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Free radical grafting kinetics of acrylamide onto a blend of starch/chitosan/alginate

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ABSTRACT

Grafting of monomer onto polymer backbone is one of the effective and accessible methods for the chemical modification of polysaccharides. Grafting of acrylamide (AAm) onto polysaccharides blend (PsB) composed of starch, chitosan and alginate has been carried out using potassium persulfate (KPS) as an initiator. The kinetics of the grafting polymerization also has been studied. The grafting parameters have been evaluated by changing the initial concentrations of AAm from 8 to 16 g, PsB from 6 to 14 g and KPS from 0.2 to 1 g. Evidence of grafting has been obtained from FTIR, XRD and TGA. The kinetics of the grafting polymerization also has been studied. The grafting rate equation of the produced hydrogel (PsB-g-AAm) hydrogel has been expressed by: $Rg = k[AAm]\,[PsB]^{0.5}\,[KPS]^{0.5}$. The grafting rate is a first order dependence to [AAm] initial concentration and square root to [PsB] and [KPS] initial concentrations in the used concentrations range.

1. Introduction

Grafting is a useful method for modifying some properties of natural and synthetic polymers. In grafting process, amount of monomer is attached onto the polysaccharide backbone, the formed product can be provided with a number of new properties such that, it swells in water media with good product yield (El-Sayed et al., 2011; Sadeghi, Heidari, & Montazeri, 2011;Shifeng, Ying, Lucile, & Da-Wen, 2012).

Using a polysaccharide blend in the hydrogel preparation shows better mechanical stability and water retention ability, compared to single polysaccharide. In addition, it gives the opportunity to more field applications.

In view of the limitations encountered using the pure polysaccharides blend in hydrogel preparation, the concept of alginate–chitosan polyelectrolyte complex was introduced. Complexation of alginate with chitosan reduces the porosity of the alginate beads which in addition, chitosan acquires a higher level of mechanical strength with the support of the alginate gel mass (Wong, Chan, Kho, & Heng, 2002).

Considerable work on the graft polymerization of natural and synthetic polymers with the vinyl monomers has been reported (Jasim, Al-Karawi, & Hussein, 2010; Patel, Patel, Patel, Patel, & Patel, 1986; Saifuddin, Nur, & Abdullah, 2011; Vieira, Cestari, Airoldi, & Loh, 2008). Grafting process was initiated through generation of free radicals along the polysaccharide backbone as well as the monomer. Among the various methods allowing the generation of radicals, redox initiation systems were widely used (Abd-Alla, Mohamed, & Hesham, 2007; Abdel-Halim, 2012; Ifuku, Iwasaki, Morimoto, & Saimoto, 2012; Mino, Koizerman, & Rasmussen, 1959).

There are many comparative work for the grafting single polysaccharides with acrylamide using the traditional conventional methods. Potassium persulfate (KPS) has been used for the grafting of AAm onto starch, SWR obtained was 605 g/g, using [KPS] of 1.5 wt% of starch, St:AAm (weight ratio) of 1:1 and 140 min at 80 °C (Charoen, Toha, Azizon, & Suda, 2010).

Much attention had been paid to the studied of kinetics of radical graft polymerization of monomers onto polysaccharides by Berlin and Kislenko. 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.

Grafting rate (Rg) of acrylonitrile (AN) onto starch using KPS and potassium permanganate ($KMnO_4$) initiator, respectively has been studied. The grafting rate equations using two different types of initiators has been achieved (Brydon, Burnett, & Cameron, 1974; Singh, Tiwari, Pandey, & Singh, 2007):

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Graft polymerization of AAm, acrylic acid (AA) and methylmeth acrylate (MMA) monomers onto starch using potassium dichromate (PDC) as an initiator has been carried out (Berlin & Kislenko, 1992), Also the grafting of AA and ethyl methacrylate (EMA) monomers onto starch using CAN has been studied (Taghizadeh & Mehrdad, 2007).

The present work is concerned with studying the graft polymerization of acrylamide onto polysaccharides blend (PsB) in aqueous media using potassium persulfate as an initiator and methylene bis-acrylamide (MBA) as a crosslinker for producing a hydrogel. Moreover, the kinetics of free radical graft polymerization of AAm onto a blend of polysaccharides has been is examined. The obtained hydrogel integrated platform for the development of hydrogel based functionality compounds.

