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Modeling of Copolymerization of Acrylonitrile onto Starch Phosphate via Ceric Ammonium Nitrate Initiation.

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ABSTRACT

The synthesis of copolymerization of maize starch phosphate with acrylonitrile, in presence of ceric ammonium nitrate as initiator, was investigated. Experiments have been previously performed in order to study the polymerization kinetics. A theoretical analysis of the undertaken process has been carried out, leading to the development of a lumped parameter mathematical model for the description of polymerization process. The model parameters were verified and validated using the experimental results to achieve a reliable tool for design, replication, scaling-up and optimization. The model is based on the continuity and mass balance, accounting for the reaction rate equations, consequently solved in terms of reaction conversions. The model verification and validation have been achieved. A full description for the behavior undertaken by each ion species involved in the synthesis is reported. Further, the dependence of temperature on kinetic parameters involved was examined and expressed in terms of Arrhenius equation. Equations representing the rate of acrylonitrinile consumption in the grafting process are derived in terms of overall rate coefficient, concentrations and temperature.

Keywords: Acrylonitrile, ceric, grafting, kinetics, modeling, starch

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INTRODUCTION

Recently, research on the use of superabsorbent polymers, usually called hydrogels, as water managing tools for the renewable of arid and desert environment have attracted great attention, [1-4]. One of the various techniques embraced to produce "hydrogels" is chemical grafting polymerization followed by saponification process. Graft polymerization is one of the most active and accessible methods of chemical modification of high molecular weight compounds, in particular, carbohydrate polymers. The unique requirement for the latter is the presence of surface reactive sites from which polymer chains can propagate. Previous studies have shown that the free-radical graft polymerization of vinyl monomers is a competent and controllable method for creating a condensed grafted polymer layer[1, 2, 5,6]. Its advantages are that it takes place in aqueous media with good yield of final product, and used a wide choice of monomers, making possible the preparation of graft copolymers with different physico-chemical properties under relevant process conditions. In graft polymerization, the generation of free-radicals along the natural macromolecule backbone as well as on the monomers is best performed by chemical methods of initiation by the use of chain-transfer initiators, such as hydrazine redox systems, transition metals, fenton reagent, persulphate, etc.

Moreover, the optimized combination of fertilizers and superabsorbent polymers may improve the nutrition of plants, mitigate the environmental impact from water-soluble fertilizers, reduce water loss by evaporation, and lower the frequency of irrigation. This is achieved through the introduction of an effective inorganic nutrient group in the product. Initiated by this particular interest, a research project has been undertaken by the authors, (Innovative Hydrogels Based on Carbohydrates to Improve Efficiency of Water-Use for Agricultural Purposes (Sandy-Lands Reclamation), project ID: 4226 (TC/3/ARP/2010/SFP-5.2), funded by the Academy of Scientific Research & Technology, Egypt[7,8], to synthesize new modified hydrogel, based on maize starch in which a phosphate group has been first incorporated, as effective cost superabsorbent in agricultural purposes.

In the present article, a mathematical model was developed and verified to identify the first essential stage in hydrogel superabsorbent synthesize, i.e. the polymerization, with main objective of producing information on the reaction course, thermodynamically and kinetically, in view of batch reactor process design.

MATERIALS AND METHOD

Kinetic Investigated Scheme

Polymerization of vinyl monomer onto starch phosphate was prepared by first generating free radicals on starch phosphate (St-P) and then allowing these radicals to serve as macro initiators for polymerization of the vinyl monomer. The most widely used methods of chemical initiation are the reaction of ceric salts, such as ceric ammonium nitrate (CAN)[9, 10, 11,12]. Further, it is known that starch ceric complex was formed during reaction of starch with ceric ions, which is reduced to cereous, a hydrogen atom is oxidized and a free radical is formed on starch. The starch free radical may then react with the monomer to initiate polymerization or may be further oxidized to generate a second radical (St-P-OX) also initiating the grafting reaction.

In this section, suggested mechanism for the preparation of grafted acrylonitrile (AN) onto phosphorylated starch, initiated by ceric ammonium nitrate, are presented and accordingly, kinetic models are developed. For the sake of simplicity, relevant assumptions are undertaken as follows[1,2]:

1- the pseudo – steady – state hypothesis is applied to the intermediate and radical species, (invariant rate coefficients approximation).
2- the long-chain hypothesis is assumed for propagation and termination reactions for both homopolymer and grafted polymer chains, thereby introducing the invariance of rate coefficients for the two reactions respectively.
3- termination by disproportionation is assumed of negligible importance.

