $T = 60^\circ\text{C}$ ,  $\text{Time} = 2.5 \text{ h}$  and  $\text{starch/water} = 1:15$

### Evidence of Graft

The produced copolymer was characterized by FT-IR spectroscopy (8101 M Shimadzu). The spectrum of the grafting sample showed both the characteristic absorption of starch at  $3000\text{-}3800 \text{ cm}^{-1}$  and characteristic absorption of acrylonitrile homopolymer at  $2240 \text{ cm}^{-1}$  which were not present in starch, this testified the existence of grafting.

## Results and Discussion

### Effect of Initiator, Monomer and Starch Concentration

The grafting reaction may be influenced by the

concentration of initiator, monomer and starch. Effects of initiator concentration within the range of  $0.001\text{-}0.009 \text{ M}$  on the percentage of grafting (graft (%)) were obtained by Kjeldahl method and the percentage of homopolymer (homo (%)) by bromometric titration are shown in Figures 1 and 2. It is observed that with increasing initiator concentration, the graft yield and homopolymer increase. The number of grafting sites on the backbone of the starch increases by the interaction of the starch with the initiator, resulting the increase in graft yield.

Effects of monomer concentration within the range of  $0.373\text{-}1.88 \text{ M}$  at constant initiator and starch concentrations on the graft (%) and the homo (%) are shown in Figures 3 and 4. It is observed that with increasing monomer concentration, the graft yield increases.

Effects of starch concentrations within the range of  $16.66\text{-}100 \text{ g/l M}$  at constant initiator and monomer concentration on the graft (%) and the homo (%) are shown in Figures 5 and 6. It is observed that with increasing starch concentration, the graft yield increases. The significant enhancement in the graft yield by increasing starch concentration, makes it understandable that as the active centers on starch molecules increase, as a result, the graft yield increases too.

### Kinetics of Graft Polymerization and Homopolymerization

The rate of graft polymerization ( $R_g$ : grafted monomer (mol/sec)) depends on the concentration of initiator, monomer and starch as following:

$$R_g = k \cdot [AN]^a \cdot [I]^b \cdot [Sta]^c$$

The plot of  $\ln(R_g)$  vs.  $\ln[I]$  is linear and plotted in Figure 7. The slope of the line is 0.499, which suggests that the order of the reaction with respect to initiator is 0.499.

The plot of  $\ln(R_g)$  vs.  $\ln[AN]$  is linear and plotted in Figure 8 and indicating that the order of the reaction with respect to monomer is 1.185.

The plot of  $\ln(R_g)$  vs.  $\ln[Sta]$  is linear and plotted in Figure 9. The slope of line is 0.497, which suggests that the order of the reaction with respect to starch is 0.497. Therefore:

$$R_g = k \cdot [AN]^{1.185} \cdot [I]^{0.499} \cdot [Sta]^{0.497} \quad (a)$$

The rate of homopolymerization ( $R_h$ : homopolymerization monomer (mol/l)) is dependent on concentrations of initiator and monomer as following:

$$R_h = k \cdot [AN]^a \cdot [I]^b \cdot [Sta]^c$$

The plot of  $\ln(R_h)$  vs.  $\ln[I]$ ,  $\ln[AN]$  and  $\ln[Sta]$  are linear with slopes 0.436, 1.359 and  $-0.0001$ ,

respectively; and plotted in Figures 10, 11 and 12, which suggested that the order of the reaction with respect to initiator, monomer, and starch are 0.436, 1.359 and -0.0001, respectively, therefore:

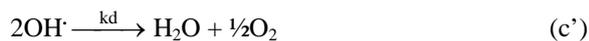
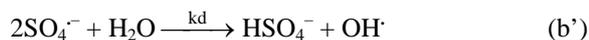
$$R_h = k \cdot [AN]^{1.359} \cdot [I]^{0.436} \quad (b)$$

**Effect of Temperature**

The grafting reaction was carried out at different temperatures ranging from 40-65°C in constant experimental conditions. Graft yields increases with increasing temperature (Fig. 13). The plot of ln(R<sub>g</sub>) vs. 1/T is linear and activation energy was obtained as 56.95 kJ/mol (Fig. 14).

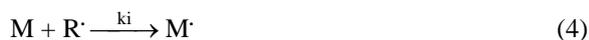
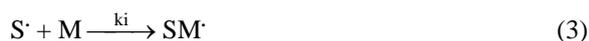
**Mechanism**

When an aqueous solution of persulfate is heated, it decomposes to produce sulfate ion radical along with other radical species [3, 6].