2. Materials and methods

2.1. Materials

Normal corn starch (Sigma–Aldrich, Germany), chitosan medium molecular weight (Sigma–Aldrich, Germany), alginic acid sodium salt from brown algae "alginate" (Routh, Germany) and acrylamide (Baker Chemical Co., USA) were the basic raw materials used for the hydrogel preparation. Potassium persulfate (KPS) (Merck, Germany) and methylenebisacrylamide (MBA) (Fluka, Germany) have been used as initiator and crosslinker, respectively. Other chemicals include: acetone, acetic acid and ethanol (El Nasr Pharmaceutical Chemicals Co.), and sodium hydroxide pellets (Laboratory chemicals, Modern Lab., Egypt). All experiments have been performed using distilled water (DW).

2.2. Methods

2.2.1. Preparation of the polysaccharides blend (PsB)

Three grams of starch were suspended in 70 ml DW and stirred for 30 min at 80 °C. 1 g of chitosan was dissolved in 70 ml acidified DW containing 1 wt% acetic acid and stirred for five hours at room temperature. 1 g of alginate was dissolved in 70 ml DW and stirred for four hours at room temperature. The three solutions have been mixed and stirred for 10 min giving the polysaccharides blend (PsB).

2.2.2. Grafting of acrylamide onto PsB

A known weight of KPS, AAm and 0.1 g of MBA have been added to PsB. The reaction mixture has been allowed to react in a water bath at 60 °C under nitrogen atmosphere. For a different grafting periods (10, 20, 30, 60, 90 and 120 min) have been conducted.

2.2.3. Graft polymerization for kinetics analysis

2.2.3.1. Determination of grafted AAm. The amount of the grafted AAm monomer onto the polysaccharides backbone (%*G*) has been estimated according to the following equation (Taghizadeh & Mafakhery, 2001):

$$\%G = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

where, W_1, W_0, and W_2 denote the weight of grafted product, original PsB and AAm, respectively. All the reaction parameters are presented in Table 1.

2.2.3.2. Effect of PsB concentration. The effect of adding different PsB weights (6, 8, 10, 12 and 14 g) using (12 g) acrylamide, (0.6 g) KPS and (0.1 g) MBA at 60 °C has been studied. AAm/PsB weight ratios of (2, 1.5, 1.2, 1 and 0.86 g/g) has been obtained.

Table 1
Experimental conditions for kinetic analysis of graft copolymerization of methyl acrylate and sago starch by ceric ion.

Exp. no.	PsB weight (gm)	Initiator KPS weight (gm)	Acrylamide weight (gm)	MBA weight (gm)
1	6	0.6	12	0.1
2	8	0.6	12	0.1
3	10	0.6	12	0.1
4	12	0.6	12	0.1
5	14	0.6	12	0.1
6	8	0.2	12	0.1
7	8	0.4	12	0.1
8	8	0.6	12	0.1
9	8	0.8	12	0.1
10	8	1	12	0.1
11	8	0.6	8	0.1
12	8	0.6	10	0.1
13	8	0.6	12	0.1
14	8	0.6	14	0.1
15	8	0.6	16	0.1

2.2.3.3. Effect of initiator concentration. The effect of adding different initiator weighs (0.2, 0.4, 0.6, 0.8 and 1 g using (8 g) PsB, (12 g) AAm and (0.1 g) MBA has been studied.

2.2.3.4. Effect of monomer concentration. The effect of adding different acrylamide weighs (8, 10, 12, 14 and 16 g) using (8 g) PsB, (0.6 g) KPS and (0.1 g) MBA has been studied giving AAm/PsB weight ratio of (1, 1.25, 1.5, 1.75 and 2 g/g).

2.3. Characterization and analysis

The prepared hydrogel has been characterized using the following methods.

2.3.1. Fourier transform infrared spectroscopy (FTIR)

JASCO FTIR-6100, Japan, using the absorbance technique (400–4000 cm^{-1} and resolution 4 cm^{-1}) was used to identify pure manganese octoate crystals.

