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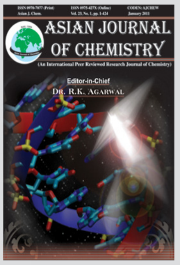

Optimized Graft Copolymerization of Pectin-g-Poly(acrylonitrile)

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In this work, large numbers of cyanide functional groups were introduced onto pectin by grafting with polyacrylonitrile. The graft copolymerization reactions were carried out under nitrogen atmosphere using ceric ammonium nitrate as an initiator. Evidence of grafting was obtained by comparing FTIR spectra of pectin and the graft copolymer as well as solubility characteristics of the products. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, acrylonitrile monomer and pectin.

Key Words: Pectin, Acrylonitrile, Graft copolymerization.

INTRODUCTION

Pectin is a naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry[1]. 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 applications.

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 substrate[2]. 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 cellulose[3]. Of the monomers grafted, acrylonitrile has been the most frequently used one, mainly due to its highest grafting efficiency[2,4], improving the thermal resistance of the graft copolymer[5] and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents[2,6].

The literature survey reveals that few of the modifications deal with chemical grafting of a pre-modified polysaccharide such as pectin. Ceric-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate[7,8], acrylonitrile/methyl methacrylate mixture[9], acrylamide (AAm)[10,11] and 4-vinylpyridine[12,13] onto pectin has been reported. However, to the best of our knowledge, no report has been published on the optimization of acrylonitrile graft polymerization onto pectin using ceric-saccharide initiating system. As a part of our research program on polysaccharide modification, herewith we report the optimized ceric ammonium nitrate-induced synthesis of pectin-g-polyacrylonitrile under an inert atmosphere.

EXPERIMENTAL

Pectin was purchased from Fluka, ceric ammonium nitrate (CAN, Fluka) was used without purification. Acrylonitrile monomer (Merck) was distilled before use.

Graft polymerization: The ceric ammonium nitrate solution was prepared by dissolving 2.74 g ceric ammonium nitrate in 50 mL of 1 N HNO_3. Generally, 3.5 mL of this stock solution (0.10 M) was used for each experiment except for the experiments by, which the effect of the initiator concentration was studied.

The pectin solution was prepared in a 100 mL two-neck flask equipped with magnetic stirrer, gas inlet and reflux condenser. Total volume of the aqueous solution was 57 mL in all experiments. To control the reaction temperature, the flask was placed in a water bath preset at desired temperature. A gentle stream of purified N_2 was purged through the system during the whole reaction time.

Desired amount of acrylonitrile monomer was added to the flask and the mixture was heated at given temperature and stirred for 10 min. Then a given volume of the initiator solution was added to the mixture. The mixture was continuously stirred at the desired temperature until completion of the reaction

(2 h). After adding hydroquinone solution (0.5 wt %, 2 mL), cooling to room temperature and adding few droplets of a molar sodium hydroxide solution to neutralize the remaining acid, the product was then precipitated in excess amount of methanol while mild stirring for 10 min. The product was filtered, thoroughly washed with methanol and dried at 50 ºC for 1 h. To separate the polyacrylonitrile homopolymer, 0.5 g of the crude product was poured in 50 mL of dimethyl formamide (DMF) and stirred gently at 30 ºC for 24 h. After centrifugating and decanting the supernatant (polyacrylonitrile in DMF), the pectin-g-polyacrylonitrile was precipitated in methanol, thoroughly washed with methanol and dried at 50 ºC to reach a constant weight. A brief proposed mechanism for ceric-induced grafting of polyacrylonitrile onto pectin (Pec) showed in **Scheme-I**.

