Kinetics and Mechanism of Free Radical Grafting of Methyl Acrylate onto Sago Starch

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ABSTRACT: The graft copolymerization was carried out by methyl acrylate with sago starch in which ceric ammonium nitrate was used as an initiator. It has been found that the rates of graft polymerization and grafting efficiency were dependent upon the concentration of ceric ammonium nitrate (CAN), methyl acrylate (MA), sago starch (AGU, anhydro glucose unit), mineral acid (H_2SO_4), and as well as reaction temperature and period. A rate equation of polymerization was established from the proposed reaction mechanism, and the rate of polymerization (R_p) was the first-order dependence of the MA monomer concentration and square root of the CAN concentration. A new kinetic model of the grafting reaction has been proposed, and a normal kinetics of methyl acrylate polymerization was observed. An equation of a predicted model relating the graft fraction of poly(methyl acrylate) with the sago starch has been derived, and validity of the predicted model was verified by the experimental results. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 784–791, 2000

Key words: rate of graft polymerization; free radical; methyl acrylate; graft fraction; homopolymer

INTRODUCTION

Graft polymerization of monomers is one of the universal, effective, and accessible methods of chemical modification of high molecular weight compounds, natural polymers in particular. The advantage of radical polymerization is that it take place in water media with good yield of the final product. Besides, it considerably widens the choice of monomers and the preparation of graft copolymers with wider ranges of physico-chemical properties under technological process conditions. Much attention had been paid to the studied

of kinetics of radical graft polymerization of monomers onto polysaccharides by Berlin and Kislenko.[1] Their investigation covering grafting efficiency and the study of the interaction kinetics of initiators with polysaccharides promotes the finding of key reactions for the determination of rate of graft copolymerization, and the development of mathematical models of process kinetics. Brydon et al.[2] investigated in detail the kinetics and mechanism of styrene monomers grafting to polybutadiene (part II). A conclusion had been derived from the polymerization of the monomers that appeared to follow the normal kinetics of reaction. The rate of polymerization showed a first-order dependence on monomer concentration and a square root of initiator concentration. An expression relating to the graft fraction with the polybutadiene and styrene monomer concentrations has been derived, and validity of their model

Table I Experimental Conditions for Kinetic Analysis of Graft Copolymerization of Methyl Acrylate and Sago Starch by Ceric Ion

Series	Experiment No.	Sago Starch [AGU] Concentration/mol L^{-1}	Initiator [CAN] Concentration/mol $L^{-1} \times 10^{-3}$	Methyl Acrylate Concentration/mol L^{-1}
A	1	0.135	8.770	0.178
A	2	0.135	8.770	0.389
A	3	0.135	8.770	0.592
A	4	0.135	8.770	0.803
B	6	0.135	1.270	0.389
B	7	0.135	3.010	0.389
B	8	0.135	5.490	0.389
B	2	0.135	8.770	0.389
C	9	0.044	8.770	0.803
C	10	0.068	8.770	0.803
C	11	0.104	8.770	0.803
C	4	0.135	8.770	0.803

The reaction periods of 10, 20, 30, 40, and 50 min were used for the A and B series experiments. The reaction period was 50 min for the C series experiments. Temperature and [H_2SO_4] were 50°C and 0.175 mol L^{-1}, respectively.

was verified by the experimental results (part I). In the present study, we have examined the kinetics of free radical graft copolymerization of methyl acrylate onto sago starch by ceric initiation.

EXPERIMENTAL

Materials

Sago starch was purchased from Tepung Sago Ind. Ltd, Malaysia. It was dried at 60°C for 24 h. The methyl acrylate monomer was obtained from the Merck Company. To remove the inhibitor, methyl acrylate was passed through columns filled with chromatographic-grade activated alumina. Ceric ammonium nitrate (BDH), methanol (Beaker), hydroquinone (BDH), and other chemicals used were of analytical reagent grades.