2.3.2. X-ray diffraction (XRD)

Philips X-Ray diffraction equipment PW/1710 with Monochrome TOR, Cu-radiation at 40 KV, 35 mA and scanning speed of 0.02°/s.

2.3.3. Thermal gravimetric analysis (TGA)

The thermal analysis was done by means of Schimadzu TGA-50H. The temperature of the powdered sample was raised 10 °C/min up to 500 °C.

3. Results and discussion

3.1. Characterization of PsB-g-AAm

3.1.1. Fourier transforms infrared spectroscopy (FTIR)

Grafting of acrylamide onto polysaccharide blend (PsB) has been confirmed by comparing FTIR spectra of pure PsB mixture with the grafted PsB as shown in Fig. 1. For the pure PsB, there are peaks at 1157, 1080, 1016, and 927 cm^{-1} due to the C=O stretching, a peak at 3390 cm^{-1} (O—H stretching) and a band at 2926 cm^{-1} (C—H stretching), the characteristic peaks of chitosan are 1600 cm^{-1} (N—H bend), 1327 cm^{-1} (C—N stretch), 1155 cm^{-1} (bridge O stretch), two peaks at 1618 and 1440 cm^{-1} (—COO— stretching) and the characteristic peak of alginate appeared at 819 cm^{-1} (Na—O). For the grafted PsB, some new absorption peaks appeared; N—H and O—H stretching absorption are merged to a strong peak around 3428 cm^{-1}. Amide (I) and Amide (II) bands are seen as one strong sharp peak at 1450 cm^{-1} while, C—H stretching vibrations are

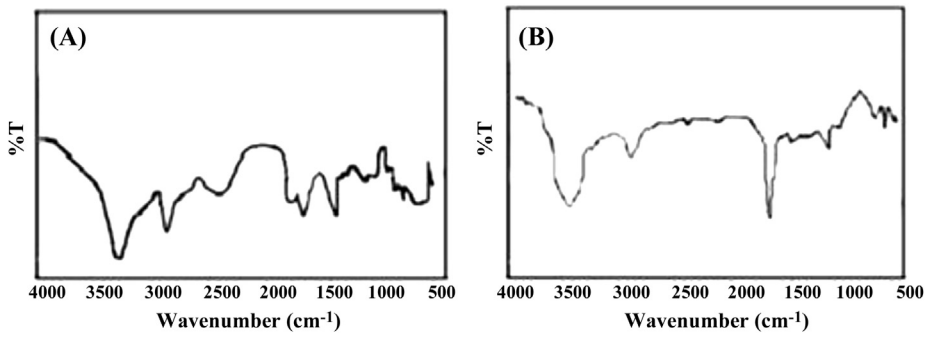

Fig. 1. FTIR for PsB; pure (A), PsB-g-AAm (B),.

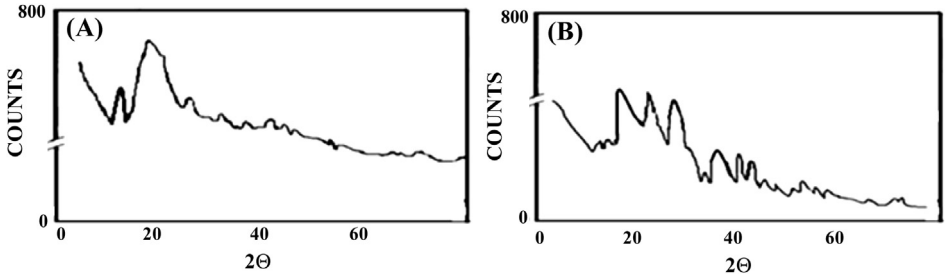

Fig. 2. XRD for PsB; raw (A), PsB-g-AAm (B).

present at 2926 cm^{-1} and 2856 cm^{-1}. $-CH_2$ vibrations appear at 1460 cm^{-1}; C—O stretching vibrations around 1048 cm^{-1}, peak at 3416 cm^{-1} is of quite reduced intensity and broadness,(due to overlapping of O–H stretching of chitosan and N—H stretching of amide groups). Presence of the N—H and C=O stretching vibrations in grafted hydrogel confirms the presence of AAm and hence confirms the evidence of grafting.