The mechanism of polymerization of AN onto St-P using CAN as initiator is proposed as follows:

Scheme of Reactions

Initiation reactions

$$St - P + Ce^{4+} \overset{k/k'}{\longleftrightarrow} \qquad [Complex] \tag*{[1]}$$

$$[Complex] \overset{k_d}{\rightarrow} St - P^o \tag*{[2]}$$

$$St - P^o + AN \overset{k_i}{\rightarrow} St - P - AN^o \tag*{[3]}$$

$$AN + Ce^{4+} \overset{k_i}{\rightarrow} AN^o + Ce^{3+} H^+ \tag*{[4]}$$

$$St - P^o + Ce^{4+} \overset{k_i}{\rightarrow} St - P - OX + Ce^{3+} + H^+ \tag*{[5]}$$

$$St - P - OX + Ce^{4+} \overset{k_i}{\rightarrow} St - P^o + Ce^{3+} + H^+ \tag*{[6]}$$

Propagation reactions

$$St - P - AN^o + AN \overset{k_p}{\rightarrow} St - P - AN_2^o \tag*{[7]}$$

$$St - P - AN_2^o + AN \overset{k_p}{\rightarrow} St - P - AN_n^o \tag*{[8]}$$

$$St - P - AN_n^o + AN \overset{k_p}{\rightarrow} St - P - AN_m^o \tag*{[9]}$$

$$AN^o + AN \overset{k_p}{\rightarrow} AN_n^o \tag*{[10]}$$

$$AN_n^o + AN \overset{k_p}{\rightarrow} AN_m^o \tag*{[11]}$$

Termination reactions

$$St - P - AN_n^o + St - P - AN_m^o \overset{k_t}{\rightarrow} St - p - AN_{n+m} St - P \tag*{[12]}$$

$$St - P - AN_n^o + AN_m^o \overset{k_t}{\rightarrow} St - p - AN_{n+m} \tag*{[13]}$$

$$AN_n^o + AN_m^o \overset{k_t}{\rightarrow} AN_{n+m} \tag*{[14]}$$

The fourteen equations of the scheme of reactions will be used to develop the mathematical model and calculate the change of concentration of every component.

METHODOLOGY AND MODEL DEVELOPMENT

Methodology

The complex reaction kinetic existing in the polymerization under study requires computer-aided applications for estimating the kinetics parameters involved in the mechanism described above. In this study, the rate equations were solved using MATLAB Simulink (The Mathworks, Release 2014b) to determine the change of the controlling reactant (AN monomer) conversion as function with time, and compared with that of calculated from experimental data previously reported by the authors[7,8].

For the sake of model development, a nomenclature for the concentration of the different interactions ions species (*i*), in terms of x_i(gmol/l), is formulated in Table 1

Table 1: Model Nomenclature of Involved Ions Species for the Suggested Mechanism

Concentration of each component	Symbol	Concentration of each component	Symbol
$[St - P]$	x_1	$[St - P - OX]$	x_{10}
$[Ce^{4+}]$	x_2	$[St - P - AN_2^o]$	x_{11}
$[St - P - Ce^{4+}]$	x_3	$[St - P - AN_n^o]$	x_{12}
$[St - P^o]$	x_4	$[St - P - AN_m^o]$	x_{13}
$[Ce^{3+}]$	x_5	$[AN_n^o]$	x_{14}
$[H^+]$	x_6	$[AN_m^o]$	x_{15}
$[AN]$	x_7	$[St - p - AN_{n+m} St - P]$	x_{16}
$[St - P - AN^o]$	x_8	$[St - p - AN_{n+m}]$	x_{17}
$[AN^o]$	x_9	$[AN_{n+m}]$	x_{18}

Model Development

The starch phosphate polymerization was carried out in an ideal batch-well mixed tank reactor, operating isothermally, where the reaction mixture properties are uniform throughout the reactor, represented as shown in Figure 1, where,(n_{if})is number of moles of component (*i*) in feed stream, (n_{ip})is number of moles of component (*i*) in product stream and (N) is the number of reactions.

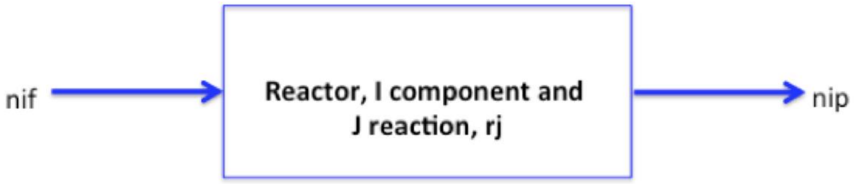


Figure 1: Mass Flow Diagram

The mass balance design equation for each reaction in a chemical engineering lumped system with *j* consecutive reactions happening at the rates r_j $(r_1, r_2, \dots r_j)$, where $j$equal 14, and the number of component is N (i=1,2, ….N) where *N* equal to18, can be derived for any incremental time (Δt) inside the reactor,as follows:

$$n_i + \Delta n_i = n_i \sigma_i V r_i \Delta t \qquad [15]$$

$$\frac{\Delta n_i}{\Delta t} = \sigma_i V r_i \qquad [16]$$

When Δ*t* goes to zero, it will be in an ordinary differential equation (ODE) form:

$$\frac{dn_i}{dt} = \sigma_i V r_i \qquad [17]$$

For multiple- reactions, this equation becomes:

$$\frac{dn_i}{dt} = V \sum_{j=1}^{N} \sigma_{ij} r_j \qquad [18]$$

Where:V is the reaction constant volume ($V = \frac{n_i}{x_i}$).