Graft Copolymerization for Kinetic Analysis

The reactions were carried out into a 250-mL three-neck flask equipped with a stirrer and condenser, and the flask was immersed into a thermostat water bath. The N_2 gas was purged into the flask to remove the oxygen during the reaction. The starch slurry was prepared from the required amount of sago starch and 50 mL distilled water, and it was preheated at 80°C for about 30 min with stirring. After it was gelatinized, the flask content was then cooled to a 50°C temperature and then 1.05 mL diluted sulfuric

acid ($H_2SO_4 : H_2O/1 : 1$) was added to the reaction mixture. After 5 min the required milliliters of 0.1M of CAN solution was added, and the reaction mixture was mixed homogeneously. Exactly 10 min later, the required amount of monomer (MA) was added to the mixture, and the mixture was stirred for a specific period. For kinetic analysis, three series of experiments, in each of the concentration of one of the three reactants (CAN, MA, and AGU), was varied, while those of the other two kept constant. The reaction parameters were presented in Table I. Each experiment was carried out under various reaction periods, i.e., 10, 20, 30, 40, and 50 min. After the desired reaction period, 2 mL of 0.1M hydroquinone solution was immediately added to each reaction for ceasing the polymerization. When the reaction was complete, the product was cooled under running tap water, and poured into 200 mL of methanol to induce precipitation. The grafted product was washed several times with methanol–water (4 : 1) and then oven dried at 50°C to a constant weight.[3,4]

Extraction of Homopolymer

Exactly 2.000 g of each of the above crude products was taken and extracted with the acetone in a soxhlets extractor for 24 h to remove the poly(methyl acrylate) homopolymer, and the pure copolymer was then dried at 50°C to a constant weight.[4]

RESULTS AND DISCUSSION

### Mechanism of Methyl Acrylate Grafting onto Sago Starch

We have received a number of reports regarding the mechanism of grafting of vinyl monomer with starch or cellulose materials.[5–8] Among them, the mechanism of the graft copolymerization of vinyl monomer onto polysaccharide was suggested by Shukla et al.[5] Mingzhu et al.[3] proposed a different opinion on the conventional mechanism of graft copolymerization. They had thoughts on the research of Ranby et al.[6] after the decomposition of the complex between Ce^{4+} and starch, the aldehydic groups presented in oxidized starch may be oxidized to generate carbonyl radicals to initiate the grafting reaction. So there is a pair of radicals—one is radical I initiating graft copolymerization, and the other is radical II, also initiating the graft reaction. This means that there are two kinds of radicals on the starch backbone to initiate the grafting of vinyl monomer onto the starch, and this mechanism is presented in Scheme 1.

Theory of Rate of Polymerization and Grafting Efficiency

Many researchers studied the reaction mechanism of vinyl monomer with starch or cellulose,[5–7] but very little investigation was made on the kinetics of the reaction. The expressions for the rate of polymerization of methyl acrylate are based on
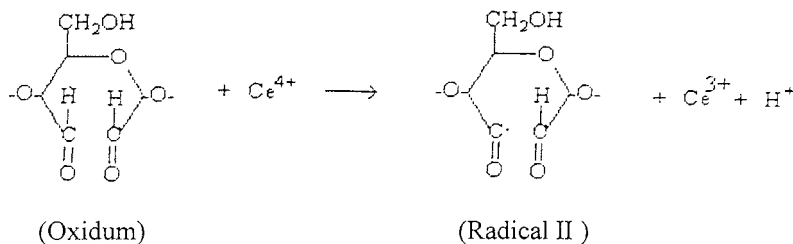
Formation of Radical I:

(Starch)   (Complex)   (Radical I)
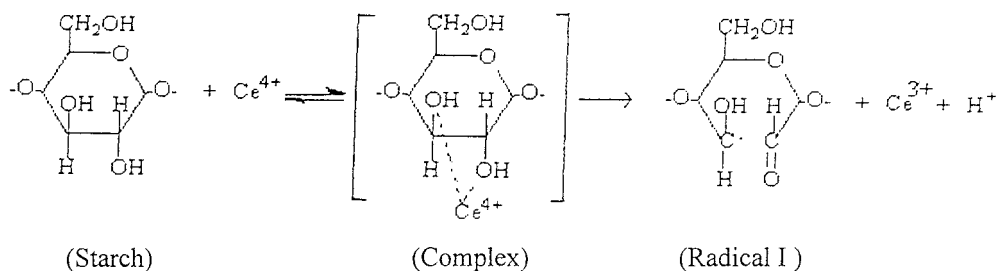
Formation of Oxidum:
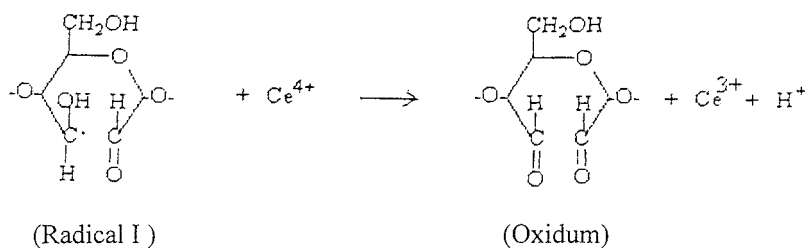
(Radical I)   (Oxidum)