3.1.2. X-ray diffraction

XRD patterns for raw and grafted polysaccharides blend (PsB) are shown in Fig. 2. For raw PsB which composed of starch, chitosan and alginate, XRD patterns presents the nature of the three polysaccharides. There are crystalline areas at 2θ equal to 14.67°, 16.97°, 19.67°, 21.97° and 23.87° due to starch and chitosan crystallinity while as, the non-crystalline area is due to the fact that raw alginate has very small crystallinity. For the grafted PsB, there are increasing crystallinity areas observed at 2θ equal to 18.7°, 21.1°, 23.4°, 28.3°, 38.7°, 43.5° and 48.7° which support the presence of AAm this is because acrylamide has a crystalline nature with characteristic peaks in the observed areas. So, increasing the crystallinity of the grafted hydrogel proof the grafting of acrylamide onto the polysaccharides backbone (Brydon, Burnett & Cameron, 1974).

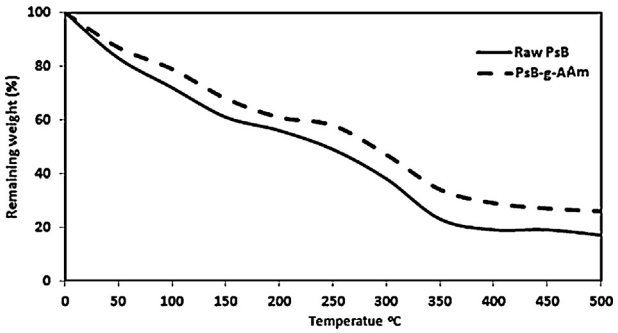

Fig. 3. TGA for raw and grafted PsB.

Table 2
Values of grafting rate and grafting rates constants for PsB_y-g-Am using conventional technique.

Initial Concentrations			Rg × 10^5 (mol/l.s)	k × 10^4 (l/mol.s)
PsB concentration [AGU] (mol/L)	Am concentration (mol/L)	KPS] concentration (mol/L)		
0.167	0.805	0.011	4.405	12.893
0.223	0.805	0.011	4.445	11.522
0.278	0.805	0.011	5.232	11.865
0.334	0.805	0.011	6.404	13.257
0.390	0.805	0.011	3.323	6.368
0.223	0.537	0.011	2.685	10.220
0.223	0.671	0.011	2.104	6.400
0.223	0.805	0.011	2.454	6.220
0.223	0.939	0.011	3.197	6.947
0.223	1.073	0.011	1.478	2.812
0.223	0.805	0.004	2.178	9.564
0.223	0.805	0.007	4.669	14.498
0.223	0.805	0.011	4.360	11.053
0.223	0.805	0.014	5.619	12.336
0.223	0.805	0.018	4.461	8.761

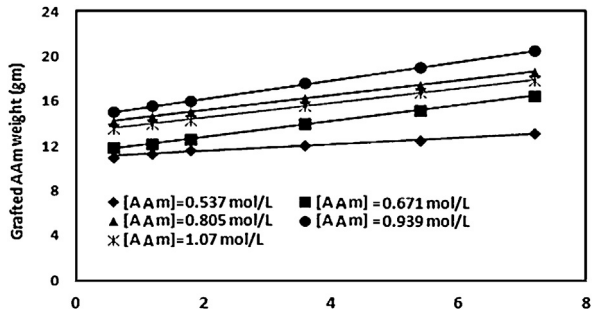

Fig. 4. Time dependence of grafted AAm weight at different initial AAm concentrations.

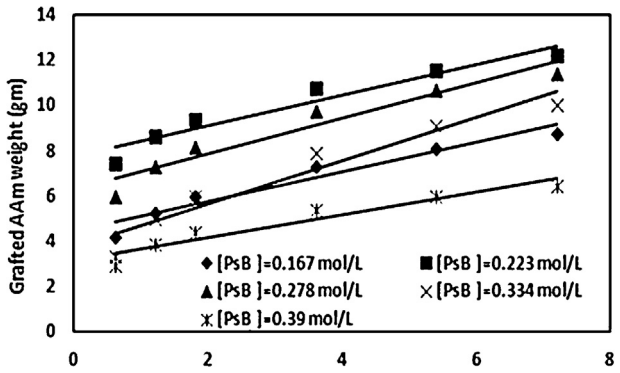

Fig. 5. Time dependence of grafted AAm weight at different initial PsB concentrations.

