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Full Length Research Paper

APS-initiated graft copolymerization of N-Vinyl pyrollidone onto gelatin: Preparation, characterization, and optimization of grafting parameters

Mohammad Sadeghi[1]*, Esmat Mohammadinasab[2] and Fatemeh Shafie[3]

Department of Chemistry, Science Faculty, Islamic Azad University, Arak Branch, Arak, Iran.

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In this work, large numbers of hydrophilic functional groups were introduced onto gelatin by grafting with N-vinyl pyrollidone monomer. The graft copolymerization reactions were carried out under nitrogen atmosphere using ammonium persulfate (APS) as an initiator. The graft copolymer was characterized by Fourier transform infrared spectra, thermo-gravimetric analysis and solubility test. The existence of a sharp intense peak at 1653 cm^{-1} in FTIR spectra of the graft copolymer, improvement of the thermal stability of gelatin-based copolymer and the solubility difference of the copolymer and the homopolymer prove the formation of graft copolymer. The effects of reaction variables, such as concentration of the initiator, monomer and gelatin, as well as, reaction temperature and time were investigated and the grafting conditions were optimized. The optimum reaction conditions resulting in maximum grafting ratio and add-on value have been determined.

Key words: Gelatin, N-vinyl pyrollidone, graft copolymerization, ammonium persulfate.

INTRODUCTION

The modification of natural polymers is a promising method for the preparation of new materials. An efficient approach to modify natural polymers in order to synthesis natural-based superabsorbent polymers, and graft polymerization of vinylic monomers onto their backbones in the presence of crosslinkers. Free radical graft copolymerization with various monomers can be carried out with different initiator systems (Heinze et al., 2001).

In fact, graft copolymerization of vinyl monomers onto polysaccharides and proteins 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 (Athawale and Rathi, 1997; Sadeghi and Hosseinzadeh, 2010a). Of the monomers grafted, acrylonitrile (AN) has been the most frequently used one, mainly due to its high grafting efficiency (Fanta and Doane, 1986; Sandle and Verma, 1987), improving the thermal resistance of the graft copolymer (Athawale and Rathi, 1999) and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents (Fanta and Doane, 1986).

Gelatin is the product obtained from the acid, alkaline, or enzymatic treatment of collagen, the chief protein component of the skins, bones, and connective tissues of animals. Gelatin is used in confectionery, water jellies and desserts, dairy products or functional food, for its versatility. Its functionalities include firming agent, formulation and processing aid, stabilizer and thickener, surface active agent, and water finishing agent. Gelatin has many uses in bakery products because of its unique function. It is particularly useful in marshmallow, icing, glazes and cream fillings. There are many non-food applications where gelatin has been found to have particular advantages. The pharmaceutical industry uses very large quantities of gelatin primarily for making hard and soft gel capsules. Gelatin functions as a protective colloid to prevent the coagulation of the suspension and to control the size of the polymer particle. Some other applications of gelatin include hair care products,

*Corresponding author. E-mail: m-sadeghi@iau-arak.ac.ir. Tel: +98-916-1613256. Fax: +98-861-3670017.

cosmetics, electroplating, and paper and textile sizing.

Poly(N-vinyl pyrrolidone) (PVP) is a synthetically derived vinyl polymer with a unique combination of properties, such as good solubility in water and a range of organic solvents, remarkable capacity to interact with a wide variety of organic and inorganic compounds, good biocompatibility, non-toxicity to living tissues and so on. PVP has been widely used in the biomedical fields, the cosmetic and food industrial sectors which are closely related to the human health for decades. PVP has also been widely used as a medical additive or polymeric modifier (Zhang and Lam, 2005; Cook et al, 2005). N-Vinyl Pyrollidone was graft copolymerized onto various natural-based polymers such as sodium carboxymethylcellulose (Yiğitoğlu et al., 2007), guar gum (Srivastava and Behari, 2006), chitosan (Yazdani-Pedram and Retuert, 1997), carrageenan (Mishra et al., 2010) and starch (Kahya et al., 2009).

The literature survey, however, reveals that few of the modifications deal with chemical grafting of a pre-modified protein such as gelatin. Ceric-initiated grafting of vinyl monomers such as methyl acrylate, ethyl acrylate and ethyl methacrylate (Okieimen et al., 1996), AN/methyl methacrylate mixture (Deshmukh et al., 1991), acrylamide (Sadeghi and Hosseinzadeh, 2010b) onto gelatin has been reported. However, to the best of our knowledge, no report has been published on the optimization graft polymerization of N-vinyl pyrollidone (NVP) onto gelatin chains using APS-Protein initiating system. In the present report, to modify the gelatin, the grafting of N-vinyl pyrollidone onto gelatin chains in the presence of ammonium persulfate (APS) as an initiator was performed in a homogeneous system. The effect of reaction variables affecting percent grafting was investigated as well. The resulted graft copolymer can be used in various applications as reported by others such as metal ions and iodine sorbents (Srivastava and Behari, 2006), in controlled drug delivery systems (Maiti et al., 2010), flocculants (Nayak et al., 2001), bonding of plastics to wood (Narayan et al., 1989) and superabsorbent polymer (Galvão et al., 2011).