Formation of Radical II:
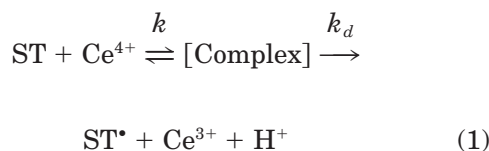

(Oxidum)   (Radical II)

Scheme 1

the following set of reactions.[1–3] For simplicity of the kinetic expression, ST and ST-OX represents starch and oxidum, respectively, and $ST^\bullet$ represents both radical I and radical II.

Initiation Reactions

Radical formation:

$$ST + Ce^{4+} \overset{k}{\rightleftharpoons} [Complex] \overset{k_d}{\longrightarrow}$$

$$ST^\bullet + Ce^{3+} + H^+ \qquad (1)$$

Reaction of free radical and monomer:

$$ST^\bullet + M \overset{k_{i1}}{\longrightarrow} STM^\bullet \qquad (2)$$

Reaction of Ce^{4+} and monomer:

$$Ce^{4+} + M \overset{k_{i2}}{\longrightarrow} M^\bullet + Ce^{3+} + H^+ \qquad (3)$$

Formation of oxidum:

$$Ce^{4+} + ST^\bullet \overset{k_{i3}}{\longrightarrow} ST\text{-}OX + Ce^{3+} + H^+ \qquad (4)$$

Reaction of Ce^{4+} and oxidum:

$$Ce^{4+} + ST\text{-}OX \overset{k_{i4}}{\longrightarrow} ST^\bullet + Ce^{3+} + H^+ \qquad (5)$$
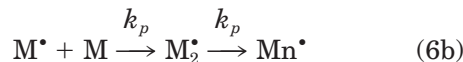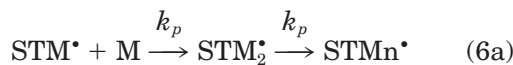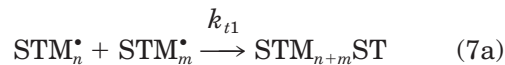
where, k is the equilibrium, k_d is the dissociation constants, and all k_is are initiation constants.

Propagation Reactions

$$STM^\bullet + M \overset{k_p}{\longrightarrow} STM_2^\bullet \overset{k_p}{\longrightarrow} STMn^\bullet \qquad (6a)$$

$$M^\bullet + M \overset{k_p}{\longrightarrow} M_2^\bullet \overset{k_p}{\longrightarrow} Mn^\bullet \qquad (6b)$$

Termination Reactions

Graft-forming termination reactions:

$$STM_n^\bullet + STM_m^\bullet \overset{k_{t1}}{\longrightarrow} STM_{n+m}ST \qquad (7a)$$

$$STM_n^\bullet + M_m^\bullet \overset{k_{t1}}{\longrightarrow} STM_{n+m} \qquad (7b)$$

Homopolymer-forming termination:

$$M_n^\bullet + M_m^\bullet \overset{k_{t1}}{\longrightarrow} M_{n+m} \qquad (8)$$

We have assumed here that three termination steps are governed by the same rate coefficient. These were reasonable, because all three basically involved the poly(methyl acrylate) radical. Termination by disproportionation was of negligible importance, and has been omitted.