$x_i$is the concentration of component *i* at any time *t*.

$\sigma_i$is a coefficient equal to -1 for any reactant and +1 for any product, according to the stoichiometric equation of reaction j.

Therefore:

$$\frac{dx_i}{dt} = V \sum_{j=1}^{N} \sigma_{ij} r_j \qquad [19]$$

At $t = 0$; $x_i = x_{if}$,and at any *t*; $x_i = x(t)_i$.

The reaction rates $r_j$are defined as the rate of changes of mass of component *i* with time, and are expressed in terms of the concentrations of the different components in the bulk space for the above proposed mechanism equations as depicted in Table 2.

Table 2: Developed Reaction Rates$(r_j)$for the Suggested Mechanism

Reaction rates			
r_1	$k\, x_1 x_2 - k' x_3$	r_8	$k_p x_{11}$
r_2	$k_d x_3$	r_9	$k_p x_{12} x_7$
r_3	$k_i x_4 x_7$	r_{10}	$k_p x_9 x_7$
r_4	$k_i x_2 x_7$	r_{11}	$k_p x_{14} x_7$
r_5	$k_i x_4 x_2$	r_{12}	$k_t x_{12} x_{13}$
r_6	$k_i x_{10} x_2$	r_{13}	$k_t x_{12} x_{15}$
r_7	$k_p x_8 x_7$	r_{14}	$k_t x_{14} x_{15}$

Based on the Simulink block solution illustrated in Figure 2, the reaction model is solved using Matlab 2014b Mathworks.

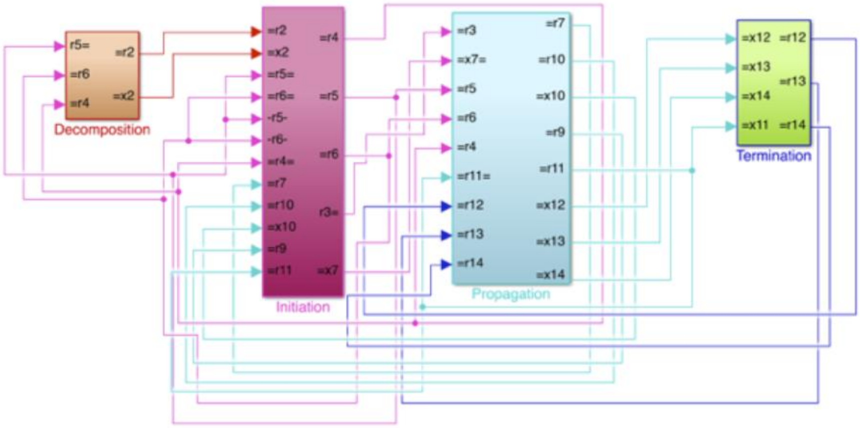


Figure 2: Matlab Systems Diagram for Acrylate Grafted Starch Phosphate Synthesis Using CAN Initiator

Model Solution and Verification

The developed mathematical model of grafting polymerization reaction was solved for the state variable change against the independent variable (time, *t*) for a specific set of parameters; or some of the parameters are being adjusted to give the best match to experimental results, using the Sum Residual Squares (SRS) (or $\sum \text{error}^2$ for *n* readings), this error approaches 9.075E-3 as depicted in Figure 3. The obtained curve fitting developed by simulink solution of model is shown in Figure 4.

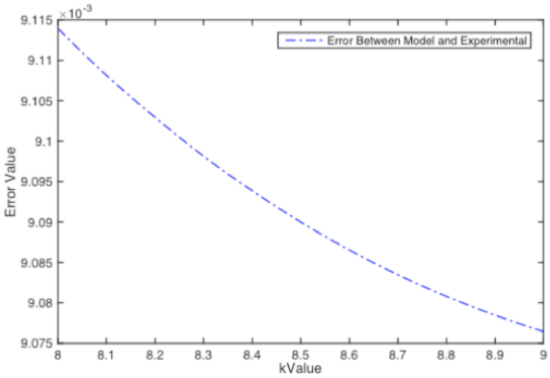


Figure 3: Minimum error between experiment results and the predicted results of model at best fitting (9.075E-3)

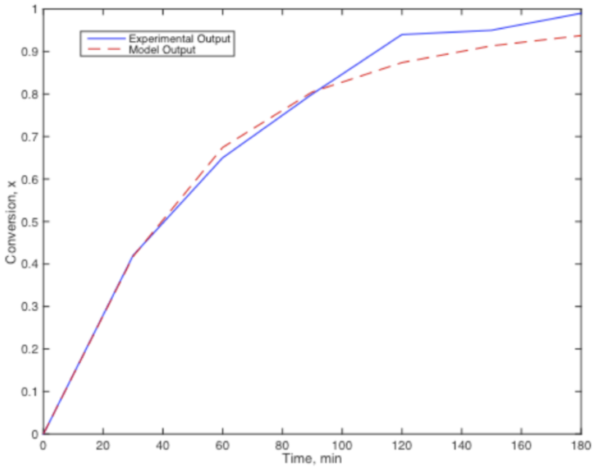


Figure 4: Best Fitting as Obtained by Simulink Model Solution

RESULTS AND DISCUSSION

Model Validation

Being the determinant of the reaction yield quantitatively, first estimates for the kinetic parameters were extracted from available published works[3,13], considered in a plausible range for the acrylonitrile monomer used.