The rate of Equation (a') is low and hence the step (a') is capable to initiate vinyl graft polymerization onto starch. The overall reaction scheme for free radical graft polymerization can be represented by the following reaction steps:

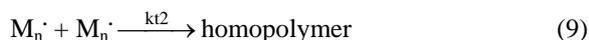
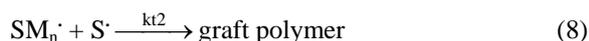
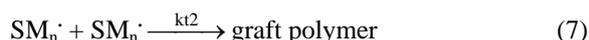
1 – Initiation



2 – Propagation



3 – Termination



S: starch, I: potassium persulfate, M: monomer.

On the basis of the above reaction schemes and the

use of quasi steady state assumption for free radicals [R<sup>·</sup>], [M<sub>n</sub><sup>·</sup>], [SM<sub>n</sub><sup>·</sup>], [S<sup>·</sup>] the following expressions were derived: [13]

$$d[SM_n^{\cdot}]/dt = 0, d[S^{\cdot}]/dt = 0 \Rightarrow [SM_n^{\cdot}] = \frac{((k_i[R^{\cdot}][S])/k_{t2})^{1/2}}{\quad} \quad (10)$$

$$d[M_n^{\cdot}]/dt = 0 \Rightarrow [M_n^{\cdot}] = ((k_i[M][R^{\cdot}])/k_{t2})^{1/2} \quad (11)$$

$$d[R^{\cdot}]/dt = 0 \Rightarrow 2(f_m + f_s)k_d[I] - k_i[M][R^{\cdot}] - k_i[S][R^{\cdot}] = 0 \quad (12)$$

$$f_m = \alpha \cdot [M] \quad (13)$$

$$f_s = \beta \cdot [S] \quad (14)$$

where f<sub>m</sub> and f<sub>s</sub> are the initiator efficiencies for M and S, respectively. Furthermore, since the initiation of monomer and surface sites are independent from each other, one may distinguish between the two types of initiations and obtain:

$$2f_m k_d [I] = k_i [M][R^{\cdot}] \Rightarrow [R^{\cdot}] = 2k_d [I] \alpha / k_i \quad (15)$$

$$2f_s k_d [I] = k_i [S][R^{\cdot}] \Rightarrow [R^{\cdot}] = 2k_d [I] \beta / k_i \quad (16)$$

By replacing Equations 15 and 16 with Equations 10 and 11:

$$[SM_n^{\cdot}] = (2k_d \beta [S][I] / k_{t2})^{1/2} \quad (17)$$

$$[M_n^{\cdot}] = (2k_d \alpha [M][I] / k_{t2})^{1/2} \quad (18)$$

Rate of polymerization:

$$R_p = R_g + R_h = k_p [M][SM_n^{\cdot}] + k_p [M][M_n^{\cdot}] \quad (19)$$

$$R_g = k_p (2k_d \beta / k_{t2})^{1/2} \cdot [M] \cdot [S]^{1/2} \cdot [I]^{1/2} \quad (20)$$

$$R_h = k_p (2k_d \alpha / k_{t2})^{1/2} \cdot [M]^3 \cdot [I]^{1/2} \quad (21)$$

Equations 20 and 21 are identical with Equations (a) and (b) respectively, established from the experiment. This indicates that the reaction mechanism suggested above, is acceptable.

**Conclusion**

Based on the results presented in this paper, we conclude that potassium persulfate can initiate the graft polymerization of starch with acrylonitrile, efficiently. Under the experimental conditions, suitable rate equations were proposed as: R<sub>g</sub> = k · [AN]<sup>1.185</sup> · [I]<sup>0.499</sup> · [Sta]<sup>0.497</sup> and R<sub>h</sub> = k · [AN]<sup>1.359</sup> · [I]<sup>0.436</sup>. The apparent activation energy was 56.95 kJ/mol.

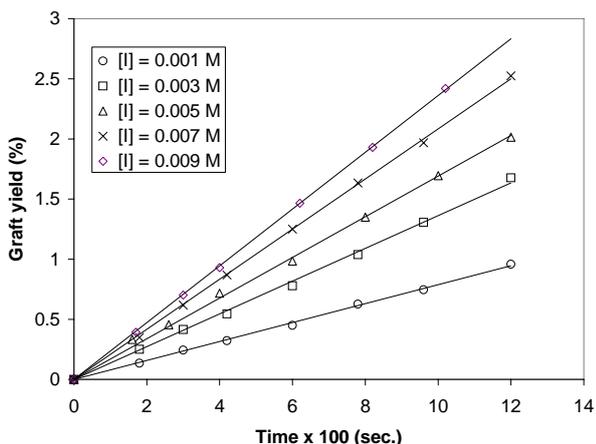


Figure 1. Effect of initiator concentration on grafting [AN] = 188 M, starch/water = 1:15, T = 60°C.