The rate of methyl acrylate polymerization can be obtained from eqs. (1)–(8) by applying the stationary-state approximation to the various radical species in the system.

$$\frac{d[ST^\bullet]}{dt} = kk_d[ST][Ce^{4+}] - k_{i1}[ST^\bullet][M]$$
$$- k_{i3}[ST^\bullet][Ce^{4+}] + k_{i4}[ST\text{-}OX][Ce^{4+}] = 0 \quad (9)$$

$$\frac{d[STM^\bullet]}{dt} = k_{i1}[ST^\bullet][M] - k_{t1}[STM^\bullet]^2$$
$$- k_{t1}[STM^\bullet][M^\bullet] = 0 \quad (10)$$

$$\frac{d[M^\bullet]}{dt} = k_{i2}[M][Ce^{4+}] - k_{t1}[M^\bullet]^2$$
$$- k_{t1}[STM^\bullet][M^\bullet] = 0 \quad (11)$$

$$\frac{d[ST\text{-}OX]}{dt} = k_{i3}[ST^\bullet][Ce^{4+}] - k_{i4}[ST\text{-}OX][Ce^{4+}] \quad (12)$$

In these equations $M^\bullet$ and $STM^\bullet$ represents homopolymer and graft polymer radicals, respectively, in the system. Because there was little attack of cerium (Ce^{4+}) to monomer (M); therefore, $k_{i2}[M][Ce^{4+}]$ in eq. (11) can be omitted, and now summing eq. (9)–(12) yields:

$$kk_d[\text{ST}][Ce^{4+}] - k_{t1}[\text{STM}^\bullet]^2$$

$$- 2k_{t1}[\text{STM}^\bullet][\text{M}^\bullet] - k_{t1}[\text{M}^\bullet]^2 = 0$$

$$\text{or } k_{t1}([\text{STM}^\bullet]^2 + 2[\text{STM}^\bullet][\text{M}^\bullet] + [\text{M}^\bullet]^2)$$

$$= k\ k_d[\text{ST}][Ce^{4+}]$$

$$\text{or } [\text{STM}^\bullet]^2 + 2[\text{STM}^\bullet][\text{M}^\bullet] + [\text{M}^\bullet]^2$$

$$= k\ k_d[\text{ST}][Ce^{4+}]/k_{t1}$$

$$\text{or } ([\text{STM}^\bullet] + [\text{M}^\bullet])^2 = k\ k_d[\text{ST}][Ce^{4+}]/k_{t1}$$

$$\text{or } [\text{STM}^\bullet] + [\text{M}^\bullet] = (k\ k_d[\text{ST}][Ce^{4+}]/k_{t1})^{1/2} \quad (13)$$

The rate of consumption of vinyl monomer is defined by:

$$R_p = k_p[\text{STM}^\bullet][\text{M}] + k_p[\text{M}^\bullet][\text{M}]$$

$$= k_p[\text{M}]([\text{STM}^\bullet] + [\text{M}^\bullet]) \quad (14)$$

Putting the value of eq. (13) into eq. (14), we obtained

$$R_p = k_p[\text{M}](k\ k_d[\text{ST}][Ce^{4+}]/k_{t1})^{1/2}$$

$$= k_p\left(\frac{kk_d}{k_t}\right)^{1/2}[\text{ST}]^{1/2}[Ce^{4+}]^{1/2}[\text{M}] \quad (15)$$

The overall rate of polymerization (R_p) of free radical process is simply the rate of chain propagation. Equation (15) is the normal kinetic relationship for a simple radical polymerization, and shows the first-order dependence of R_p on [M], and the half-order dependence of $[Ce^{4+}]$ and [ST] held by this system.

On the basis of the simple kinetic behavior and of the effect of the methyl acrylate monomer ratio on the graft fraction (GF), it appears that the most important factor affecting GF was consumption between monomer and sago starch for initiator radicals. This provides the foundation for the following derivation of GF was defined by Brydon et al.[2]

Fraction of monomer consumed by STM$^\bullet$ radicals

$$= \frac{k_p[\text{M}][\text{STM}^\bullet]}{k_p[\text{M}]([\text{STM}^\bullet] + [\text{M}^\bullet])} \quad (16)$$