Entering the aforementioned ordinary differential equations for the polymerization reaction, into the software and simulating at reaction conditions: St-P: AN (20grmol: 20grmol), CAN (1cm^3/l), polymerization temperature 35^{o}C, produces the following results:

Figure 5 illustrates the appropriateness of the predicted data compared to those of experimental results, relevant to the conversion of the acrylonitrile monomer as function with reaction time- previously reported by the authors as mentioned above and depicted in Table 3.It should be mentioned that the polymerization of AN onto St-P was monitored by N-content (Kjeldahl method).

Table 3: The Effect of Polymerization Time of AN onto St-P [6]

Time, min	N%, Nitrogen%	Conversion%
0	0	0
30	1.6	12
60	5.3	40
120	12.4	94
180	13	99
Over night	13	99

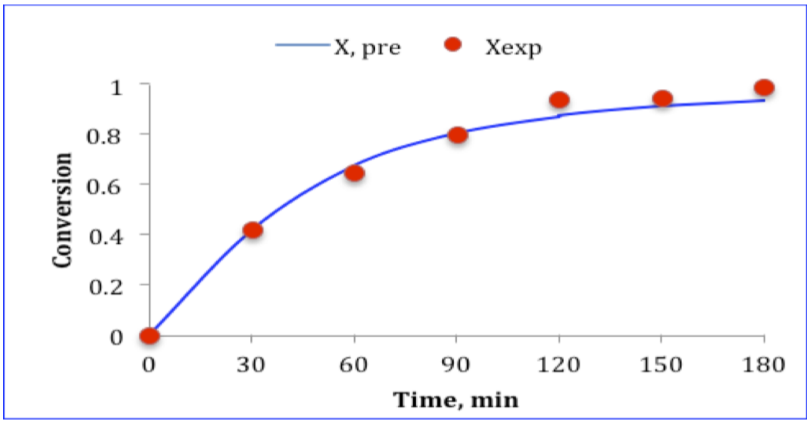


Figure 5: Time Evolution of Monomer Concentration During Polymerization.

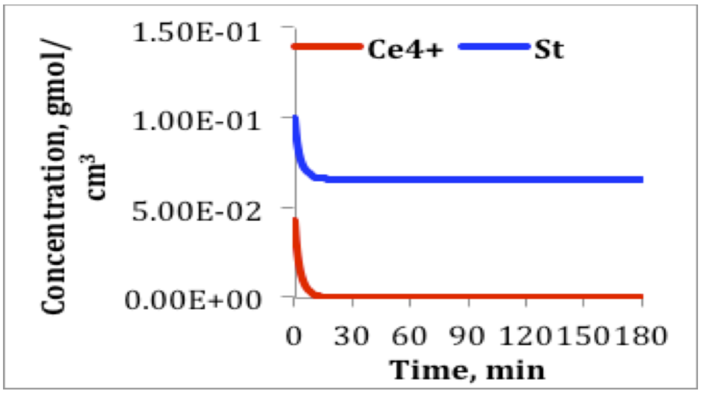
It is clear that the reaction proceed smoothly until reaching asymptotic conversion (99 %).
The best fitting of the experiment readings and predicted results occurred at the following kinetic parameters Table4.

Table 4: The Best Fitting of Experimental and Predicted Results

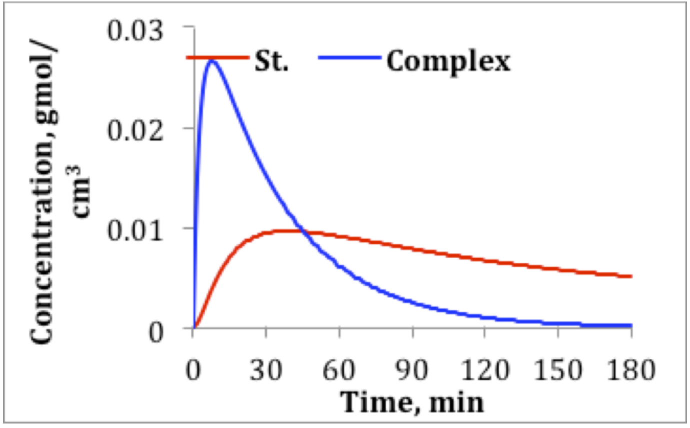
Reaction constant	Value
k, cm^{3}mol^{-1}min^{-1}	9
k', cm^{3}mol^{-1}min^{-1}	3.00E-3
k_d, min^{-1}	0.03
k_i, cm^{3}mol^{-1}min^{-1}	0.79
k_p, cm^{3}mol^{-1}min^{-1}	200
k_t, cm^{3}mol^{-1}min^{-1}	8000

Once the predicted conversion results are fitted with the corresponding experimental data, therefore, all variables can be predicted directly from the model solution at the same obtained k values of the reactions, consequently, we can study the behavior of the integrated system and the profile of each intermediate compounds.