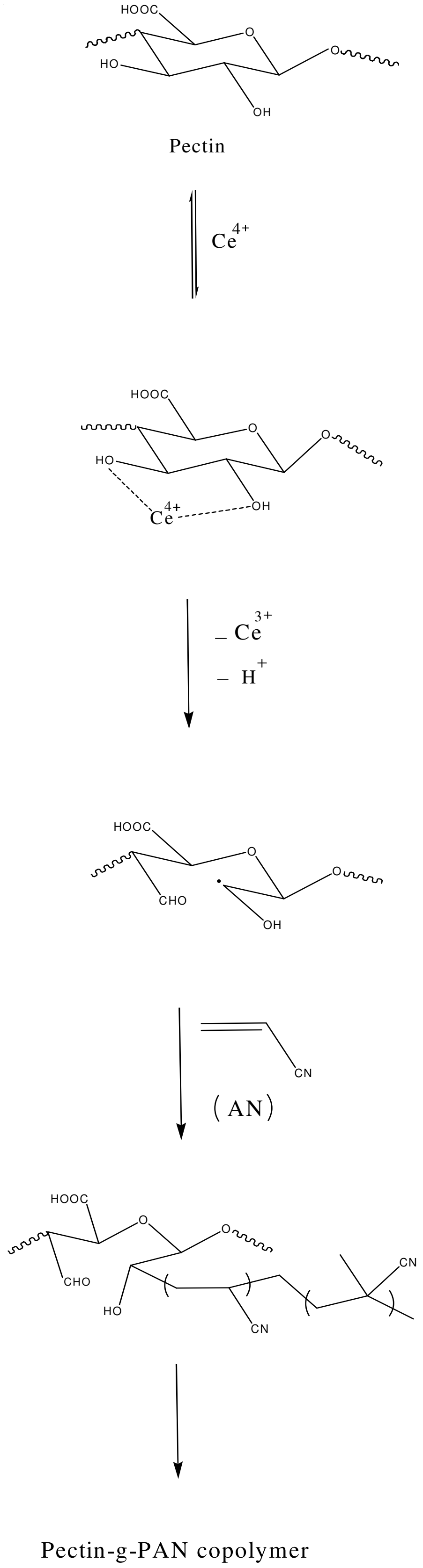
Instrumental analysis: The pectin-g-polyacrylonitrile samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer.

RESULTS AND DISCUSSION

Grafting evidences: The simplest method to prove the formation of pectin-g-polyacrylonitrile is based on the solubility difference of the graft copolymer and the homopolymer, polyacrylonitrile. Pectin and polyacrylonitrile are soluble in water and DMF, respectively. When a reaction product was Soxhlet-extracted with DMF and alternately with water for 24h, an insoluble solid was still remained. A pectin/polyacrylonitrile physical mixture was dissolved completely when it was treated in the same way. Therefore, it is obvious that the graft copolymer obtained was not a simple physical mixture, but some chemical bonds must exist between the pectin substrate and polyacrylonitrile macromolecules.

The polyacrylonitrile grafting was also confirmed by the differences between FTIR spectra of the substrate and that of the graft copolymer. Fig. 1 shows the FTIR spectra of the pectin substrate, polyacrylonitrile and the pectin-g-polyacrylonitrile graft copolymer freed from homopolyacrylonitrile. The existence of a sharp intense peak at 2246 cm^{-1} in IR spectra of the graft copolymers is an evidence of grafting. This absorption band arises from stretching vibration mode of the nitrile (C≡N) groups. Most of the other peaks are related to the carbohydrate backbone. Since polyacrylonitrile could be extracted nearly completely from a physical mixture of polyacrylonitrile and polysaccharide by DMF, the presence of appreciable amounts of nitrile groups in our reaction products after extraction is an additional proof for grafting of polyacrylonitrile onto the polysaccharide.

Optimization of polymerization: Since polymerization variables determine the extent of grafting and homopolymer amount, certain factors affecting the grafting parameters were investigated to achieve the optimum condition of polymerization. Therefore, we optimized the grafting of acrylonitrile onto pectin in homogenous aqueous media by changing temperature, the initial concentration of monomer, initiator and the relative amount of the substrate. Within the range of the amount of the reactants used, our preliminary studies showed no considerable dependence between the reaction time and the grafting extent.



