

Studies of Kinetic Polymerization of Pectin-g-polyAAM in Homogeneous Solution

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In this work, we have focused on study of kinetics of polymerization of graft copolymerization pectin and acrylamide (AAM) in a homogeneous solution. The relation kinetics of polymerization pectin-g-polyAAM with effective parameters was investigated as well. The kinetics of the graft copolymerization showed a second order kinetics of reaction. In addition, the effect temperature onto polymerization was also studied.

Key Words: Pectin, Acrylamide, Effective parameters, Modify structure, Kinetics of polymerization.

INTRODUCTION

Pectin is a naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry. It has been used successfully for many years in the food and beverage industry as a thickening agent, a gelling agent and a colloidal stabilizer. Pectin also has several unique properties that have enabled it to be used as a matrix for the entrapment and/or delivery of a variety of drugs, proteins and cells. However, it may need to be further modified for some special applications¹⁻³.

Among the diverse approaches that are possible for modifying polysaccharides, grafting of synthetic polymer is a convenient method to add new properties to a polysaccharide with minimum loss of the initial properties of the substrate². Graft copolymerization of vinyl monomers onto polysaccharides using free radical initiation has attracted the interest of many scientists. Up to now, considerable works have been devoted to the grafting of vinyl monomers onto the substrates, specially cellulose³. Of the monomers grafted, acrylonitrile (AN) has been the most frequently used one, mainly due to its highest grafting efficiency², improving the thermal resistance of the graft copolymer⁴ and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents².

The literature survey, however, reveals that few modifications deal with chemical grafting of a pre-modified polysaccharide such as pectin. APS-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate⁵, acrylonitrile/methyl methacrylate mixture⁶ and 4-vinylpyridine⁶ onto pectin has been reported. However, to

the best of our knowledge, no report has been published on the kinetic graft polymerization of pectin with AAM using APS-saccharide initiating system. Hence, the objectives of this study was investigate kinetics polymerization of pectin and polyacrylamide.

EXPERIMENTAL

Pectin (chemical grade, MW 50000) was purchased from Merck Chemical Co. (Germany). Acrylamide (AAM, Merck) was used after recrystallization. Ammonium persulfate (APS, Merck) was used as received. All other chemicals were of analytical grade.

Synthesis of copolymer: A facial one step preparative method was used for synthesis of Pec-polyacrylamide copolymer. Pectin (0.50-1.5 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 50-500 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath. After complete dissolution of pectin to form a homogeneous solution, a definite amount of ammonium persulfate solution (0.15 g in 5 mL H₂O) was added to pectin solution and was allowed to stir for 10 min. After adding ammonium persulfate, certain amounts of monomer (AAM 1.50 g in 5 mL H₂O) was added to the pectin solution. After 90 min, the reaction product was allowed to cool to ambient temperature. The produced material was poured to excess non solvent ethanol (200 mL) and kept for 3 h remove water. Then ethanol was decanted and the product scissored to small pieces. Finally, the filtered copolymer is dried in oven at 60 °C for 10 h.

RESULTS AND DISCUSSION

Reaction rate: The rates of polymerization (R_p) and graft copolymerization (R_g) may be evaluated as measures of the rate of monomer disappearance by using the following equations¹⁸:

$$R_p (\text{mol s}^{-1} \text{ m}^{-3}) = \frac{\text{Weight of total polymer formed}}{\text{Molecular weight of monomer} \times [\text{reaction time (s)}] \times \text{volume (m}^3\text{)}} \quad (1)$$

$$R_g (\text{mol s}^{-1} \text{ m}^{-3}) = \frac{\text{Weight of grafted polymer}}{\text{Molecular weight of monomer} \times [\text{reaction time (s)}] \times \text{volume (m}^3\text{)}} \quad (2)$$