Figures 6 demonstrate the dissociation of the ceric ion to generate the free radicals initiating the polymerization reactions. As it is expected, a rapid depletion rate of Ce $^{4+}$ is observed at the early beginning of the reaction; Figure 6-a accompanied by a sudden increase with simultaneous decrease in the complex formed at almost the same time interval with the appearance of the starch phosphate free- radicals which after 50 min. begins to be consumed by the monomer forming the initial graft free- radical (Figure 6-b).



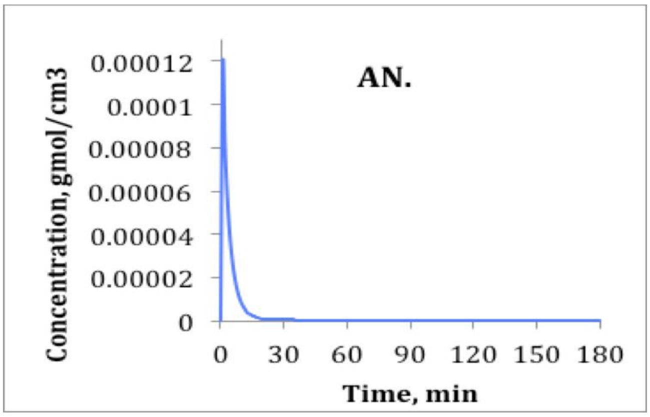
(a)



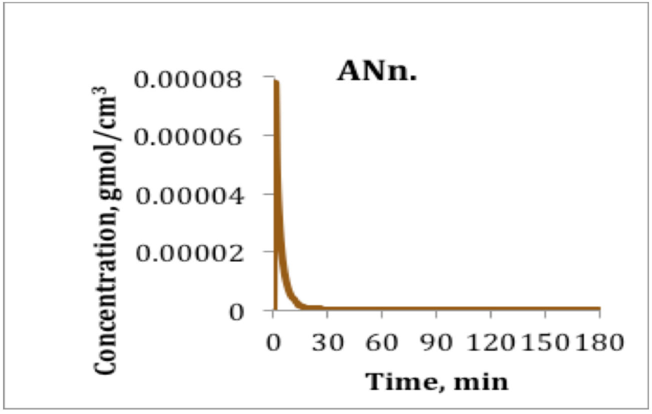
(b)

Figures 6: Dissociation Profile of Ce^{4+} and the Formed Complex

Figure 7 illustrates the instantaneous appearance and disappearance of the acrylonitrile and homopolymerfree radicals initiating the propagation reactions of the grafting process as shown in Figure 8. It is worth noting that all these reactions proceed simultaneously within the first fifteen minutes of the polymerization time.



(a)



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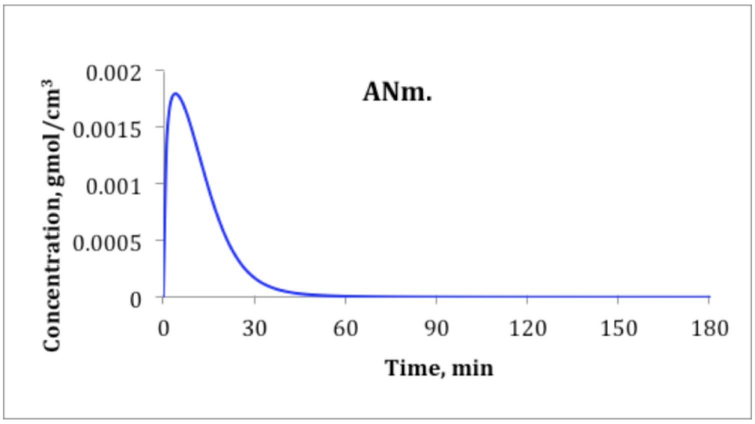
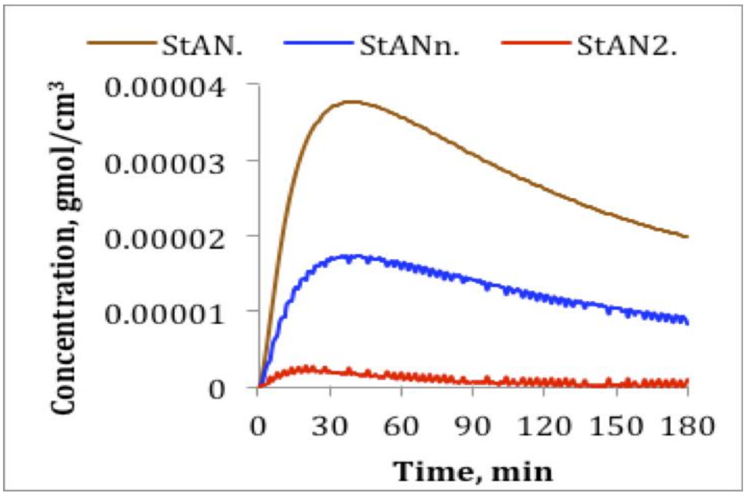
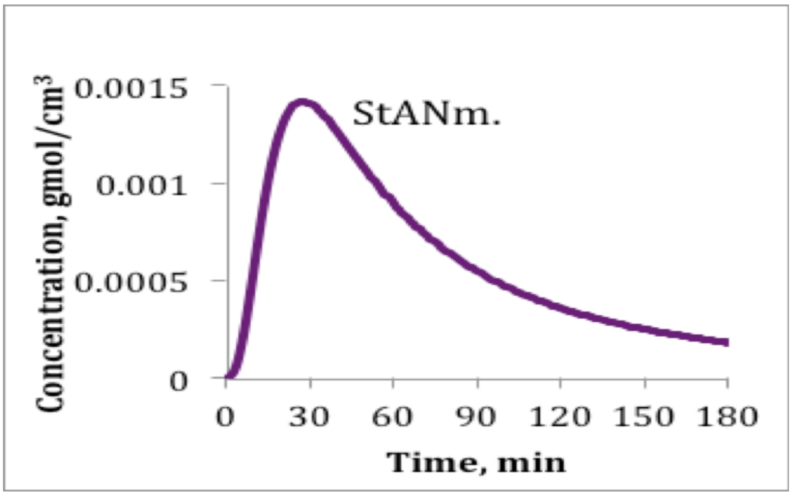