(a)

Scheme-I: A brief proposed mechanism for ceric-induced grafting of polyacrylonitrile onto Pectin (Pec)

The conversion as well as the grafting parameters, *i.e.,* homopolymer content (Hp), grafting ratio (Gr) and the

TABLE-1
GRAFTING PER CENT VARIANCES WITH CONCENTRATION OF CERIC AMMONIUM NITRATE (CAN) VARIANCE

CAN (M)	W_0	W_1	W_2	T (ºC)	Time (min)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.008	1.00	4.50	3.40	60.00	60.00	240.00	24.00	70.50	75.50
0.010	1.00	4.90	3.80	60.00	60.00	280.00	22.40	73.60	77.50
0.080	1.00	6.10	5.50	60.00	60.00	450.00	9.80	81.80	90.10
0.100	1.00	6.40	6.20	60.00	60.00	520.00	3.10	84.00	96.80
0.120	1.00	5.10	5.40	60.00	60.00	440.00	6.80	81.40	93.10
0.150	1.00	5.60	5.10	60.00	60.00	410.00	8.90	80.20	91.70

TABLE-2
GRAFTING PARAMETERS FROM THE GRAFT POLYMERIZATION[a] OF ARCRYLONITRILE ONTO PECTIN AT DIFFERENT TEMPERATURES

T (ºC)	W_0	W_1	W_2	Time (min)	Gr (%)	Hp (%)	Add (%)	Ge (%)
40.00	0.50	3.80	2.00	60.00	300.00	47.30	75.00	52.60
45.00	0.50	4.80	2.60	60.00	420.00	45.80	80.70	54.10
50.00	0.50	5.10	4.20	60.00	740.00	17.60	88.00	82.30
55.00	0.50	5.80	5.10	60.00	920.00	12.00	90.10	87.90
60.00	0.50	5.50	4.80	60.00	860.00	12.60	89.50	87.20
65.00	0.50	5.40	4.10	60.00	720.00	24.00	87.80	75.90
70.00	0.50	4.30	3.10	60.00	520.00	27.90	83.80	72.00
75.00	0.50	4.00	2.50	60.00	400.00	37.50	80.00	62.50

[a] Reaction conditions: Pectin 0.5 g, water 50 mL, acetonitrile 3 mL, ceric ammonium nitrate 0.1 M.

grafting add-on values was calculated using the following equations:

$$Gr = W_3/W_0 \quad (1)$$

$$Hp = W_2/(W_2 + W_3) \quad (2)$$

$$\text{Add-on} = (W_3 - W_0)/W_3 \quad (3)$$

where W_0, W_1, W_2, W_3 and W_4 are weight of the initial substrate, the monomer charged, the homopolymer extracted, the homopolymer-free graft copolymer and polyacrylonitrile side-chains separated, respectively.

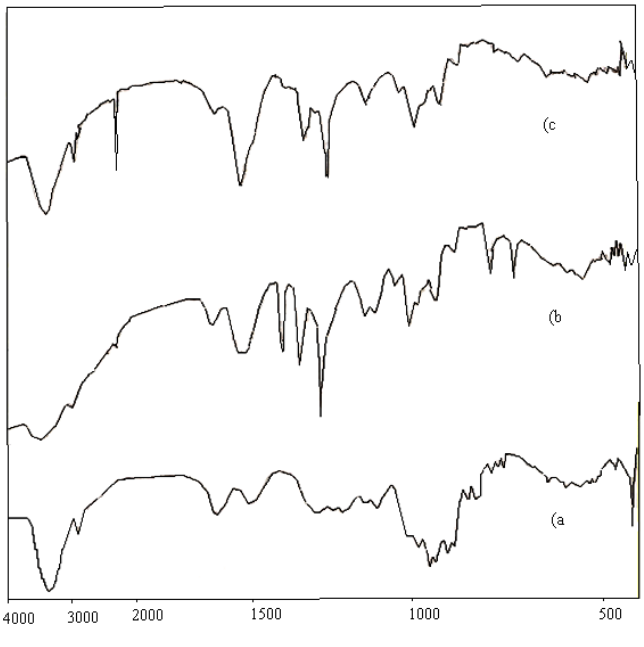


Fig. 1. FT-IR spectra of (a) pectin (b) copolymer and homopolymer (c) optimum copolymer.

