

Kinetics of graft copolymerization of acrylonitrile onto sago starch using free radicals initiated by ceric ammonium nitrate

M. R. Lutfor, M. Z. A. Rahman, S. Sidik, A. Mansor, J. Haron & W. M. Z. Wan Yunus

To cite this article: M. R. Lutfor, M. Z. A. Rahman, S. Sidik, A. Mansor, J. Haron & W. M. Z. Wan Yunus (2011) Kinetics of graft copolymerization of acrylonitrile onto sago starch using free radicals initiated by ceric ammonium nitrate, *Designed Monomers and Polymers*, 4:3, 252-259, DOI: [10.1163/156855501750536233](https://doi.org/10.1163/156855501750536233)

To link to this article: <https://doi.org/10.1163/156855501750536233>



Published online: 02 Apr 2012.



Submit your article to this journal [↗](#)



Article views: 201



View related articles [↗](#)

Kinetics of graft copolymerization of acrylonitrile onto sago starch using free radicals initiated by ceric ammonium nitrate

M. R. LUTFOR*, M. Z. A. RAHMAN, S. SIDIK, A. MANSOR,
J. HARON and W. M. Z. WAN YUNUS

Department of Chemistry, Faculty of Science and Environmental Studies, University of Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Abstract—This article reports an experimental investigation on the graft copolymerization of acrylonitrile monomer onto sago starch in which ceric ammonium nitrate was an initiator. The grafting reactions were initiated by the known free radical method. It was observed that the rate of graft polymerization and the grafting efficiency were dependent on the concentration of ceric ammonium nitrate (CAN), acrylonitrile (AN), sago starch (AGU, anhydro glucose unit), and the reaction period. The equation for the rate of polymerization (R_p) is a first-order dependence of the monomer (AN) concentration and the square root of the CAN concentration. The experimental results were used to verify the kinetic equation relating the graft fraction of poly(acrylonitrile) on sago starch.

Keywords: Free radical; acrylonitrile; graft fraction; rate of graft polymerization.

1. INTRODUCTION

The chemical modification of high-molecular-weight compounds such as starch and cellulose using graft copolymerization is a unique and effective method. However, the simultaneous generation of both a homopolymer and a graft copolymer in graft copolymerization is due to the competitive reactions of homopolymeric radicals and backbone polymeric radicals towards monomer molecules. Although the free radical graft copolymerization mechanism has been known for some time, there are few articles describing the kinetics of graft copolymerization which realistically predict the molecular structure reaction rate [1, 2]. Brydon *et al.* [2] produced a styrene monomer grafted onto polybutadiene in benzene solution at 60°C with benzoyl peroxide as the initiator. They proposed a primary radical initiation grafting

*To whom correspondence should be addressed.

Kinetics of graft copolymerization of acrylonitrile onto sago starch using free radicals initiated by ceric ammonium nitrate

M. R. LUTFOR*, M. Z. A. RAHMAN, S. SIDIK, A. MANSOR,
J. HARON and W. M. Z. WAN YUNUS

Department of Chemistry, Faculty of Science and Environmental Studies, University of Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia

Abstract—This article reports an experimental investigation on the graft copolymerization of acrylonitrile monomer onto sago starch in which ceric ammonium nitrate was an initiator. The grafting reactions were initiated by the known free radical method. It was observed that the rate of graft polymerization and the grafting efficiency were dependent on the concentration of ceric ammonium nitrate (CAN), acrylonitrile (AN), sago starch (AGU, anhydro glucose unit), and the reaction period. The equation for the rate of polymerization (R_p) is a first-order dependence of the monomer (AN) concentration and the square root of the CAN concentration. The experimental results were used to verify the kinetic equation relating the graft fraction of poly(acrylonitrile) on sago starch.

Keywords: Free radical; acrylonitrile; graft fraction; rate of graft polymerization.