Fraction of monomer consumed by M$^\bullet$ radicals

$$= \frac{k_p[\text{M}][\text{M}^\bullet]}{k_p[\text{M}]([\text{STM}^\bullet] + [\text{M}^\bullet])} \quad (17)$$

A proportion of monomer consumed by homopolymer radicals was incorporated in the graft in the crosstermination reaction. This fraction was given by

$$= \frac{k_{t1}[\text{STM}^\bullet][\text{M}^\bullet]}{k_{t1}[\text{STM}^\bullet]([\text{STM}^\bullet] + [\text{M}^\bullet])} \quad (18)$$

Thus, the total fraction of monomer combined with starch, GF was given by

$$\text{GF} = \frac{k_p[\text{M}][\text{STM}^\bullet]}{k_p[\text{M}]([\text{STM}^\bullet] + [\text{M}^\bullet])}$$

$$+ \frac{k_{t1}[\text{STM}^\bullet][\text{M}^\bullet]}{k_{t1}[\text{M}^\bullet]([\text{STM}^\bullet] + [\text{M}^\bullet])}$$

$$\times \frac{k_p[\text{M}][\text{M}^\bullet]}{k_p[\text{M}]([\text{STM}^\bullet] + [\text{M}^\bullet])} \quad (19)$$

which was simplified to

$$\text{GF} = \frac{[\text{STM}^\bullet]}{[\text{STM}^\bullet] + [\text{M}^\bullet]}$$

$$+ \frac{[\text{STM}^\bullet]}{[\text{STM}^\bullet] + [\text{M}^\bullet]}\left\{\frac{[\text{M}^\bullet]}{[\text{STM}^\bullet] + [\text{M}^\bullet]}\right\}$$

$$= \frac{[\text{STM}^\bullet]([\text{STM}^\bullet] + [\text{M}^\bullet]) + [\text{STM}^\bullet][\text{M}^\bullet]}{([\text{STM}^\bullet] + [\text{M}^\bullet])^2} \quad (20)$$

Therefore,

$$1 - \text{GF} = \frac{[\text{M}^\bullet]^2}{([\text{STM}^\bullet] + [\text{M}^\bullet])^2} \quad (21)$$

and

$$\frac{1}{(1 - \text{GF})^{1/2}} = 1 + \frac{[\text{STM}^\bullet]}{[\text{M}^\bullet]} \quad (22)$$

The ratio $[\text{STM}^\bullet]/[\text{M}^\bullet]$ was obtained by rearranging of eqs. (9)–(12) and dividing:

$$\frac{[\text{STM}^\bullet]}{[\text{M}^\bullet]} = \frac{kk_d[\text{ST}]}{k_{i2}[\text{M}]} \quad (23)$$

Therefore,

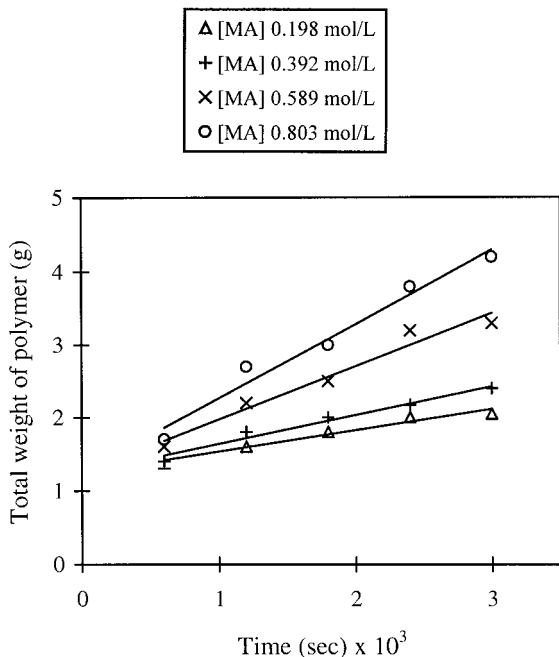$$\frac{1}{(1 - \text{GF})^{1/2}} = 1 + \frac{kk_d[\text{ST}]}{k_{i2}[\text{M}]} \quad (24)$$