Effect of initiator concentration: The grafting dependence on ceric ammonium nitrate concentration can be concluded from Table-1 and Fig. 2, respectively. The highest grafting ratio (520 %) was achieved at 0.1 mol/L of ceric ammonium nitrate where homopolymer content was 3.1 %. Increased ceric ammonium nitrate concentration resulted in more radical sites on the polysaccharide backbone that in turn led to higher grafting ratio and add-on values and lower homopolymer formation. However, since the ceric ammonium nitrate initiator solution is used as dilute HNO_3, at ceric ammonium nitrate concentration higher than 0.1 mol/L, a more acidic pH probably causes partially termination of the macroradicals on pectin. As a result, increased free radicals on pectin are compensated by partial termination of the macroradicals. Thus, grafting ratio and add-on values were diminished at higher amounts of the initiator.

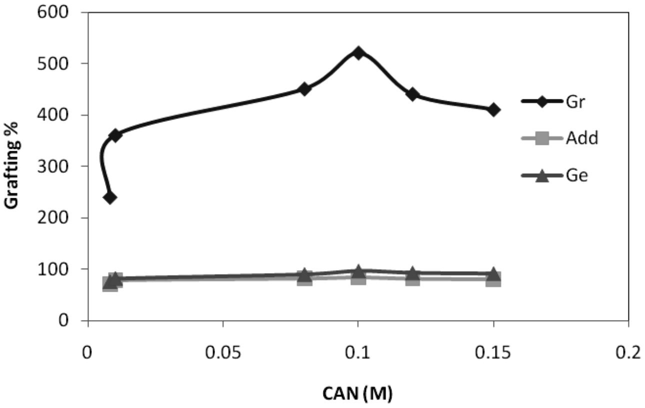


Fig. 2. Grafting percent variances with concentration of ceric ammonium nitrate variance.

Effect of Temperature: To study the influence of the reaction bath temperature on the grafting parameters, the grafting of acrylonitrile onto pectin was carried out at six temperatures ranging from 40 to 75 ºC. The results are given in Table-2 and Fig. 3, respectively. Grafting percentage is increased with

TABLE-3
GRAFTING PARAMETERS FROM THE GRAFT POLYMERIZATION[a] OF ARCRYLONITRILE ONTO PECTIN AT DIFFERENT AMOUNT OF THE MONOMER

AN (mL)	W_0	W_1	W_2	T (ºC)	Time (min)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.50	1.00	3.20	2.20	60.00	60.00	120.00	31.20	54.50	67.70
1.50	1.00	3.50	2.70	60.00	60.00	170.00	22.80	62.90	77.10
2.00	1.00	4.10	3.20	60.00	60.00	220.00	21.90	68.70	78.00
2.50	1.00	4.60	4.10	60.00	60.00	310.00	10.80	75.60	89.10
3.00	1.00	5.20	4.70	60.00	60.00	370.00	9.60	78.70	90.00
3.50	1.00	3.80	3.10	60.00	60.00	210.00	22.50	67.70	81.50
4.50	1.00	3.50	2.30	60.00	60.00	130.00	34.20	56.50	65.70
5.00	1.00	3.30	1.70	60.00	60.00	70.00	0.48	41.70	51.50

[a]Reaction conditions: Pectin 0.5 g, water 50 mL, ceric ammonium nitrate 0.1 M, temperature 55 ºC, Gr = Grafting ratio.