1. INTRODUCTION

The chemical modification of high-molecular-weight compounds such as starch and cellulose using graft copolymerization is a unique and effective method. However, the simultaneous generation of both a homopolymer and a graft copolymer in graft copolymerization is due to the competitive reactions of homopolymeric radicals and backbone polymeric radicals towards monomer molecules. Although the free radical graft copolymerization mechanism has been known for some time, there are few articles describing the kinetics of graft copolymerization which realistically predict the molecular structure reaction rate [1, 2]. Brydon *et al.* [2] produced a styrene monomer grafted onto polybutadiene in benzene solution at 60°C with benzoyl peroxide as the initiator. They proposed a primary radical initiation grafting

*To whom correspondence should be addressed.

mechanism and found that the rate coefficient for the primary radical attacking the monomer molecules was slightly higher than that for the primary radical attacking the backbone polymer. They also found that the polymerization of the monomers appeared to follow the normal kinetics of the reaction; the rate of polymerization also showed a first-order dependence on the monomer concentration and the square root of the initiator concentration. In our earlier paper [3], we derived a new model for the kinetic equation of methyl acrylate grafted onto sago starch; their concentrations were derived and the validity of the predicted model was verified by experimental results. In the present study, we have investigated how the nature of the initiator (CAN), the monomers (AN), the backbone polymer (sago starch), and other factors influence the rate of graft copolymerization.

2. EXPERIMENTAL

2.1. Materials

Acrylonitrile monomer was purchased from Fluka. The inhibitor was removed from the monomer using columns filled with chromatographic grade activated alumina. Sago starch was obtained from Tepung Sago Ind. Ltd., Malaysia. Ceric ammonium nitrate (BDH), hydroquinone (BDH), methanol (Beaker), and the other chemicals used were of analytical reagent grade.

2.2. Graft copolymerization

Graft copolymerizations were carried out in a 250 ml three-neck flask equipped with a stirrer, condenser, and a thermostated water bath. The starch slurry was prepared from 2.50 g of sago starch with 100 ml of distilled water and transferred into the flask. The slurry was preheated at 80°C for about 30 min and N₂ gas was passed into the flask to remove oxygen. The flask contents were cooled to 50°C and then 2.0 ml of diluted H₂SO₄ (water–H₂SO₄; 1 : 1) was added to the reaction mixture. About 5 min later, the required volume of 0.1 M CAN was added and 10 min later, the required amount of acrylonitrile monomer was added to the mixture. For the kinetic analysis, three series of experiments, in each of which the concentration of one of the three reactants (CAN, AN, AGU) was varied, while the other were two kept constant, were carried out; the parameters are shown in Table 1. Each experiment was carried out under various reaction periods, i.e. 10, 20, 30, 40, and 50 min. After a specific reaction period, 4.0 ml of 0.1 M hydroquinone solution was added to each reaction to stop the polymerization. The product was then poured into 300 ml of methanol to induce precipitation. The grafting products were washed several times with methanol–water (4 : 1) and dried at 50°C to a constant weight [4, 5].

Table 1.

Experimental conditions for the kinetic analysis of graft polymerization reactions by acrylonitrile onto sago starch

Series	Run No.	[AGU] (mol l ⁻¹)	[CAN] (mol l ⁻¹ × 10 ⁻³)	[AN] (mol l ⁻¹)
P	1	0.146	9.520	0.300
P	2	0.146	9.520	0.506
P	3	0.146	9.520	0.650
P	4	0.146	9.520	0.720
Q	5	0.146	2.380	0.506
Q	6	0.146	3.501	0.506
Q	7	0.146	4.761	0.506
Q	2	0.146	9.520	0.506
R	8	0.060	9.520	0.650
R	9	0.105	9.520	0.650
R	3	0.146	1.520	0.620

Reaction periods of 10, 20, 30, 40, and 50 min were used for the P and Q series of experiments and 50 min for the R series. Temperature: 50 °C; [H₂SO₄]: 0.190 mol l⁻¹.

