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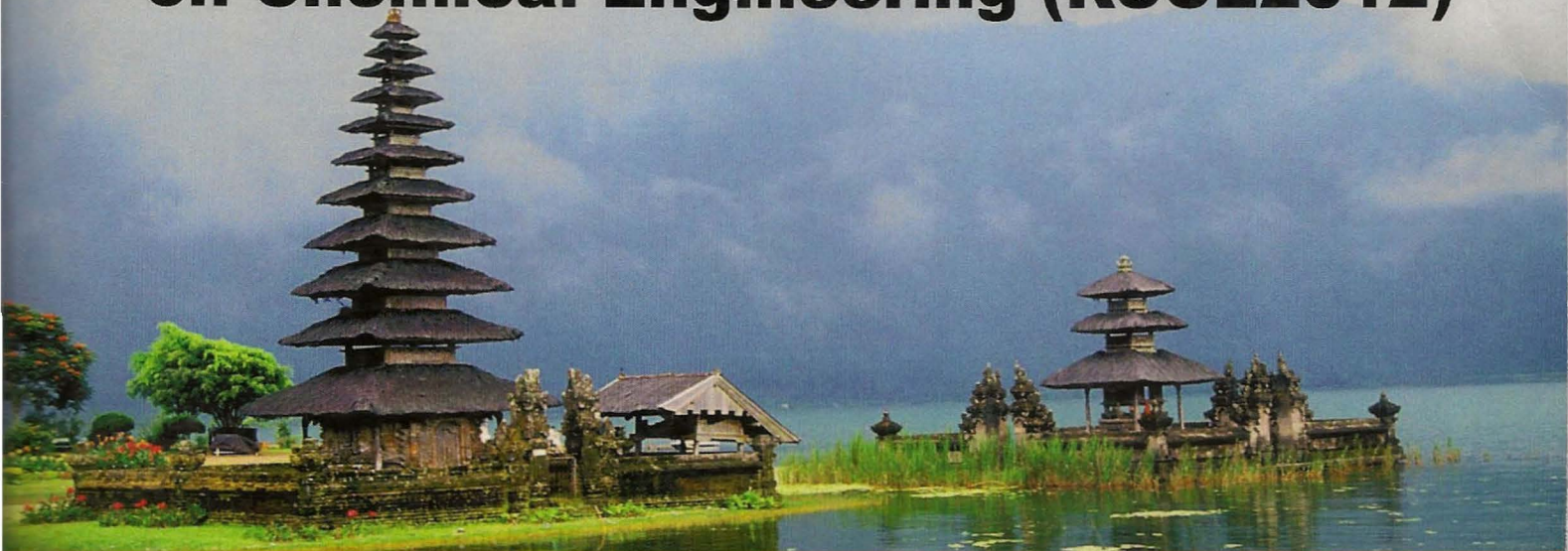# 19th Regional Symposium
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D. Polymer, Petrochemical and
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Kinetic Evaluation of the Graft Copolymerization of Acrylic Acid onto Starch Based on Concentration Measurements and on Torque Observation

Judy R.Witono[1a*], Hero J. Heeres[2b], Leon P.B.M.Janssen[3b], Inge W. Noordergraaf[4b]

[a] Department of Chemical Engineering
Parahyangan Catholic University, Bandung 40141 Indonesia
[b] Department of Chemical Engineering
University of Groningen, Groningen 9700AB The Netherlands

*Corresponding Author's E-mail: judy@unpar.ac.id

Abstract

The utilization of natural polymers to replace synthetic polymers is an important factor in our world nowadays. One of the promising materials in terms of using 'green' feedstock is the graft copolymer of cassava starch with (poly-) acrylic acid. A study of reaction kinetics has been made to improve understanding of the reaction mechanism. It is one of the chemical reaction engineering aspects that need to be considered for any future reactor design.