3.1.3. *Thermal gravimetric analysis (TGA)*

TGA for raw and grafted PsB prepared on the basis of %weight loss due to thermal decomposition are presented in Fig. 3.

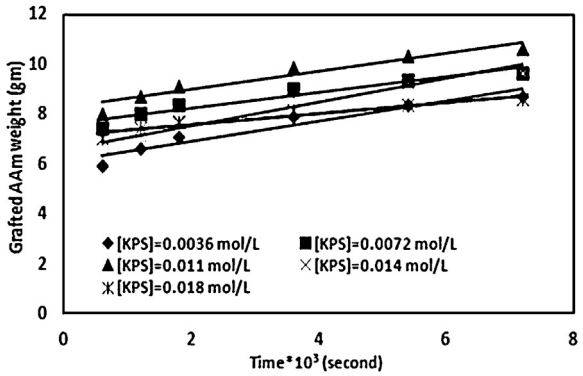

Fig. 6. Time dependence of grafted AAm weight at different initial KPS concentrations.

As observed in Fig. 3 PsB before the grafting process curve shows an initial stage at a temperature ranging from ambient temperature to 80 °C giving %weight loss of 15% which is due to the dehydration process in such a hydrophilic superabsorbent polymer. The major weight loss of 52% occurs within temperature ranging from 160 °C to 280 °C. The third stage of decomposition is rather slow and results in about 8% weight loss within temperature ranging from 280 °C to 480 °C due to the polysaccharide chains degradation. TGA for the grafted polysaccharide hydrogel may be divided into three stages as follows: the first stage is assigned to the loss of water and the second stage corresponds to the decomposition (thermal and oxidative) of polysaccharide and the 3rd stage vaporization and elimination of volatile products.

Up to 480 °C the average weight losses for the raw and the grafted PsB hydrogels were 88% and 75%, respectively which confirms that the grafted PsB is more thermally stable than the raw PsB.