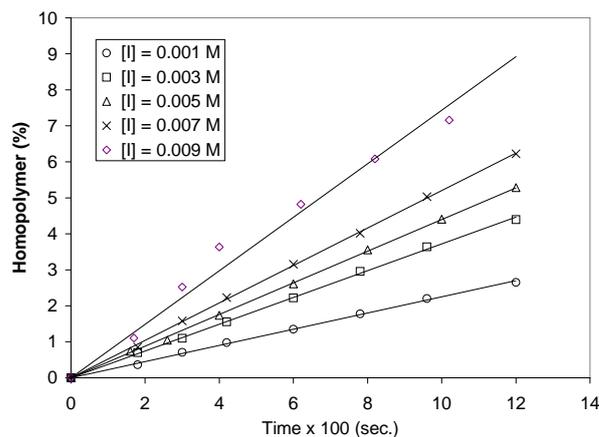


Figure 2. Effect of initiator concentration on homopolymerization [AN]=1.88 M, starch/water =1:15, T=60°C.

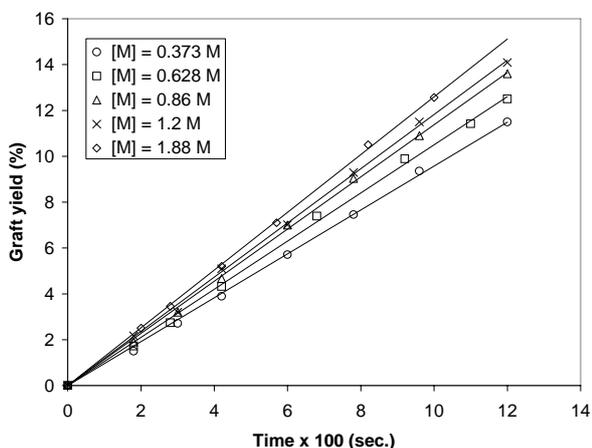


Figure 3. Effect of monomer concentration on grafting [I] = 0.009 M, starch/water = 1:15, T = 60°C.

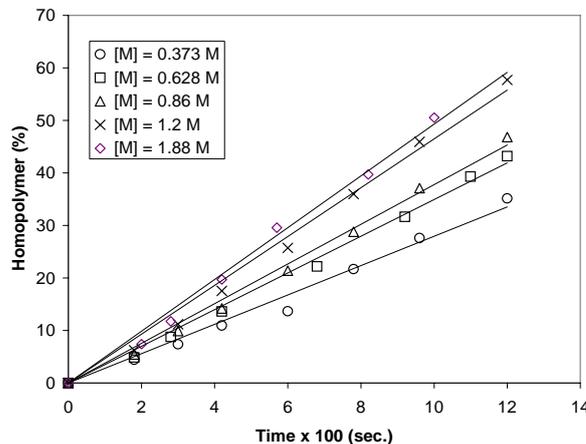


Figure 4. Effect of monomer concentration on homopolymerization [I] =0.009 M, starch/water = 1:15, T = 60°C.

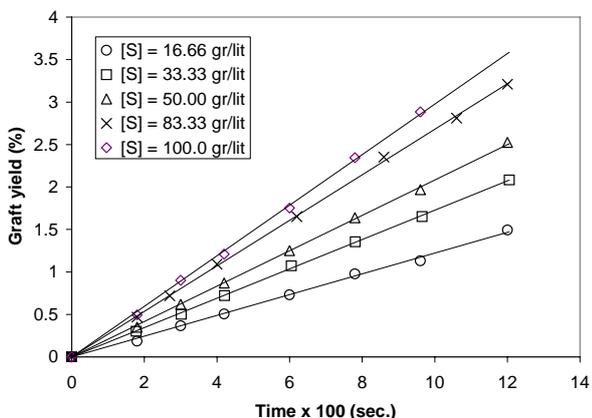


Figure 5. Effect of starch concentration on grafting [AN] = 1.88 M, [I] = 0.009, T = 60°C.