A new model for graft copolymerization is proposed which is derived from the possible steps of the grafting reaction. The accompanying rate constants could be estimated from experimental data. For two different mol ratios of starch with respect to acrylic acid i.e. St:AA = 1 and 0.5, the ratio of these rate constants is 0.09 and 0.04 respectively. These values are clearly below 1, which means that unfortunately the formation of homopolymer, the unwanted side product, is much faster than the graft reaction. Although the newly derived model has shortcomings due to some necessary assumptions, it does provide for a prediction of the concentrations of relevant species over time. These predictions compare well to actual data from dedicated experiments. The rate of the grafting reaction shows pseudo 1st (first) order dependence in monomer concentration while homopolymerization reactions show pseudo 1.5 order dependence in monomer concentration.

The validity of the model is further confirmed by the observation of the torque during the reaction with pregelatinized starch, which shows an exponential growth. These data also provide information on the viscosity development during the reaction, another important factor in reactor design.

Keywords: Starch grafting with acrylic acid; Kinetic model; Torque; Order of the grafting reaction.

1. Introduction

The importance of utilization of natural resources like starch and cellulose as a substitute for fossil resources derived materials is growing rapidly. To meet the product properties of many end-products, modifications of either starch or cellulose are inevitable. A well established chemical modification of these bio-polymers is graft copolymerization. For example, (Stannett et al., 2002) reported that grafting cellulose (cotton) with acrylic acid, led to an increase in water absorbency of native cellulose from 4 cm^3/g to 26 cm^3/g. Cassava starch is one of the starch sources which is abundantly available in tropical regions. In 2008 Indonesia produced over 21 million ton (30% of the total production in Asia) (FAO, 2008).

The influence of the reaction conditions and an optimization of these for cassava starch grafting with acrylic acid have been studied (Witono et al. 2012). Some kinetic models of various radical graft copolymerization reactions have been published already (Chaimberg & Cohen, 1994; Gopalan et al., 1995; Sahloul & Penlidis, 2004; Sunday, 1988; Wang, 1988; Wong et al., 1995; Mcmanus et al., 1998). However, these are not grafting reactions onto starch and therefore the models can not directly be applied to our system. Still, from this literature there appears to be a general agreement on the mechanism of graft polymerization. By the action of an initiator, radicals are created at the substrate polymer and chains of new polymer grow from these sites. This is just a special form of free radical add-on polymerization. The general approach to the modeling of such polymerizations was originally introduced by (Dostal, 1936), later followed by (Mayo & Lewis, 1944) . They proposed a linear model, but this model does not cover the important aspect of the reactivity ratio when there are two polymerization reactions that proceed in parallel. Other, non-linear models were proposed by (Finemann & Ross, 1950; Kelen & Tǔdǒs, 1974 and Tidwell & Mortimer 1965). The general agreement is that the non-linear approach is more suitable, although it enforces more sophisticated computing work (Zhou, 2004). Our, basically new, model for starch graft polymerization has been developed according to these findings.

2. Experimental
2.1. Materials

The native cassava starch used in this study was produced by PT. Sungai Budi, Lampung and was kindly supplied by PT. AVEBE Indonesia, Cikampek, Indonesia with a purity of 99.93%. Acrylic acid (glacial, 99.5%, stabilized with 200±20 ppm monomethyl ether of hydroquinone - MEHQ) was kindly supplied by BASF PETRONAS Chemicals, Sdn. Bhd., Malaysia and was used without further purification. FAS (Ferrous Ammonium Sulfate), H_2O_2 (Hydrogen Peroxide) 30% and acetone were reagent grade chemicals and were used as received.