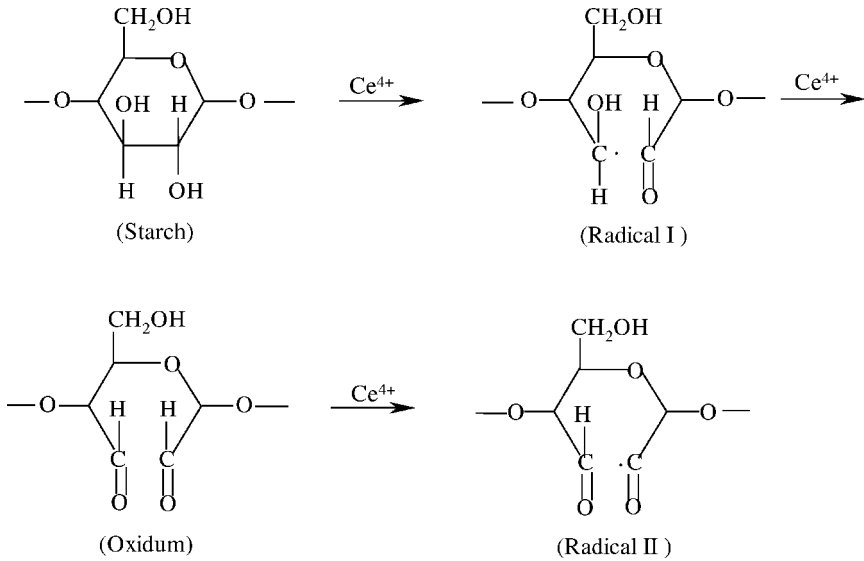
2.3. Extraction of the homopolymer

The crude products (2.000 g) of polyacrylonitrile (PAN) grafted sago starch were weighed accurately and extracted with DMF in a Soxhlet extractor for 12 h to remove PAN homopolymer. The pure products were oven-dried at 50 °C to a constant weight. The grafted copolymers were characterized by FT-IR, TG, and the DSC technique, which is presented elsewhere [5].

3. RESULTS AND DISCUSSION

3.1. Mechanism of acrylonitrile grafting onto sago starch

A great deal of attention has been paid to the mechanism of various monomers with starch/cellulose materials and a considerable body of literature was found [6–8]. According to the mechanism suggested by Ranby [8], the transition metal ions attack the starch (AGU) and a free radical is produced on the starch molecule, as shown in Scheme 1 (radical I). Mingzhu *et al.* [4] proposed a new mechanism, which is the modification of the mechanism suggested by Ranby [8]. After decomposition of the Ce⁴⁺–starch complex, the aldehyde groups in the starch may be oxidized to generate carbonyl radicals to initiate grafting, as shown in Scheme 1 (radical II). Therefore, two kinds of radicals were created on the starch backbone and both radicals may initiate graft copolymerization [3].



Scheme 1.

3.2. Rate of polymerization and grafting efficiency

We derived expressions for the rate of polymerization and grafting efficiency in our earlier paper [3]. The rate of polymerization can be expressed by

$$R_p = k_p \frac{k k_d}{k_t} [\text{ST}]^{1/2} [\text{Ce}^{4+}]^{1/2} [\text{M}], \quad (1)$$

where k_p , k , k_d , and k_t are the propagation, equilibrium, dissociation, and termination constant, respectively. ST and M represent the sago starch and acrylonitrile monomer, respectively. Equation (1) is the normal kinetic relationship for a simple radical polymerization. It shows that the rate of polymerization (R_p) is a first-order dependence of the monomer concentration [M] and a half-order dependence of $[\text{Ce}^{4+}]$ and [ST], respectively.

The graft fraction (GF) is the consumption between monomer and sago starch for initiator radicals; and the derivation of GF has been given in our earlier paper [3]. The effect of the acrylonitrile monomer ratio on GF is given in the following equation:

$$\frac{1}{(1 - \text{GF})^{1/2}} = 1 + \frac{k k_d [\text{ST}]}{k_{12} [\text{M}]}. \quad (2)$$

Equation (2) correctly indicates that GF becomes zero at zero starch or at infinitely high monomer concentrations.