(c)

Figure 7: Evolution of AN Free Radicals with Time



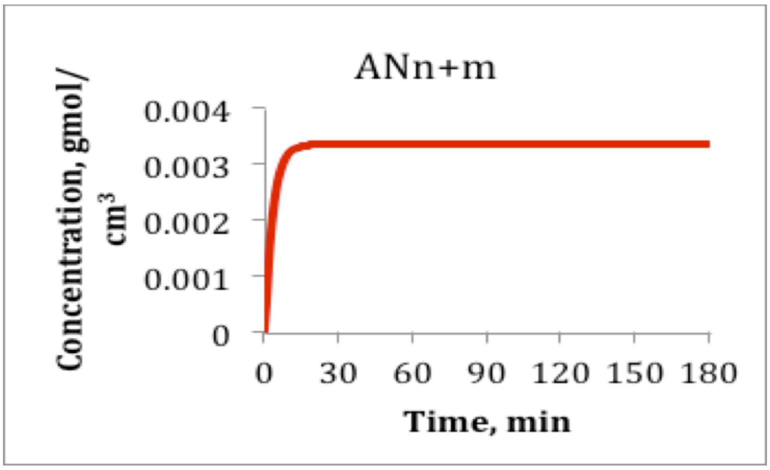
(a)



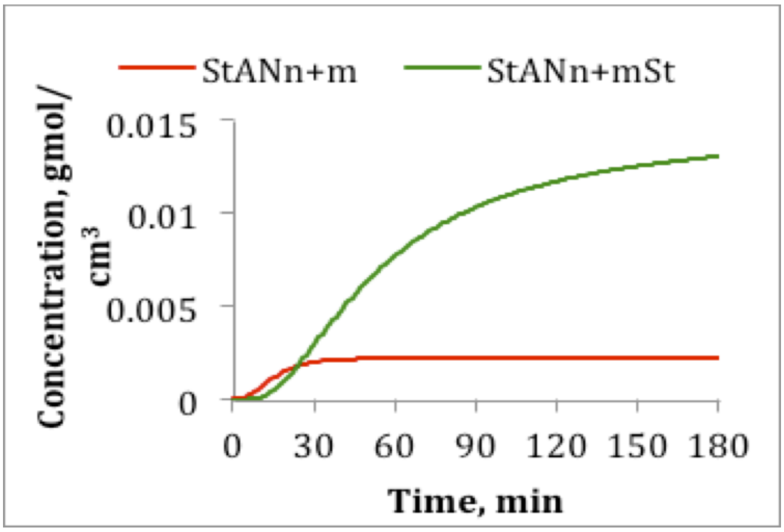
(b)

Figure 8: Generation and Disappearance of Grafted Free Radical with Polymerization Time

Further, Figure 9 shows the termination reaction rates of the growing polyacrylonitrile and starch phosphate grafted products. It should be noticed the time compatibility between the disappearance of the intermediate species and the appearance of the polymerization products, implying the reliability of the simulated differential equations and subsequently the proposed polymerization mechanism of the system under investigation.