EXPERIMENTAL

Materials

Gelatin (Parvar Novin-E Tehran Co.) was industrial grade which is available in market and has nearly 25% insoluble phosphate salt. Ammonium persulfate (APS, Merck) was used without purification. N-vinyl pyrollidone monomer (Merck) was used after vacuum distillation. All other chemicals were of analytical grade.

Graft copolymerization procedure

A general one step preparative method for synthesis of graft copolymer was conducted as follows. A pre-weighed amount of gelatin (1.5 g) was dissolved in 50 mL distilled water and filtered to remove its insoluble phosphate salt. Then the solution was added to a 1 L reactor equipped with a mechanical stirrer (RZR 2021, a three-blade propeller type, Heidolph, Schwabach, Germany) and stirred at (300 rpm) for 10 min. The reactor was immersed in a thermostated water bath preset at a desired temperature (65^{o}C). Then a definite amount of APS solution (0.1 g in 5 mL H_2O) was added to gelatin solution and was allowed to stir for 10 min. After adding APS and complete dissolution of the mixture to form a homogeneous solution, certain amounts of N-vinyl pyrollidone (0.50 to 3.50 mL) monomer was added to the reaction mixture. After 60 min, the mixture was heated at a given temperature and stirred for 15 min. The mixture was continuously stirred at the desired temperature until completion of the reaction (60 min). After adding hydroquinone solution (0.5 wt%, 2 ml), cooling to room temperature, the product was precipitated in excess amount of methanol while mild stirring for ten minutes. The product was filtered, thoroughly washed with methanol and dried at 65^{o}C for one hour. To separate the poly N-vinyl pyrollidone (NVP) homopolymer, 0.50 g of the crude product was poured in 50 mL of dimethyl formamide (DMF) and stirred gently at 35°C for 48 h. After centrifugation and decanting the supernatant (NVP in DMF), the gelatin-*g*-PNVP was precipitated in methanol, thoroughly washed with methanol, and dried at 50^{o}C to reach a constant weight.