TABLE-4
GRAFTING PARAMETERS FROM THE GRAFT POLYMERIZATION[a] OF ARCRYLONITRILE ONTO PECTIN AT DIFFERENT CONCENTRATION OF THE SUBSTRATE

Pec (Gr)	W_1	W_2	T (ºC)	Time (min)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.20	3.80	2.00	60.00	60.00	300.00	47.30	75.00	52.60
0.30	4.80	2.60	60.00	60.00	420.00	45.80	80.70	54.10
0.40	5.40	4.10	60.00	60.00	720.00	24.00	87.80	75.90
0.50	5.60	5.30	60.00	60.00	960.00	4.50	90.50	94.60
1.00	5.80	5.20	60.00	60.00	420.00	10.30	80.70	89.60
1.50	6.00	4.80	60.00	60.00	220.00	20.00	68.70	80.00
2.00	6.30	4.50	60.00	60.00	125.00	28.50	55.50	71.40
2.50	6.40	4.20	60.00	60.00	68.00	34.30	40.40	65.60
3.00	6.60	4.00	60.00	60.00	33.30	39.30	25.00	60.60

[a]Reaction conditions: water 35 mL, acetonitrile 3 mL, ceric ammonium nitrate 0.1 M, temperature 55 ºC.

increasing the temperature from 40 to 55 ºC and then decreased. At 55 ºC, maximum grafting (grafting ratio 920 %), minimum homopolymer content (12 %) and highest add-on value (90.1 %) was obtained. Improvement of grafting up to 55 ºC can be attributed to the following factors: increased the number of free radicals formed 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[14]. However, grafting was decreased as the bath temperature was raized beyond 55 ºC. This can be accounted for in terms of chain radical termination at higher temperatures. Premature termination of growing chains and instability of the ceric-saccharide complex[5] are presumably another reasons for reduced amount of grafting beyond 55 ºC. The polyacrylonitrile homopolymer formation is minimal at the bath temperature of 55 ºC.

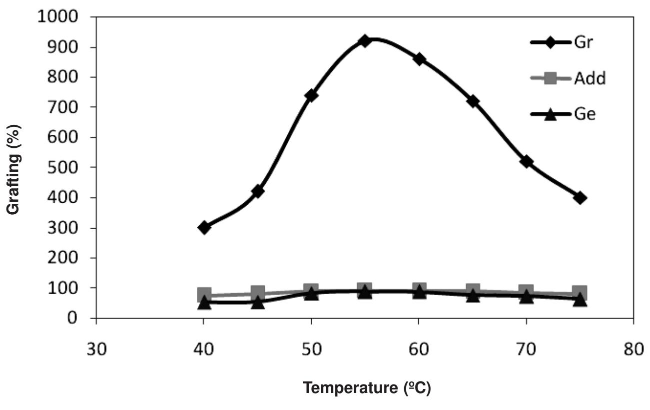


Fig. 3. Grafting per cent variances with temperature variance

Effect of monomer concentration: The effect of monomer amount on the grafting reaction was studied at various concentrations of acrylonitrile while other influential factors were unchanged. The grafting parameter variations are changed by the amount of charged monomer. The results are given in Table-3 and Fig. 4, respectively. The grafting extent is significantly increased due to more availability of monomer for grafting. However, beyond a certain grafting value, *i.e.*, 370 % at acrylonitrile 3 mL, the trend is inversed. The conversion and the grafting efficiency are decreased and homopolymer content is increased noticeably from 9.6 to 48 %. Thus, acrylonitrile in an amount of acrylonitrile 3 mL was recognized as an optimum monomer concentration. Once the monomer units are added, an excess of monomer can only increase the optimum volume of the reaction mixture. The resulting reduced relative concentration of the initiator and substrate leads to decreased conversion and grafting efficiency.

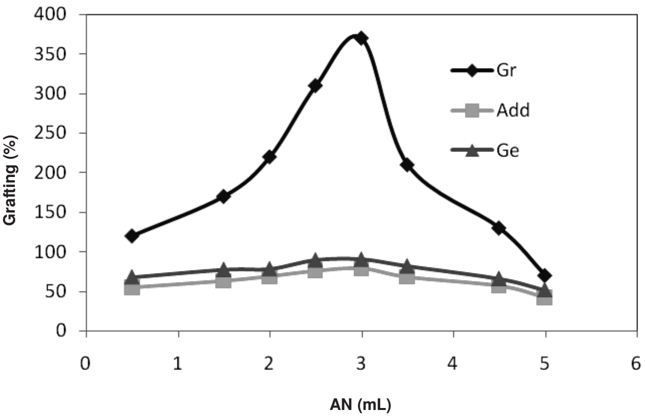


Fig. 4. Grafting per cent variances with amount of acrylonitrile monomer variance