The calculation of R_p values may be of significant importance in confirming a proposed reaction mechanism and kinetics. Therefore, we investigated the relation between rate of graft copolymerization and concentration of APS, AAm and pectin. Figs. 1-3 show that the plots of R_p versus the monomer concentration, [AAm], half-order of the initiator concentration, $[\text{APS}]^{1/2}$ and the polysaccharide concentration, $[\text{pec}]^{1/2}$, are linear. This is in agreement with a modified kinetic scheme already explored for CAN-initiated acrylonitrile grafting onto carboxymethyl cellulose⁸. The statement of rate of polymerization according to the **Scheme-I** is as follows:

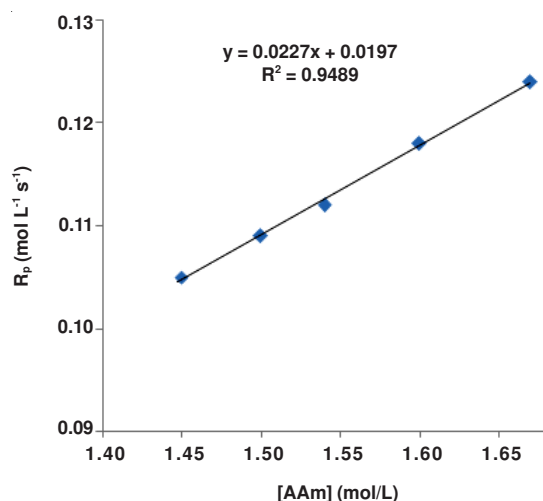


Fig. 1. Plot of R_p versus monomer concentration

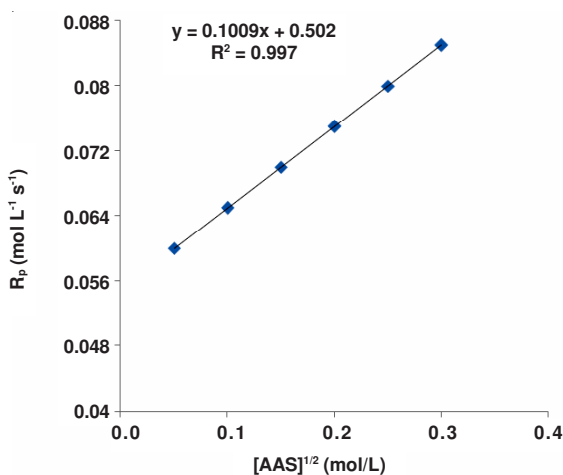


Fig. 2. Plot of R_p versus initiator concentration

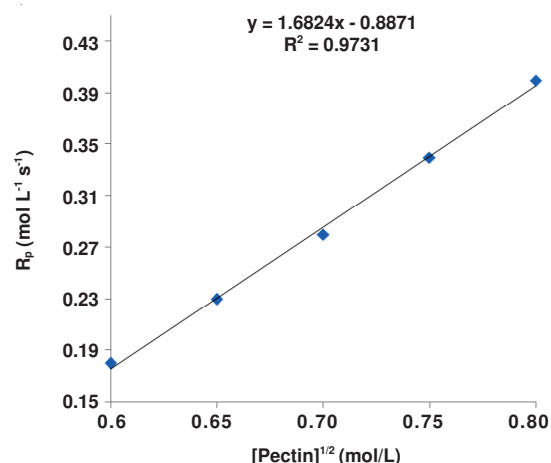


Fig. 3. Plot of R_p versus polysaccharide concentration

$$R_p = k_p \left(\frac{Kk_d}{k_t} \right)^{1/2} [\text{pec}]^{1/2} [\text{APS}]^{1/2} [\text{AAm}] \quad (3)$$

The coefficient K is the equilibrium constant, k_p , k_d and k_t are the rate constants for propagation, pec-APS complex dissociation and termination reactions, respectively. Therefore, we preliminarily conclude that the APS-initiated grafting of AAm onto pectin is also fitted with this kind of rate statement.

The overall activation energy (E_a) of the graft polymerization reaction was calculated by using of the eqn. 3 and the slope of the plot $\ln R_g$ versus $1/T$ (Fig. 4) based on Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization was found to be 16.85 kJ/mol.