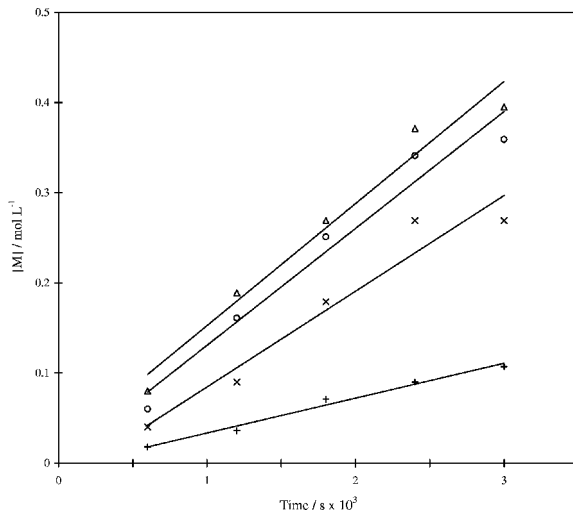


Figure 1. Plot of the quantity of polymerized monomer formed (expressed as mol of monomer units per l) as a function of time for the series 'P' experiment. Temperature: 50°C; [H₂SO₄]: 0.190 mol l⁻¹; [AGU]: 0.146 mol l⁻¹; [CAN]: 9.52 × 10⁻³ mol l⁻¹. Δ [AN]: 0.720 mol l⁻¹; + [AN]: 0.300 mol l⁻¹; \times [AN]: 0.506 mol l⁻¹; \circ [AN]: 0.650 mol l⁻¹.

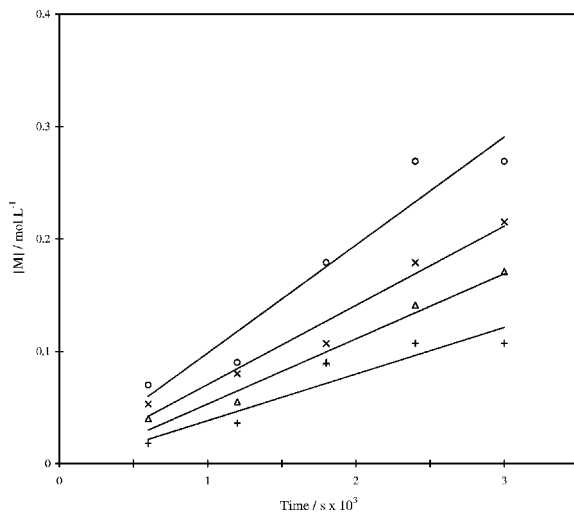


Figure 2. Plot of the quantity of polymerized monomer formed (expressed as mol of monomer units per l) as a function of time for the series 'Q' experiment. Temperature: 50°C; [H₂SO₄]: 0.190 mol l⁻¹; [AN]: 0.506 mol l⁻¹; [AGU]: 0.146 mol l⁻¹. Δ [CAN]: 0.0035 mol l⁻¹; + [CAN]: 0.0023 mol l⁻¹; \times [CAN]: 0.0047 mol l⁻¹; \circ [CAN]: 0.0095 mol l⁻¹.

3.3. Verification of the rates of polymerization

The quantity of polymerized monomer can be expressed in mol of monomer unit per litre, according to Berlin and Kislenko [1]. Therefore, plots of the monomer concentration [M] as a function of time for series P and Q experiments are presented