RESULTS AND DISCUSSION

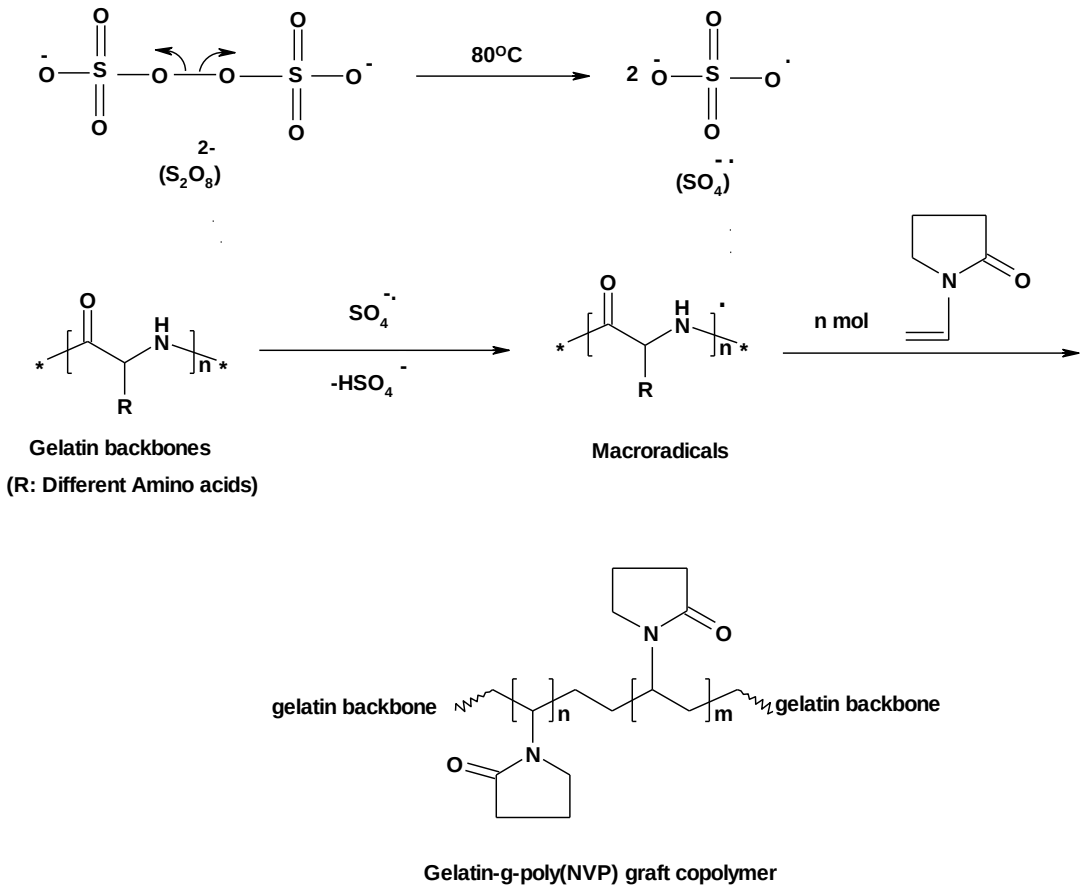
Grafting mechanism

A general reaction mechanism for NVP grafting onto gelatin backbones is shown in Scheme 1. The monomer, N-vinyl pyrollidone, was grafted onto gelatin backbones in a homogeneous medium using APS as a radical initiator. At the first step, the thermally dissociating initiator, that is, APS, is decomposed under heating to produce sulfate anion-radical. Then, the anion-radical abstracts hydrogen from one of the functional groups in side chains (that is, COOH, SH, OH, and NH_2) of the substrate to form corresponding radical. So, these macroradicals initiated monomer grafting onto gelatin backbones led to a graft copolymer (Okieimen, 2003; Leza et al., 1990).

Grafting evidences

FTIR analysis

The poly (N-vinyl pyrrolidone) grafting was confirmed by the differences between FTIR spectra of the pure gelatin and that of the graft copolymer. Figure 1 shows the FTIR spectra of the gelatin substrate and the gelatin-g-poly (N-vinyl pyrrolidone) graft copolymer freed from homopolymers. Some characteristic peaks such as carbonyl stretching bands of amide and carboxylate are given in Table 1. By comparing the spectrum of hydrogel with gelatin, some new absorption bands are observed in addition to characteristic protein absorption bands. From spectrum of gelatin-*g*-poly (N-vinyl pyrrolidone) hydrogel, it is clearly indicated that it contains functional groups of both, gelatin and poly (N-vinyl pyrrolidone). The existence of a rather sharp intense peak at 1653 cm^{-1} (C=O, carboxamide groups related to NVP) in IR spectra of the



Scheme 1. A brief proposed mechanism for APS-induced grafting of N-vinyl pyrollidone onto gelatin.

graft copolymers is a certain evidence of grafting. This peak however, is overlapped with carboxamide linkage of gelatin. Most of the other peaks are related to the gelatin with the functional groups (that is, COOH, SH, OH, and NH_2) in side chains onto gelatin backbone. Since poly(N-vinyl pyrrolidone) could be extracted nearly completely from a physical mixture of PNVP and gelatin by DMF, the presence of appreciable amounts of carboxamide groups in our reaction products after extraction is an additional proof for grafting of poly(N-vinyl pyrrolidone) onto gelatin. As a result, the FTIR analysis was used significantly to support the tentative mechanism of grafting reaction (Figure 1 and Table 1).

Thermal characterization

The grafting was also supported by thermogravimetric analysis (Figure 2). TGA of gelatin (Figure 2a) shows a weight loss in two distinct stages. In the TGA curve gelatin-*g*-poly (N-vinyl pyrrolidone) copolymer about 10 to 12% loss in weight is observed below 130°C. This was attributed to the removal of the absorbed water. Figure 2 shows that degradation also of native gelatin is faster than that of grafted gelatin. About 45% weight loss takes place in the temperature of 280°C for gelatin. A residual weight of 72% observed at 280°C for gelatin-*g*-poly (N-vinyl pyrrolidone) copolymer. In general, the copolymer had lower weight loss than gelatin. This means that the grafting of gelatin increases the thermal stability of gelatin in some extent.

Solubility test

The simplest method to prove the formation of gelatin-*g*-poly (N-vinyl pyrrolidone) is based on the solubility difference of the graft copolymer and the homopolymer, poly (N-vinyl pyrrolidone). Gelatin and homopolymer are soluble in water and DMF, respectively. When a reaction product was Soxhlet-extracted with DMF and alternately with water for 48 h, an insoluble solid still remained. A gelatin/PNVP 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 gelatin substrate and poly (N-vinyl pyrrolidone) macromolecule.