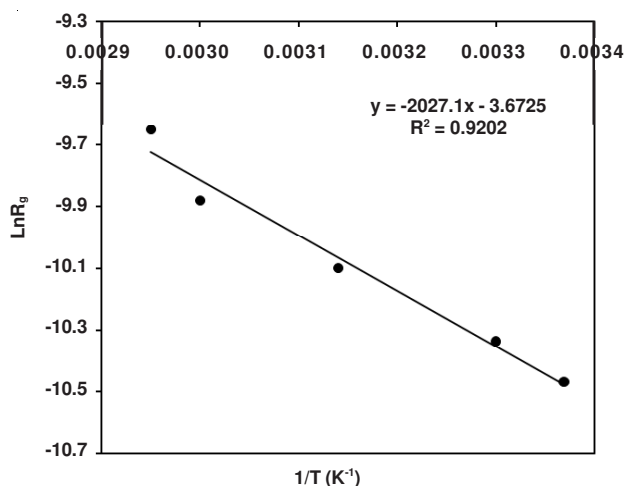
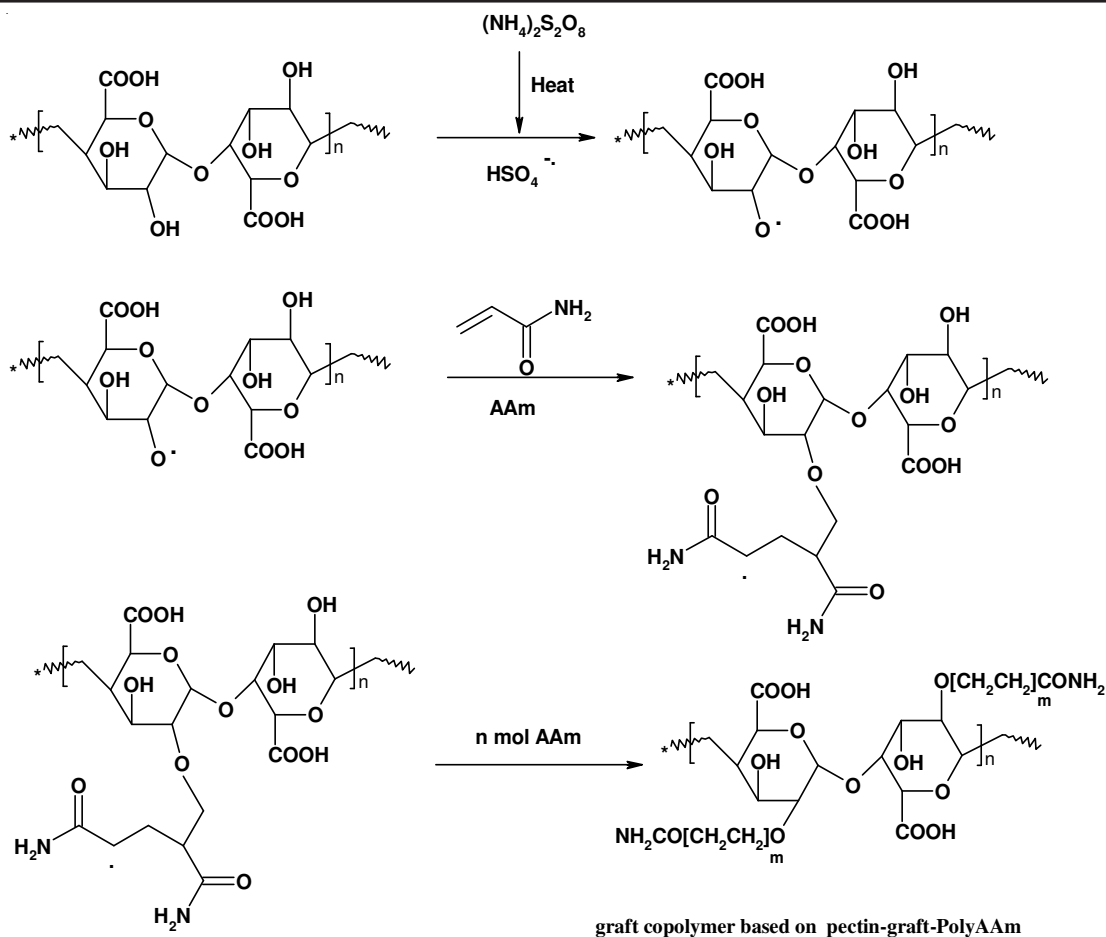