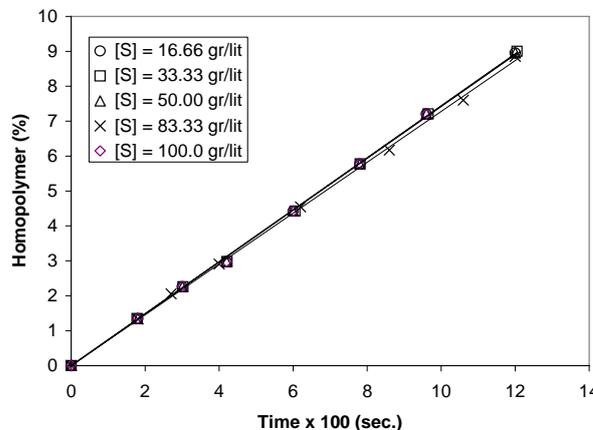
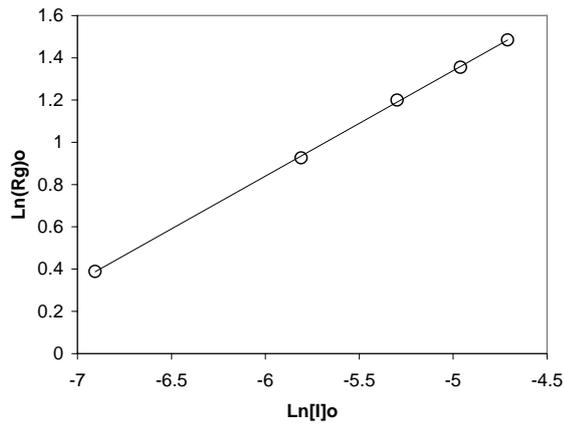
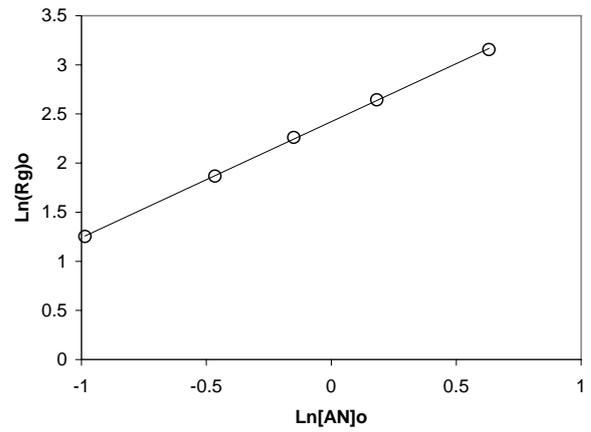


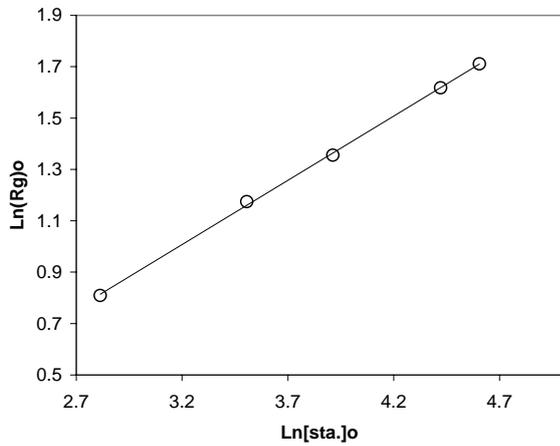
Figure 6. Effect of starch concentration on homopolymerization [AN] = 1.88 M, [I] = 0.009, T = 60°C.



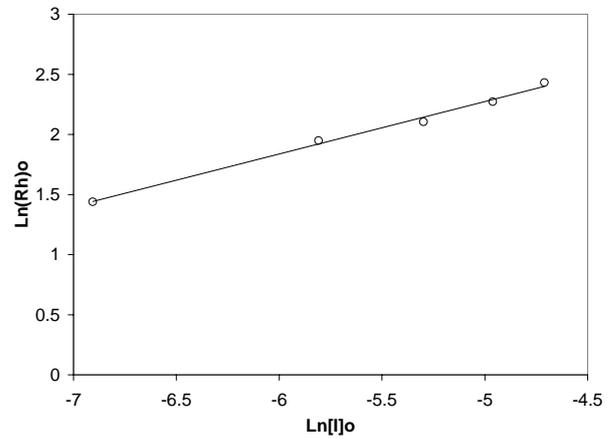
**Figure 7.** Plotting  $\ln(Rg)_o$  vs.  $\ln[I]_o$ , other conditions are as in Figure 1.