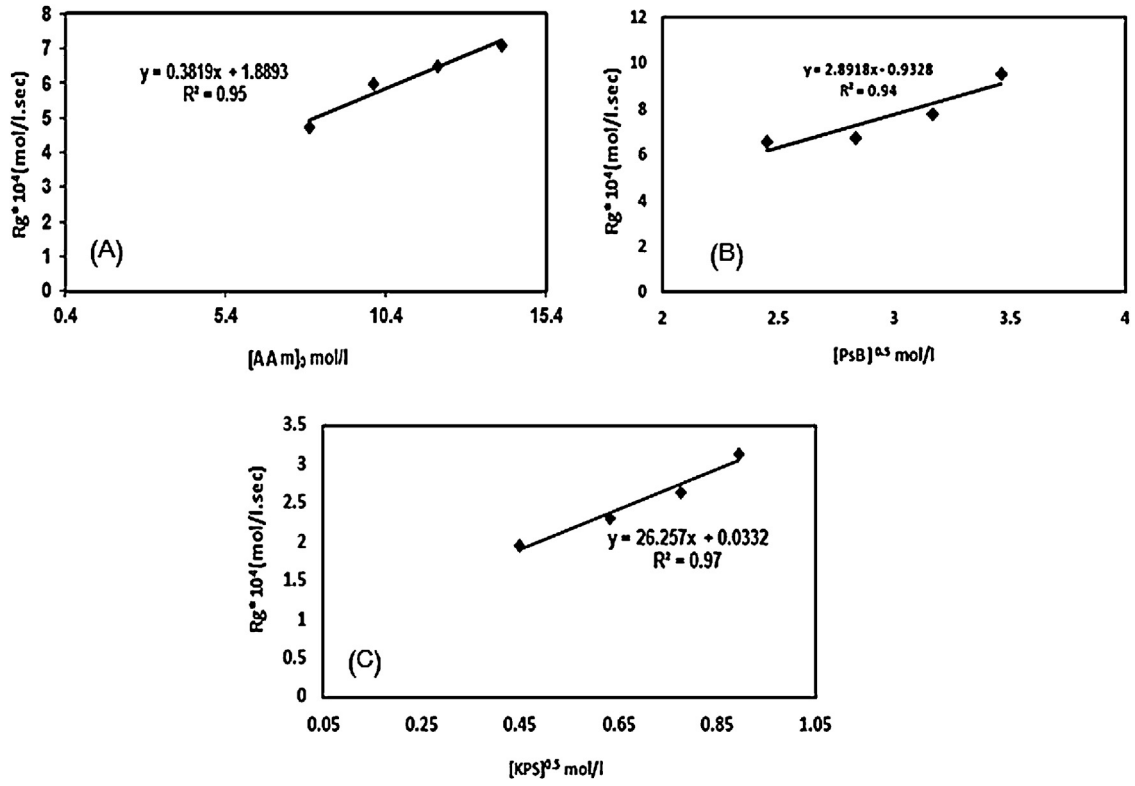

Fig. 7. Effect of (A) initial AAm monomer concentration; (B) initial square root of PsB concentration; (C) initial square root of KPS concentration on grafting rate.

3.2. Grafting rate kinetics

The grafting rate kinetics of AAm monomer onto the polysaccharides blend (PsB) using KPS initiator has been investigated.

Figs. 4–6 represent the plot of the grafted AAm monomer weight (g) as a function of grafting time (s) which has been calculated as equation (1) at different initial concentrations of AAm, PsB and KPS, respectively. The reactants used for different AAm weights (8, 10, 12, 14 and 16) are: PsB = 8 g, KPS = 0.6 g and MBA = 0.1 g while, the reactants used for different PsB weights (6, 8, 10, 12 and 14 g) are: AAm = 12 g, KPS = 0.6 g and MBA = 0.1 g and the reactants used for different KPS weights (0.2, 0.4, 0.6, 0.8 and 1 g) are: PsB = 8 g, AAm = 12 g, and MBA = 0.1 g. Linear relations are obtained with correlation coefficient up to 98%. It is well noted that maximum grafted weights were obtained at 12, 8 and 0.6 g for [AAm],[PsB] and [KPS], respectively at the investigated concentration ranges. Values of Rg were ranging from 2.4×10^5 to 3.2×10^5, 4.4×10^5 to 6.4×10^5 and 2.1×10^5 to 5.6×10^5 mol/l.s for the effect of [Am], [PsB] and [KPS] concentrations, respectively as depicted in Table 2.

The slopes of Figs. 4–6 have been used to study the effect of initial AAm monomer concentration, initial square root of PsB concentration and initial square root of KPS concentration on grafting rate as shown in Fig. 7A–C.

It can be concluded that under the experimental conditions, a grafting rate equation is well expressed by the rate equation: $Rg = K[AAm][PsB]^{0.5}[KPS]^{0.5}$ for the grafting of AAm monomer onto the polysaccharides blend [PsB] which is a first order dependence to [AAm] concentration and square root of [PsB] and [KPS] concentrations. The values of grafting rate constant (k) were estimated and ranged from 2.8×10^4 to 10×10^4, 6.3×10^4 to 12.8×10^4 and 8.7×10^4 to 14.5×10^4 l/mol.s for the effect of [Am], [PsB_y] and [KPS] concentrations, respectively as mentioned in Table 2. Changing in the grafting rate constant values may be attributed to the fact that k is not only a function on the temperature rising but also, k may be affected by increasing the reaction medium viscosity. There for, the initial rate of radical polymerization of acrylamide onto PsBy is considered in relation to the viscosity of the system (Ashok, Singh, & Munish, 2009; Berlin & Kislenko, 1992; Taghizadeh & Mehrdad, 2007).

4. Conclusion

According to the previously mentioned results it can be concluded that:

The characterization tests studied revealed the formation hydrogel based on grafting of acrylamide onto the target polysaccharides blend according to FTIR, XRD and TGA analysis.

Under the experimental conditions, a grafting rate equation has been estimated for the grafting of AAm monomer onto the polysaccharides blend [PsB], which shows a first order dependence of the rate on [AAm] concentration and square root of [PsB] and [KPS] concentrations.

The grafting rate equation of PsB–g–AAm hydrogel produced via changing the initial concentrations of AAm, PsB and KPS is well expressed by the rate equation: $Rg = k[AAm][PsB]^{0.5}[KPS]^{0.5}$.

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