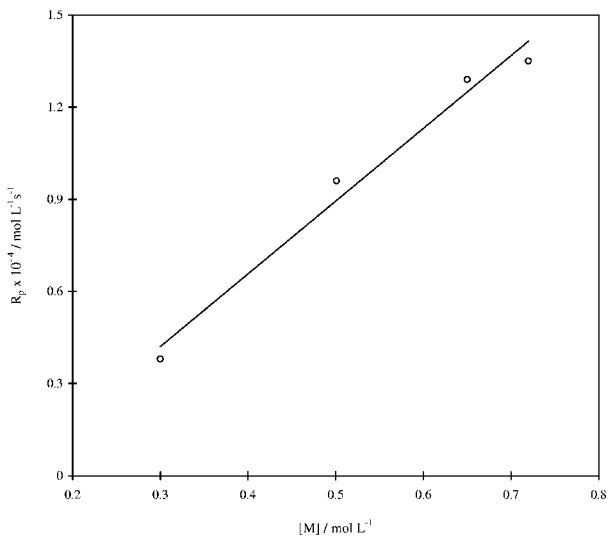


Figure 3. Rates of polymerization (R_p) from Fig. 1 as a function of the monomer concentration. Other conditions as in Fig. 1.

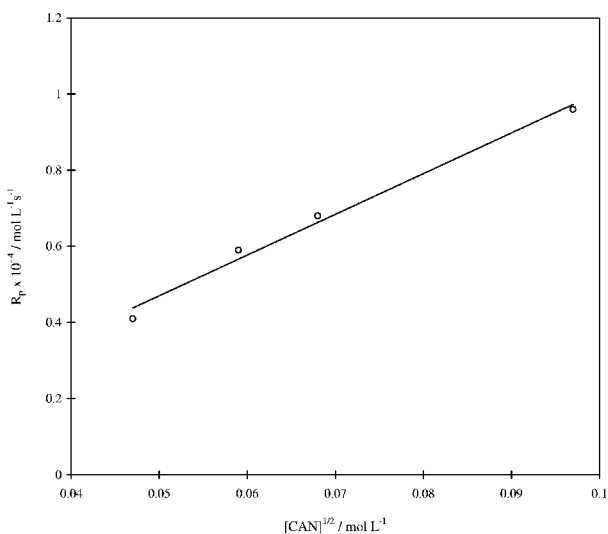


Figure 4. Rates of polymerization (R_p) from Fig. 2 as a function of the square root of the initiator concentration $[CAN]$. Other conditions as in Fig. 2.

in Figs 1 and 2, respectively. The rates of polymerization (R_p) were calculated from Fig. 1 and the values of R_p were plotted as a function of the monomer (AN) concentration in Fig. 3. The rate of polymerization shows a first-order dependence of the acrylonitrile monomer concentration. Similarly, the rates of polymerization were obtained from Fig. 2; R_p shows a half-order dependence of the initiator concentration $[CAN]$ in Fig. 4. The R_p results were obtained from the P and Q series

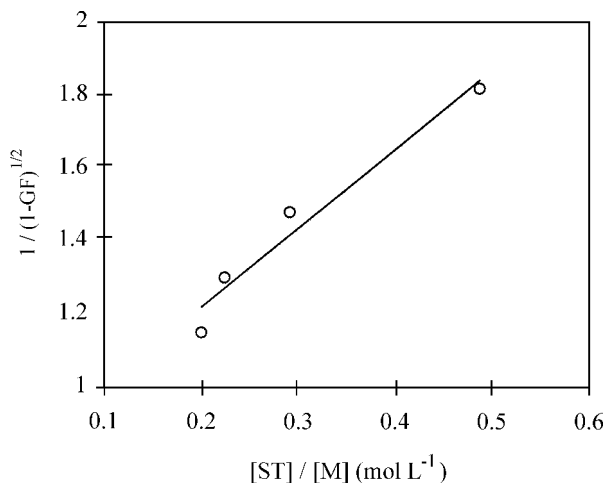


Figure 5. Dependence of the grafted fraction of polymerized acrylonitrile on the ratio of sago starch to monomer concentration according to equation (2).

of experiments and the acrylonitrile consumption follows normal kinetics according to equation (1). Therefore, the equation for the rate of polymerization was verified using the experimental results and the proposed reaction mechanism.