[MA] 0.198 mol/L
[MA] 0.392 mol/L
[MA] 0.589 mol/L
[MA] 0.803 mol/L

Figure 1 Plot of PMA polymer formed as a function of time for series "A" experiments. Temperature, 50°C; $[H_2SO_4]$, 0.175 mol L^{-1}; [AGU], 0.135 mol L^{-1}; [CAN], 8.77×10^{-3} mol L^{-1}.
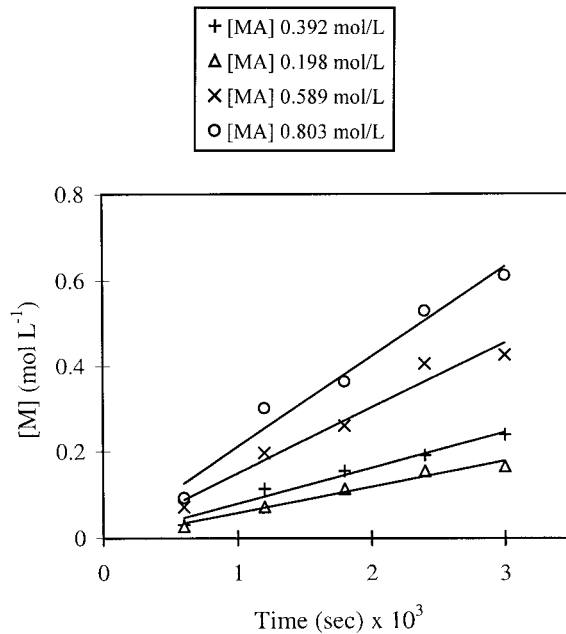
[MA] 0.392 mol/L
[MA] 0.198 mol/L
[MA] 0.589 mol/L
[MA] 0.803 mol/L

Figure 3 Plot of quantity of polymerized monomer (expressed as mol of monomer units per liter) as a function of time for series "A" Experiments. Other condition as in Figure 1.

Equation (24) correctly indicates that GF becomes zero at zero starch or at infinitely high monomer concentrations.
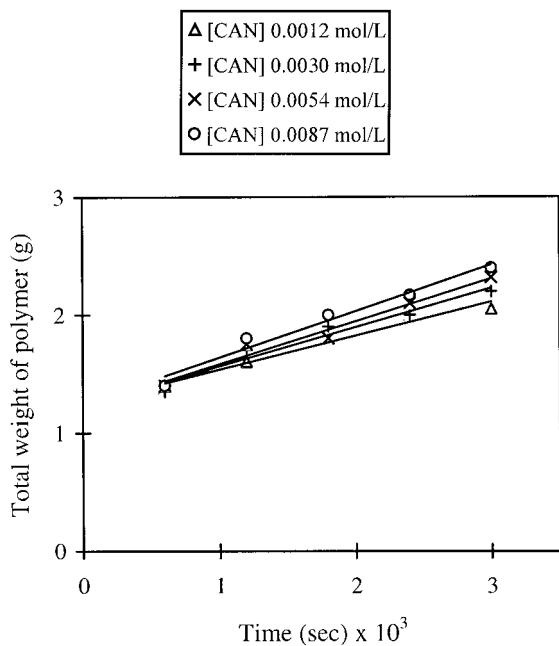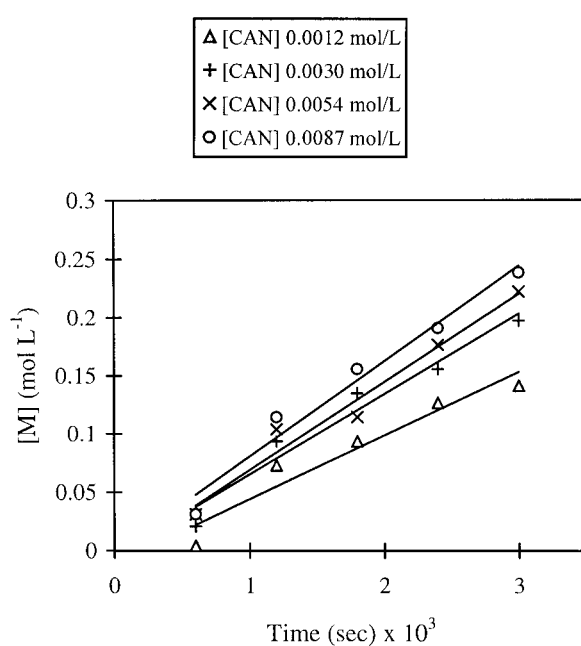
[CAN] 0.0012 mol/L
[CAN] 0.0030 mol/L
[CAN] 0.0054 mol/L
[CAN] 0.0087 mol/L