2.2. Procedure

The kinetic model derived in this work has been tested with data from dedicated batch graft polymerization runs conducted in the stainless steel reactor as reported before (Witono et al., 2012). The highly viscous reaction mass makes reliable sampling during the reaction almost impossible. Therefore, it was chosen to make several runs at the same conditions and to stop each run at a different time, in order to assess the course of the graft parameters over time. To avoid possible influences from poor mixing especially at the shorter reaction times, samples were collected from five different locations in the gelled mass after the reaction was stopped, and mixed together to get a representative sample for the whole of the reactor contents. This approach made it necessary to perform 18 separate runs, for just two different conditions of the starting parameters.
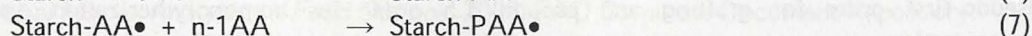
In order to monitor the polymerization reaction also with another system, we observed the course of torque (using a Heidolph overhead stirrer RZR 2102 control) during the reaction. In the batch reactor, the shear rate was controlled by maintaining a constant stirring speed of 300 rpm. The increase of torque (shear stress) is automatically compensated by the instrument and the torque value is recorded. The interface of this system was connected to a computer using Labview software to store the relevant data.

3. Results and Discussion
3.1. Estimation of the reactivity ratio of graft and homopolymer radicals from experimental data

Since the graft copolymerization proceeds through free-radical polymerization, the reaction is very fast and non-selective. The formation of homopolymer simultaneously with the graft product is

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therefore inevitable. In their book, (Mishra et al., 1998) confirm that a radical grafting reaction is similar to radical vinyl polymerization. It is a free radical chain reaction in three steps: initiation, propagation and termination. There are several schemes (Lutfor et al, 2000; Park & Song, 1999; Vázquez et al., 1989; Brockway & Mosser, 1963) introduced, which are also depend on the initiator used. The scheme proposed (by Brockway and Moser, 1963) is chosen in this work i.e.:

$$H_2O_2 + Fe^{2+} \rightarrow HO\bullet + OH^- + Fe^{3+} \tag{1}$$
$$HO\bullet + AA \rightarrow AA\bullet \tag{2}$$
$$AA\bullet + n\text{-}1\,AA \rightarrow AA_n\bullet \tag{3}$$
$$HO\bullet + starch\text{-}H \rightarrow Starch\bullet + H_2O \tag{4}$$
$$AA_n\bullet + starch\text{-}H \rightarrow Starch\bullet + PAA \tag{5}$$
$$Starch\bullet + AA \rightarrow Starch\text{-}AA\bullet \tag{6}$$
$$Starch\text{-}AA\bullet + n\text{-}1AA \rightarrow Starch\text{-}PAA\bullet \tag{7}$$
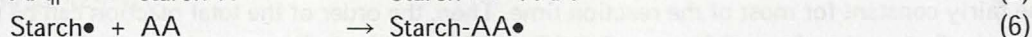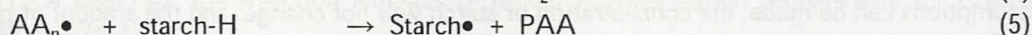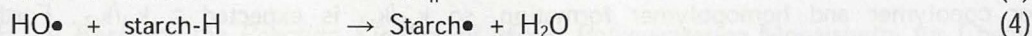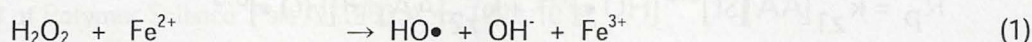
The fraction of monomer (AA) this is incorporated in the grafted polymer is the grafting efficiency (GE):

$$GE = \frac{\text{monomer grafted onto starch}}{\text{monomer grafted onto starch} + \text{monomer consumed by homolymer}} \tag{20}$$

By substituting the rates of copolymerization and homopolymerization from the propagation and termination steps the definition of the graft efficiency can be rearranged, finally leading to:

$$\frac{1}{(1-GE)^{0.5}} = 1 + \frac{k_{i1}[St]}{k_{i2}[AA]} \tag{8}$$

Where k_{i1} & k_{i2} are the respective initiation reaction constant of starch and monomer.