3.4. Poly(acrylonitrile) grafting efficiencies

The poly(acrylonitrile) graft fraction GF, the fraction of polymerized acrylonitrile chemically bound to the sago starch, is proposed by Brydon *et al.* [9] to be $GF = [(total\ weight\ of\ polyacrylonitrile\ graft\ polymer) - (weight\ of\ homopolymer\ (PAN))]/(total\ weight\ of\ polyacrylonitrile\ graft\ polymer)$.

The values of $1/(1 - GF)^{1/2}$ are plotted against the reciprocal monomer concentration (from series P) at a constant sago starch concentration (from series R) in Fig. 5. The data points fit a straight line well and an ordinate intercept of unity was attained at a certain monomer concentration. The required straight line and intercept of unity were obtained at concentrations of monomer up to $0.650\ mol\ l^{-1}$ and equation (2) was tested by Fig. 5. The slope of the line in Fig. 5 yields the ratio kk_d/k_{i2} and the value of the slope obtained is 2.17. The ratio kk_d/k_{i2} expresses the relative rates of initiator (Ce^{4+}) attack on the sago starch and monomer. The rate of initiation of polymerization was therefore faster than the rate of homopolymer radical formation. From the experimental results, the value of the slope obtained was greater than 1 ($kk_d/k_{i2} = 2.17$), therefore the ratio indicated that Ce^{4+} attack on starch was preferred rather than the monomer molecule in the competitive reactions. However, the Ce^{4+} attack on monomer is not small at higher monomer concentrations. Beyond a monomer concentration of $0.650\ mol\ l^{-1}$, the highest amount of homopolymer is formed in the copolymerization. The predicted model was not satisfactory when there was excessive homopolymer formation in the grafted copolymer products. Therefore, a straight line was observed up to $0.650\ mol\ l^{-1}$ monomer; beyond

this monomer concentration, the data deviated from a straight line in Fig. 5. The free radical formation using Ce^{4+} onto sago starch molecule is preferable, rather than the monomer molecule, and it was most similar to the results of Brydon *et al.* [2] and our previous investigation [3].

4. CONCLUSION

A rate equation for polymerization has been established from the proposed reaction mechanism and the experimental results. The proposed model of equation (2) was tested using the plot of $1/(1 - GF)^{1/2}$ against the reciprocal monomer concentration (from series P) and the sago starch concentration (from series R), respectively. The required straight line and ordinate intercept of unity were attained at a certain limit of monomer concentration (0.650 mol l^{-1}). There is a limitation when excessive homopolymer is formed in the grafted products; then the proposed kinetic model is not valid beyond a monomer concentration of 0.650 mol l^{-1} .

Acknowledgement

This research was supported by an IRPA grant (No. 09-02-04-0057) from the Ministry of Science, Technology and Environment, Malaysia, 1997.

REFERENCES

1. A. A. Berlin and V. N. Kislenko, *Prog. Polym. Sci.* **17**, 765 (1992).
2. A. Brydon, G. M. Burnett and G. G. Cameron, *J. Polym. Sci. Polym. Chem. Ed.* **12**, 1011 (1974).
3. M. R. Lutfor, S. Sidik, W. M. Z. Wan Yunus, M. Z. Rahman, A. Mansor and M. J. Haron, *J. Appl. Polym. Sci.* **77**, 784 (2000).
4. L. Mingzhu, R. Cheng and M. A. Cheng, *J. Polym. Sci. Part A* **31**, 3181 (1993).
5. M. Lutfor Rahman, Ph.D. Thesis, University Putra Malaysia, Ch. 4, pp. 85, 94 (1999).
6. R. J. Ceresa, *Block and Graft Copolymerization*, Vol. 1. John Wiley, New York (1973).
7. J. S. Shukla and G. K. Sharma, *J. Polym. Sci. Polym. Chem. Ed.* **25**, 595 (1987).
8. B. Ranby, *Macromolecules* **17**, 2512 (1984).
9. A. Brydon, G. M. Burnett and G. G. Cameron, *J. Polym. Sci. Polym. Chem. Ed.* **11**, 3255 (1973).