Figure 2 Plot of PMA polymer formed as a function of time for series "B" experiments. Temperature, 50°C; $[H_2SO_4]$, 0.175 mol L^{-1}; [AGU], 0.135 mol L^{-1}; [MA], 0.389 mol L^{-1}.

[CAN] 0.0012 mol/L
[CAN] 0.0030 mol/L
[CAN] 0.0054 mol/L
[CAN] 0.0087 mol/L

Figure 4 Plot of Quantity of polymerized monomer (expressed as mol of monomer units per liter) as a function of time for series "B" experiments. Other conditions as in Figure 2.

Verification of Rates of Polymerization

The rates of graft polymerization of styrene to polybutadiene were thoroughly investigated by Brydon et al.[2,9] According to their recommendation, we have plotted the gross weight of grafted poly(methyl acrylate) polymer formed as a function of polymerization time for series A and B experiments presented in Figures 1 and 2, respectively. In the said diagrams each line of both figures intersects the ordinate at a point corresponding to the initial weight of sago starch used in the reaction.

Berlin and Kislenko[1] suggested that the quantity of polymerized monomer can be calculated and expressed in mol of monomer unit per liter. In this study, we also calculated the quantity of polymerized methyl acrylate monomer as mol per liter, and the monomer [M] concentrations were plotted as a function of time for series A and B experiments are presented in Figures 3 and 4,

respectively. The initial rates from Figure 3 yielded the points in Figure 5, which show a first-order dependence of rate of polymerization (R_p) of methyl acrylate monomer concentration. Initial rate from Figure 4 was used to show the dependence of R_p on the square root of the initiator [CAN] concentration in Figure 6. These results of series A and B experiments showed that the methyl acrylate consumption at least follows normal kinetics relationship according to eq. (15), which are not affected by the sago starch concentration.

Poly(methyl acrylate) Grafting Efficiencies

The poly(methyl acrylate) graft fraction GF was the fraction of polymerized methyl acrylate chemically bound to the sago starch and given by the relationship[9]:

$$GF = \frac{\text{Total weight of poly(methyl acrylate)} - \text{weight of homopolymer (PMA)}}{\text{Total weight of poly(methyl acrylate)}}$$

The validity of eq. (24) was tested in Figure 7 in which $1/(1 - GF)^{1/2}$ was plotted against reciprocal monomer concentration (from series A) and sago starch concentration (from series C). In this case, the data points fit quite well in a straight line and ordinate intercept of unity was attained at a certain concentration of monomer. The required straight line and intercept unity was obtained at the concentration of monomer up to 0.803 mol L^{-1}.

The slope of the line in Figure 7 yield the ratio kk_d/k_{i2}. The ratio kk_d/k_{i2} expresses the relative rates of initiator (Ce^{4+}) attack on the sago starch and the monomer. The value of the slope obtained are 5.23; therefore, the rate of initiation of polymerization was faster than the rate of the homopolymer radical formation. There is a satisfactory concordance that supports the validity of the proposed theory. The values of the ratio (slope) obtained by Brydon et al.[2] was a minor difference to justify the assumption in their kinetic treatment. In comparison to our experimental results, the value of the slope obtained was a large enough difference ($kk_d/k_{i2} = 5.23$), which significantly supported the proposed kinetic theory. We were also aware of when one of the kinetic steps in eq. (13) was omitted, because we thought it a little attack of Ce^{4+} to the monomer. This argument