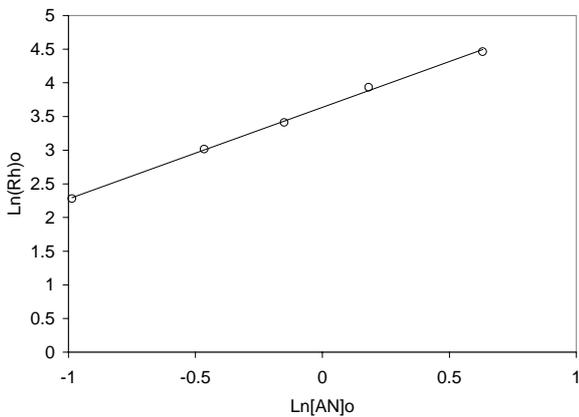
**Figure 8.** Plotting  $\ln(Rg)_o$  vs.  $\ln[AN]_o$ , other conditions are as in Figure 3.



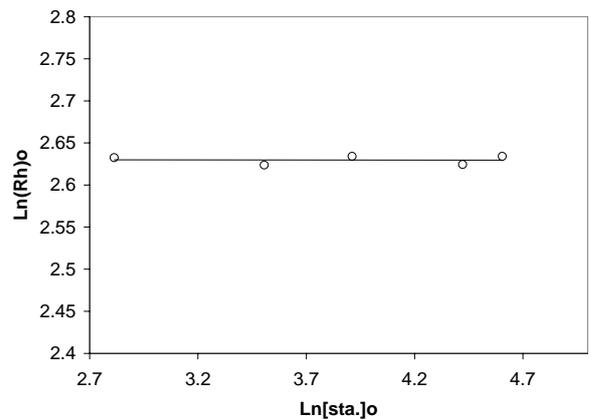
**Figure 9.** Plotting  $\ln(Rg)_o$  vs.  $\ln[sta.]_o$ , other conditions are as in Figure 5.



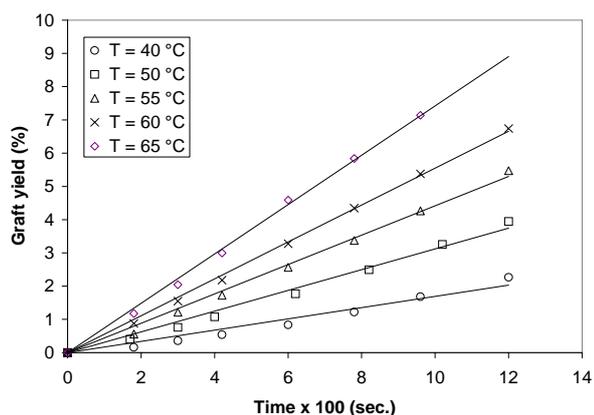
**Figure 10.** Plotting  $\ln(Rh)_o$  vs.  $\ln[I]_o$ , other conditions are as in Figure 2.



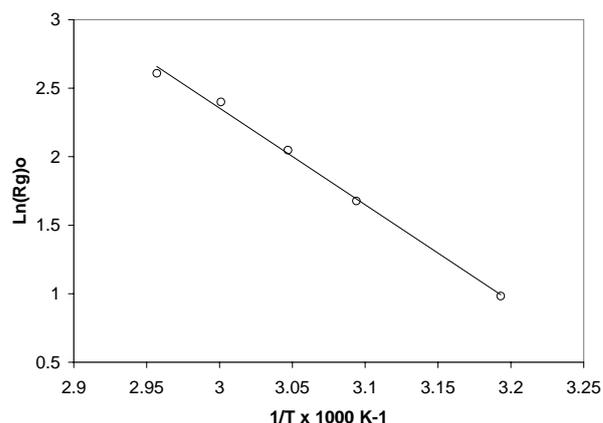
**Figure 11.** Plotting  $\ln(Rh)_o$  vs.  $\ln[AN]_o$ , other conditions are as in Figure 4.



**Figure 12.** Plotting  $\ln(Rh)_o$  vs.  $\ln[sta.]_o$ , other conditions are as in Figure 6.



**Figure 13.** Effect of temperature on grafting [AN] = 1.88 M, [I] = 0.009, starch/water = 1:15.



**Figure 14.** Plotting  $\ln(Rg)_0$  vs.  $1/T$ , other conditions are as in Figure 13.

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