By observing the data from our experiments, the concentration of acrylic acid and starch at every specific period of time, and plotting it to $1/(1\text{-}GE)^2$ based on the equation 8, the ratio k_{i1}/k_{i2} could be determined (see fig.1 (a) and (b)). From these graphs it was seen that the experimental data only fit into the model at the first part of the graph (up to around 10-15 minutes of reaction time). The data from the experiments are on the total amount reacted up to that time, whereas the formulas are in the differential form. Therefore, in the first minutes of the reaction the data will be closer to the differential than later on in the reaction. Also, the effect of 'cross terminations' (PAA• reacting with SgPAA•, which would contribute to the total grafting) will still be limited then. For these reasons it is the most appropriate to determine the ratio k_{i1}/k_{i2} from the data at the early phase of the reaction. For a mol ratio starch to acrylic acid =1, the value is ca 0.09 and for the mol ratio starch to acrylic acid = 0.5 it is 0.04.
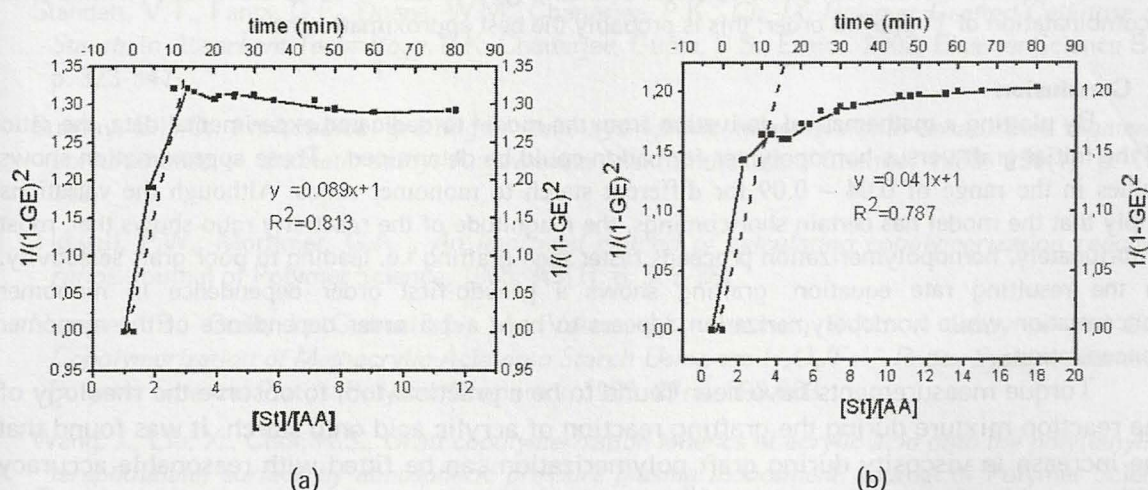

Figure 1. Plot of the experimental data and model calculations (dotted lines) based on equation (8), at the molar ratios of starch to monomer 1(a) and 0.5 (b).

The ratio k_{i1}/k_{i2} is well below one in both cases, which shows that the reactivity of starch is much lower than that of the monomer for the OH• radicals.

By further developing the kinetic equations for copolymer and homopolymer, a simplified reaction rate formula could be derived:

$$R_p = k_{z1}[AA][St]^{0.5}[HO•]^{0.5} + k_{z2}[AA]^{1.5}[HO•]^{0.5} \qquad (9)$$

Where $k_{z1} = k_p(k_{i1}/k_t)^{0.5}$ and $k_{z2} = k_p(k_{i2}/k_t)^{0.5}$. It can reasonably be assumed that k_p and k_t are the same for copolymer and homopolymer formation, so k_{z1}/k_{z2} is expected $\approx k_{i1}/k_{i2}$.. Further logical assumptions can be made: the concentration of starch will not change, and the amount of radicals will be fairly constant for most of the reaction time. Then, the order of the total reaction can be regarded as pseudo-first order for grafting and pseudo 1.5 order for homopolymerization, in monomer concentration.