(a)



(b)

Figure 9: Evolution of Polymerized Terminated Products as Function with Time

Temperature Dependence of Reaction Rates Constant

Once the essential features of the grafted phosphorylated starch with acrylonitrile synthesis is kinetically controlled, crucial related properties can be predicted, namely the influence of temperature change on the dynamics of the polymerization. The effect of the reaction temperature of the polymerization of AN onto $St - P$ is illustrated in Figure10 according to the obtained experimental results [7,8] presented in Table 5 ,

Table 5: Effect of Reaction Temperature on the Polymerization of AN onto Starch Phosphate

Temperature (°C)	N (Nitrogen)%	Conversion%
25	12.1	92
35	12.9	98
45	7.9	60
55	4.62	35
65	2.64	20

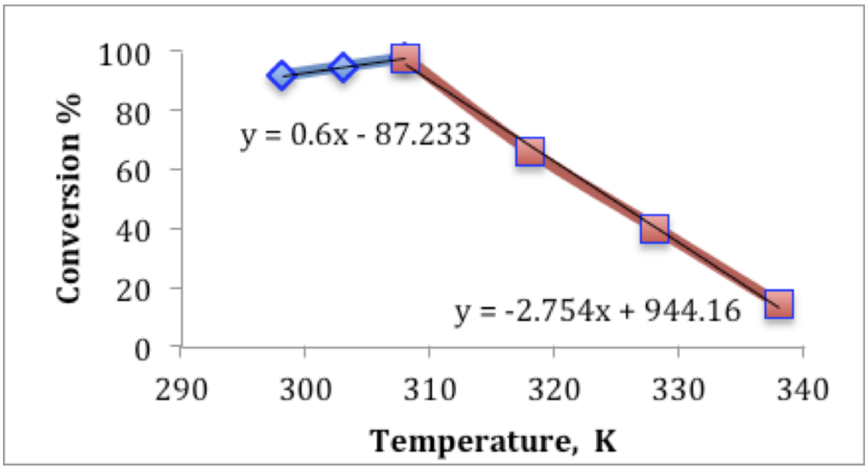


Figure 10: Effect of Temperature Reaction Conversion

It is clear that there is a critical temperature up to which total conversion increases and decreases thereafter. The observed increase is probably due to enhanced diffusion of monomer molecule to the increased macro radical sites. However, by further increasing of temperature, the transition state may be attributed to both the fast primary radicals termination and the fact that, at higher temperatures there is an increase in the rate of oxidative degradation of starch due to the existence of CAN as a powerful oxidizing agent.

The observed transition point was then defined as being the intersection of two straight-lines-represented by the data- and was determined equal to 308.8°K. Simulations were then performed considering only different temperatures up to this reversal point to predict the reaction conversions at 298, 303 and 308°K as shown in Figure 11. These results elucidates that the reaction conversion is weakly temperature dependent, hence, the conversion can be considered as a step function with temperature, yielding an asymptotic line. The predicted values of the kinetic parameters are depicted in Table 6.

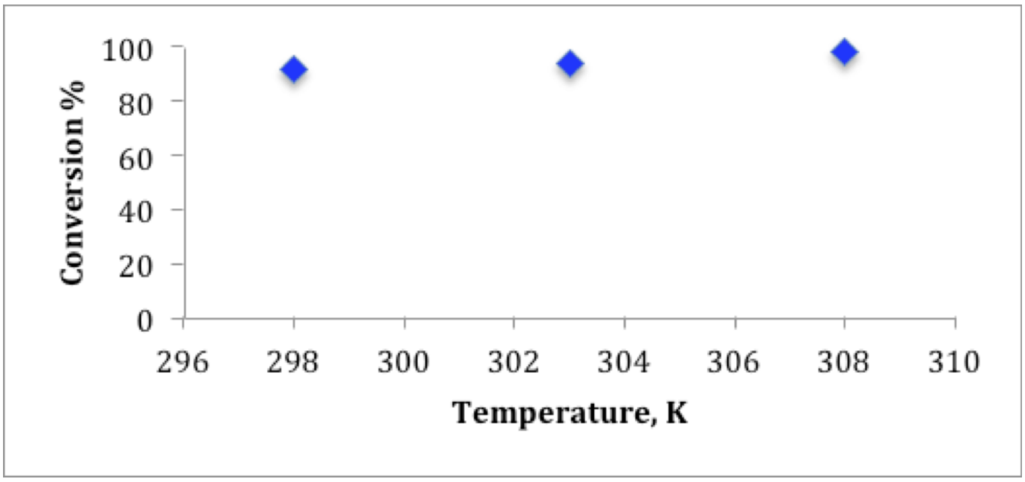


Figure 11: Dependence ofAN Conversion on Temperature

Table 6: Predicted Rate Coefficients at Different Temperatures

T, °K	k, cm^3mol^{-1} min^{-1}	k, cm^3mol^{-1} min^{-1}	k_d, min^{-1}	k_i, cm^3mol^{-1} min^{-1}	k_i, cm^3mol^{-1} min^{-1}	k_i, cm^3mol^{-1} min^{-1}
298	3	5.00×10^{-4}	0.025	0.71	190	7500
303	9	3.00×10^{-3}	0.03	0.79	200	8000
308	4.2	3.10×10^{-3}	0.035	1.7	220	8500

The temperature dependence of reaction rates can be expressed satisfactory by the Arrhenius equation, ($k = Ae^{-E/RT}$), which by integrating its logarithmic form givesa linear relation-ship between (-ln k) and (1/T), with slope (E/R), where (E) is the activation energy required for the reaction to proceed at temperature (T,°K), (R) is the universal gas constant and with intercept (A)defined as the collisions frequency factor between reactants molecules. Consequently, the application of Arrhenius equation for the system under study yields the following expressionsTable7 indicating that in this temperature range, the process is directly influenced by temperature:

Table 7: Individual Apparent Activation Energy and Frequency Factor for the Polymerization Reactions

Arrhenius equation *	E, Kj mol^{-1}
$k = 90309.686\ e^{-(3080.6/T)}$.	25.612
$k' = 4.00802x10^{20}\ e^{-(16424/T)}$.	136.550
$k_d = 797.913\ e^{-(3089/T)}$.	25.682
$k_i = 2.95519x10^{11}\ e^{-(7993/T)}$.	66.454
$k_p = 17101.133\ e^{-(1343.2/T)}$.	11.167
$k_t = 354335.683\ e^{-(1148.9/T)}$.	9.552

*R=8.314 x 10^{-3}Kj $mol^{-1o}K^{-1}$.

Recalling that the Arrhenius exponent is the ratio of activation energy (E) to the average kinetic energy (RT), and that higher temperature and lower (E) accelerate reaction rates, it can be seen from Table 7: 1-The forward reaction of the starch phosphate ceric complex formation equation [1] highly predominates rather than the reversible one. 2- The activation energy of the complex decomposition between starch phosphate and ceric ion is similar to that of complex formation, although the rate of the later is highly greater than that of the former due to higher frequency factor. 3- The lowest observed activation energy concerns the termination steps with consequent the highest reaction rates.

The overall rate of acrylonitrile consumption (R_{AN}) was, previously, defined and reported by the authors [7, 8]. Applying the steady-state approximation to the various free-radical species from equations [1-14], and solving the derived reaction rates algebraically, yielded the following rate expression:

$$R_{AN} = K_{ov} C_{AN} C_{St-PO}^{.5} C_{Ce4+}^{0.5} \qquad [20]$$

Where K_{ov} is the overall reaction rate constant determined as follows:

$$K_{ov} = k_p \{(k\, k_d) / (k'\, k_t)\}^{0.5} \qquad [21]$$

By determining K_{ov} values at different temperatures by substituting in equation [21] the predicted data, Table V, a linear relation-ship results as illustrated in Figure 12, by linear regression, it gives the following equation:

$$K_{ov} = -1.017\, T + 329.74 \qquad [22]$$

Equations [20-22] can be considered as empirical equations defining the rate expression of acrylonitrile consumption in the graft polymerization with ceric ion onto starch phosphate, where (C) in $mol.cm^{-3}$, (k) in $cm^3mol^{-1}min^{-1}$, (T) in K and K_{ov} in $(cm^3mol^{-1})^{0.5}$ min^{-1}.

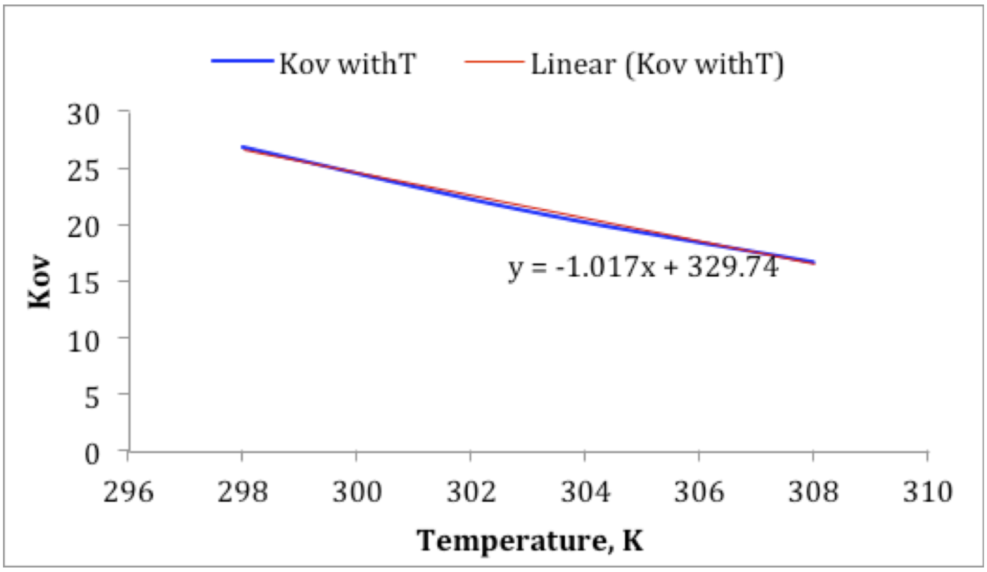


Figure 12: Temperature Dependence Grafting Temperature on Overall Rate Coefficient

CONCLUSION

The present work provides an examination on the graft copolymerization to modify starch phosphate into acrylated grafted phosphoralized starch with participation of ceric salt. A simple kinetic model was developed in terms of a set of ordinary differential rate equations, based on a suggested mechanism including many different simultaneous reactions. This model was applied to simulate the undertaken synthesis by means of Matlab functions solver and gives dependable results reliable with experimental data. Agreement of the predicted kinetic parameters and operation with measurements previously performed indicate that the proposed model is able to control kinetically the system under study.

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