TABLE-4
GRAFTING PARAMETERS FROM THE GRAFT POLYMERIZATION[a] OF ARCRYLONITRILE ONTO PECTIN AT DIFFERENT CONCENTRATION OF THE SUBSTRATE

Pec (Gr)	W_1	W_2	T (ºC)	Time (min)	Gr (%)	Hp (%)	Add (%)	Ge (%)
0.20	3.80	2.00	60.00	60.00	300.00	47.30	75.00	52.60
0.30	4.80	2.60	60.00	60.00	420.00	45.80	80.70	54.10
0.40	5.40	4.10	60.00	60.00	720.00	24.00	87.80	75.90
0.50	5.60	5.30	60.00	60.00	960.00	4.50	90.50	94.60
1.00	5.80	5.20	60.00	60.00	420.00	10.30	80.70	89.60
1.50	6.00	4.80	60.00	60.00	220.00	20.00	68.70	80.00
2.00	6.30	4.50	60.00	60.00	125.00	28.50	55.50	71.40
2.50	6.40	4.20	60.00	60.00	68.00	34.30	40.40	65.60
3.00	6.60	4.00	60.00	60.00	33.30	39.30	25.00	60.60

[a]Reaction conditions: water 35 mL, AN 3 mL, Ceric ammonium nitrate 0.1 M, temperature 55 ºC.

Effect of pectin concentration: Related to the grafting dependence on pectin amount is summarized in Table-4 (Fig. 5). Maximum grafting and the lowest homopolyacrylonitrile formation was observed at 0.5 g pectin, while others reactants including, monomer, initiator and temperature were kept constant. Beyond this value, both grafting ratio and add-on values are considerably reduced. This behaviour is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (from 0.25 to 0.50 g pE). However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of macroradicals leading to decreased grafting ratio and add-on values. It may also be attributed to deactivation of the macroradical growing chains (*e.g.*, by transfer reactions, combination and/or interaction with the primary radicals) soon after their formation.

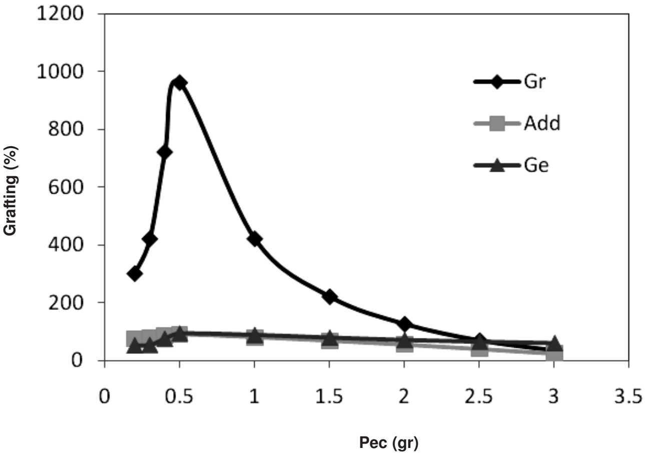


Fig. 5. Grafting percent variances with amount of pectin variance.

Conclusion

A doubly modified polysaccharide, pectin-g-polyacrylonitrile, was prepared using ceric-initiated graft polymerization of acrylonitrile onto pectin. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, the monomer acrylonitrile and the substrate pectin. The effect of the individual factors was investigated by calculating the grafting parameters, *i.e.*, grafting ratio, add-on value and homopolymer content. Under optimum conditions (pectin 0.5 g, acrylonitrile 3 mL, ceric ammonium nitrate 0.1 mol/L, reaction bath temperature 55 ºC, reaction time 1 h), the grafting parameters were achieved as 920, 90, 1 and 12 %, respectively.

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