3.2. Torque profiles during reaction

In figure 2, torque profiles during the polymerization reactions are plotted against time.
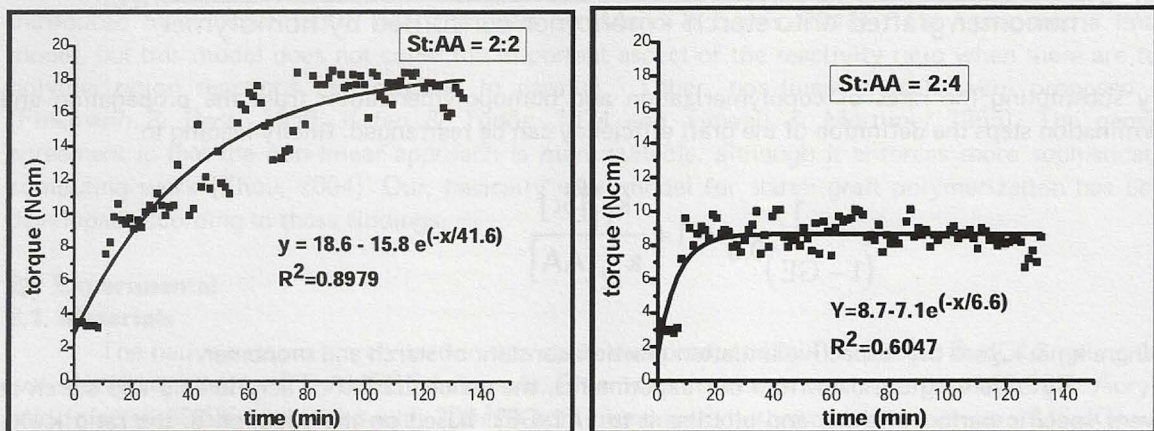

Figure 2. The torque change against time during grafting reaction at different mol ratio of starch to monomer

Observing the torque profile during the grafting reaction at different ratios of starch to the monomer in figure above, we see that they exhibit an exponential growth. The torque increases rapidly because the rate of polymerization is high. These results show that the development of torque and thus viscosity during the polymerization reaction can be fitted with reasonable accuracy by a combined first order equation. Since we had no software available (yet) to test the complete kinetic formula with a combinatation of 1st and 1.5 order, this is probably the best approximation now.

4. Conclusion

By plotting a mathematical derivation from the model to dedicated experimental data, the ratio of the initial graft versus homopolymer formation could be determined. These approximation shows values in the range of $0.04 - 0.09$ for different starch to monomer ratios. Although the variations imply that the model has certain shortcomings, the magnitude of the reactivity ratio shows that, most unfortunately, homopolymerization proceeds faster than grafting i.e. leading to poor graft selectivity. In the resulting rate equation, grafting shows a pseudo-first order dependence in monomer concentration while homopolymerization appears to have a 1.5 order dependence of the monomer concentration.

Torque measurements have been found to be a practical tool to observe the rheology of the reaction mixture during the grafting reaction of acrylic acid onto starch. It was found that the increase in viscosity during graft polymerization can be fitted with reasonable accuracy with a combined equation that has a 1st order dependency of the monomer concentration. This

result shows that for non-Newtonian fluid, the reaction kinetics as derived from concentration measurments can be more or less confirmed by torque measurement during the reaction.

References

Brockway, C.E., Mosser, K.B., *Grafting of Poly(methyl Methacrylate) to Granular Corn Starch.* Journal of Polymer Science: Part A, 1963. **1**: p. 1025-1039.

Chaimberg, M., Cohen, Y., *Kinetic modeling of free-radical graft polymerization.* AIChE Journal, 1994. **40**(2): p. 294-311.

Dostal, H., *A Basis for the Reaction Kinetics of Mixed Polymerization* Monatshefte fur Chemie, 1936. **69**: p. 424-426.

FAO, *Global Market Analysis*, in *Food Outlook.* 2008, FAO Corporate Document Repository.

Finemann, N., Ross, S.D., *Linear method for determining monomer reactivity ratios in copolymerization.* Journal of Polymer Science, 1950. **5**: p. 259-262.

Gopalan, A., Vasudevan, T., Manisankar, P., Paruthimalkalaignan, C., Ramasubramanian, A., Hariharan, S.S., *Graft copolymerization of polyacrylonitrile (PAN) onto polyester (PET) and simultaneous homopolymerization: A kinetic study. I.* Journal of Applied Polymer Science, 1995. **56**(10): p. 1299-1311.