was true, that whenever experimental results fitted in eq. (24) and plotted in Figure 7, the ratio indicated the Ce^{4+} attack on starch was preferred rather than the monomer molecule in the competitive reactions. However, the Ce^{4+} attack on the monomer is not small at a higher monomer concentration, and beyond the 0.803 mol L^{-1} monomer, the highest amount of the homopolymer is
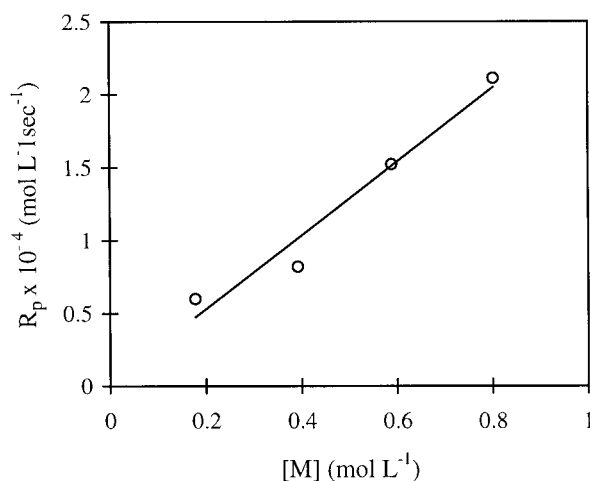

Figure 5 Rates of polymerization from Figure 3 as a function of monomer concentration. Other condition as in Figure 1.

formed in copolymerization. The predicted model was not satisfied at excessive homopolymer formation in the grafted copolymer products, i.e., it was unable to draw a straight line by the deviated points in Figure 7 due to a lot of homopolymer formation.

This study proves that the free radical formation by Ce^{4+} onto the sago starch molecule is preferable rather than the monomer molecule, and these findings also similar to Brydon et al.[2,9]

CONCLUSION

Under the experimental condition, a suitable rate equation was proposed. The rate equation of polymerization established from the experimental results was similar to the equation derived from the proposed reaction mechanism. The validity of eq. (24) was tested in which $1/(1 - GF)^{1/2}$ was plotted against the sago starch concentration (from series C) and the reciprocal monomer concentration (from series A), respectively. In each case, the required straight line and ordinate intercept of the unity was attained at a certain limit of monomer concentration. Our proposed kinetic
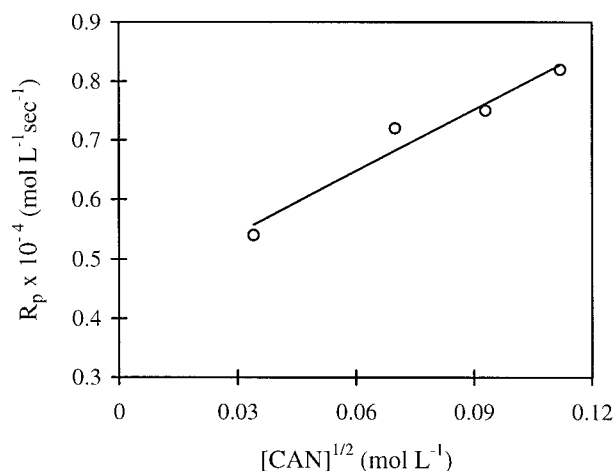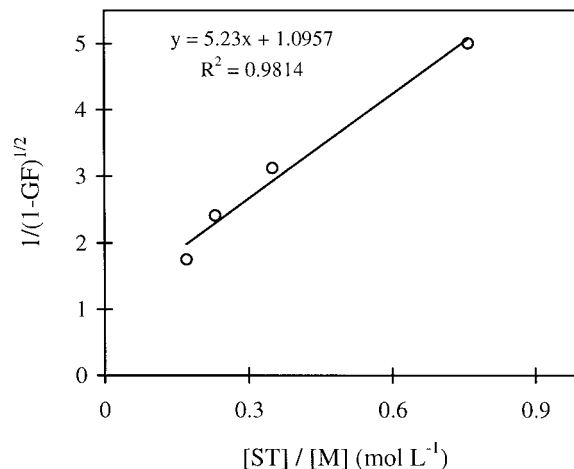

Figure 7 Dependence of grafted fraction of polymerized methyl acrylate on the ratio of sago starch to monomer concentration according to Eq. (24).

model for the grafting reaction was satisfactorily supported by the experimental results until there was no excessive homopolymer formation.

Figure 6 Rates of polymerization from Figure 4 as a function of square root of initiator [CAN] concentration. Other conditions as in Figure 2.

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