Fig. 4. Plot of $\ln R_g$ versus $1/T$ for estimating the activation energy of the graft polymerization reaction

Effect of temperature: To study the influence of the reaction bath temperature on the grafting parameters, the grafting of AAm onto pectin was carried out at six temperature ranging from 40-75 °C. The results are given in Table-1. As shown in Fig. 5, grafting percentage (Gr %) is increased with increasing the temperature from 40-55 °C and then decreased. At 55 °C, maximum grafting (Gr 557 %), minimum homopolymer content (12 %) and highest add-on value (95.3 %) was obtained. Improvement of grafting up to 55 °C can be attributed to the following factors: increased the number of free radicals formed



Scheme-I: A brief proposed mechanism for APS-induced grafting of polyacrylamide onto pectin

TABLE-1
GRAFTING PARAMETERS FROM THE GRAFT
POLYMERIZATION OF ACRYLAMIDE ONTO
PECTIN AT DIFFERENT TEMPERATURES

T (°C)	Time (min)	PC (%)	Gr (%)	Hp (%)	Add (%)	Ge (%)
40.00	60.00	66.66	177.00	37.10	75.70	66.22
45.00	60.00	72.70	216.00	22.60	80.40	94.10
50.00	60.00	84.80	413.00	17.60	88.00	122.30
55.00	60.00	95.70	557.00	12.00	95.10	170.00
60.00	60.00	90.20	438.00	13.40	88.50	164.20
65.00	60.00	87.30	402.00	19.00	83.80	109.00
70.00	60.00	79.00	312.00	24.70	81.80	77.00
75.00	60.00	65.80	203.00	31.30	78.00	68.50

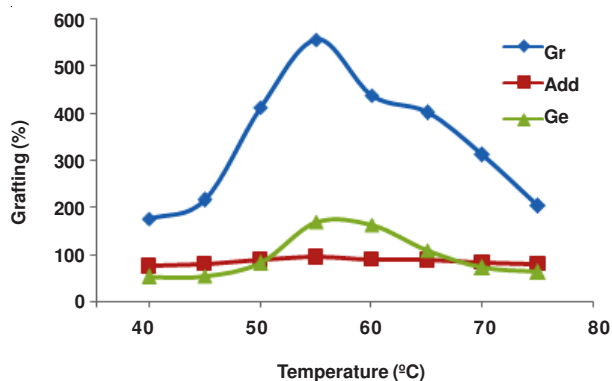


Fig. 5. Effects of reaction temperature on the graft copolymerization. Reaction conditions: pectin 1.5 wt %, APS 0.05 M, AAm 0.35 M, time 2 h

on the pectin backbone, increased propagation of the graft copolymerization onto pectin, enhanced diffusion of monomer and initiator into and onto backbone structure and increased in mobility of the monomer molecules and their higher collision probability with the backbone macroradicals. However, graft yield was decreased as the bath temperature was raised beyond 55 °C. This can be accounted for in terms of chain radical termination at higher temperatures. Premature termination of growing chains and instability of the APS-saccharide complex are presumably another reasons for reduced amount of grafting beyond 55 °C. The homopolymer formation is minimal at the bath temperature of 55 °C⁷.

In summary, a novel copolymer, Pec-g-polyacrylamide, was synthesized in an aqueous solution by graft copolymerization of acrylamide monomer onto pectin backbone using ammonium persulfate as an initiator in water solution.

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