Kelen, T., Tudos, F., *New improved linear graphical method for detemining copolymerization reactivity ratios.* Reaction Kinetics Catalysis Letter, 1974. **1**: p. 487-492.

Lutfor, M.R., Rahman, M.Z.A., Sidik, S., Mansoor, A., Haron, J., Wan Yunus, W. M. Z., *Kinetics and mechanism of free radical grafting of methyl acrylate onto sago starch.* Journal of Applied Polymer Science, 2000. **77**(4): p. 784-791.

Mayo, F.R., Lewis, F.M., *Copolymerization. I. A Basis for Comparing the Behavior of Monomers in Copolymerization; The Copolymerization of Styrene and Methyl Methacrylate.* Journal of American Chemical Society 1944. **66**: p. 1594-1601.

Mcmanus, N.T., Penlidis, A., Rempel, G.L., *A Kinetic Investigation of the Copolymerization of Acrylonitrile and Vinyl Acetate in Bulk.* Developments in Chemical Engineering and Mineral Processing, 1998. **6**(3-4): p. 153-170.

Mishra, M.K., Yagci, Y., *Handbook of radical vinyl polymerization.* 1998: Marcel Dekker, Inc.

Park I.H., S.S.Y., Song B.K., *Gratf polymerization of acrylic acid onto corn starch in aqueous isopropanol solution.* Die Angewandte Makromolekulare Chemie, 1999. **267**: p. 20-26.

Sahloul, N., Penlidis,A, *High temperature copolymerization of styrene/ethyl acrylate: Reactivity ratio estimation in bulk and solution.* Advances in Polymer Technology, 2004. **23**(3): p. 186-195.

Stannett, V.T., Fanta, G.F., Doane, W.M., Chatterjee, P.K., *Ch. IX. Polymer Grafted Cellulose and Starch*, in *Absorbent Technology*, P.K. Chatterjee, Gupta, B.S., Editor. 2002, Elsevier Science B.V. p. 323-347.

Sunday, E.H.O., *Free radical grafting of some hydrophilic monomers onto unsaturated segmented polyurethanes - a kinetic study.* Angewandte Makromolekulare Chemie, 1988. **156**(1): p. 151-162.

Tidwell, P.W., Mortimer, G.A. , *An improved method of calculating copolymerization reactivity ratios.* Journal of Polymer Science, 1965. **A3**(1): p. 369-387.

Vázquez, B., Goňi, I., Gurruchaga, M., Valero, M., Guzmán, G.M., *A Study of the Graft Copolymerization of Methacrylic Acid onto Starch Using the H_2O_2/Fe^{++} Redox System.* Journal of Polymer Science: Part A: Polymer Chemistry, 1989. **27**: p. 595-603.

Wang, J., Liu, X., Choi, H.S., *Graft copolymerization kinetics of acrylic acid onto the poly(ethylene terephthalate) surface by atmospheric pressure plasma inducement.* Journal of Polymer Science Part B: Polymer Physics, 2008. **46**(15): p. 1594-1601.

Witono,J.R., Noordergraaf,I.W., Heeres,H.J., Janssen,L.P.B.M. Graft Copolymerization of acrylic Acid to Cassava Starch – Evaluation of the Influences of Process Parameters by an Experimental Design Method. *Carbohydrate Polymers, Accepted 2012.*

Wong Shing, J.B., Baker, W.E., Russell, K.E., *Kinetics and mechanism of the grafting of 2-(dimethylamino)ethyl methacrylate onto hydrocarbon substrates.* Journal of Polymer Science Part A: Polymer Chemistry, 1995. **33**(4): p. 633-642.

Zhou, X., *Evaluation of instantaneous and cumulative models for reactivity ratio estimation with multiresponse scenarios*, in *Chemical Engineering*. 2004, University of Waterloo: Ontario, Canada. p. 157.