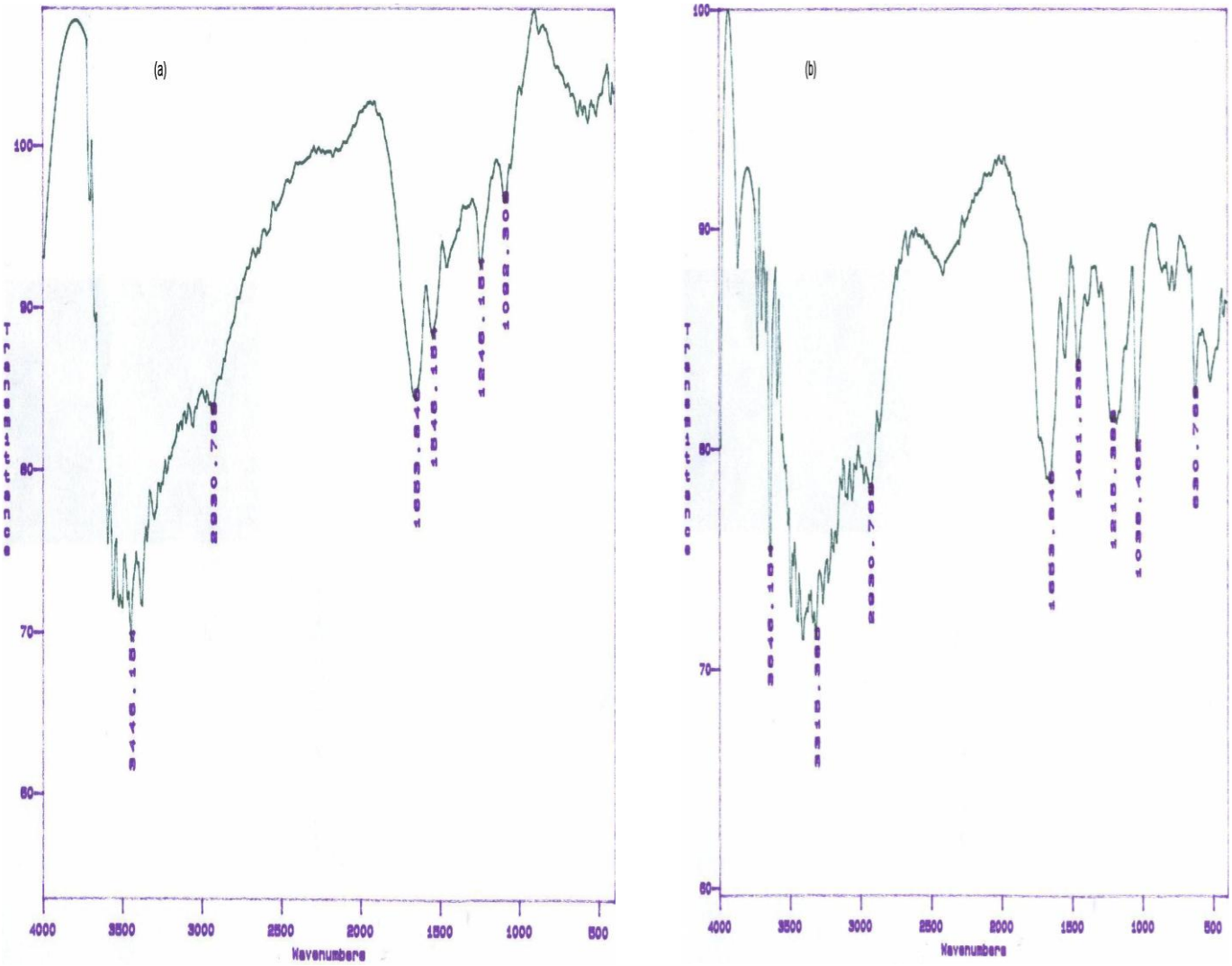


Figure 1. FTIR spectra of (a) pure gelatin (b) gelatin-g-poly(N-vinyl pyrollidone.

Table 1. Characteristic IR peaks present in the samples.

Functional groups	Absorption (cm^{-1})[a]	Absorption (cm^{-1})[b]
Carboxylic acid	1675-1725	1697
Carboxamide	1630-1690	1653
Carboxylate (symmetric)	1430-1465	1451
Carboxylate (asymmetric)	1525-1580	1545
Hydroxyl	3200-3400	3446
Amide	3400-3600	3546

[a] Literature values. [b] Observed values

Optimization of copolymerization reaction

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 N-vinyl pyrollidone onto gelatin in homogenous aqueous media

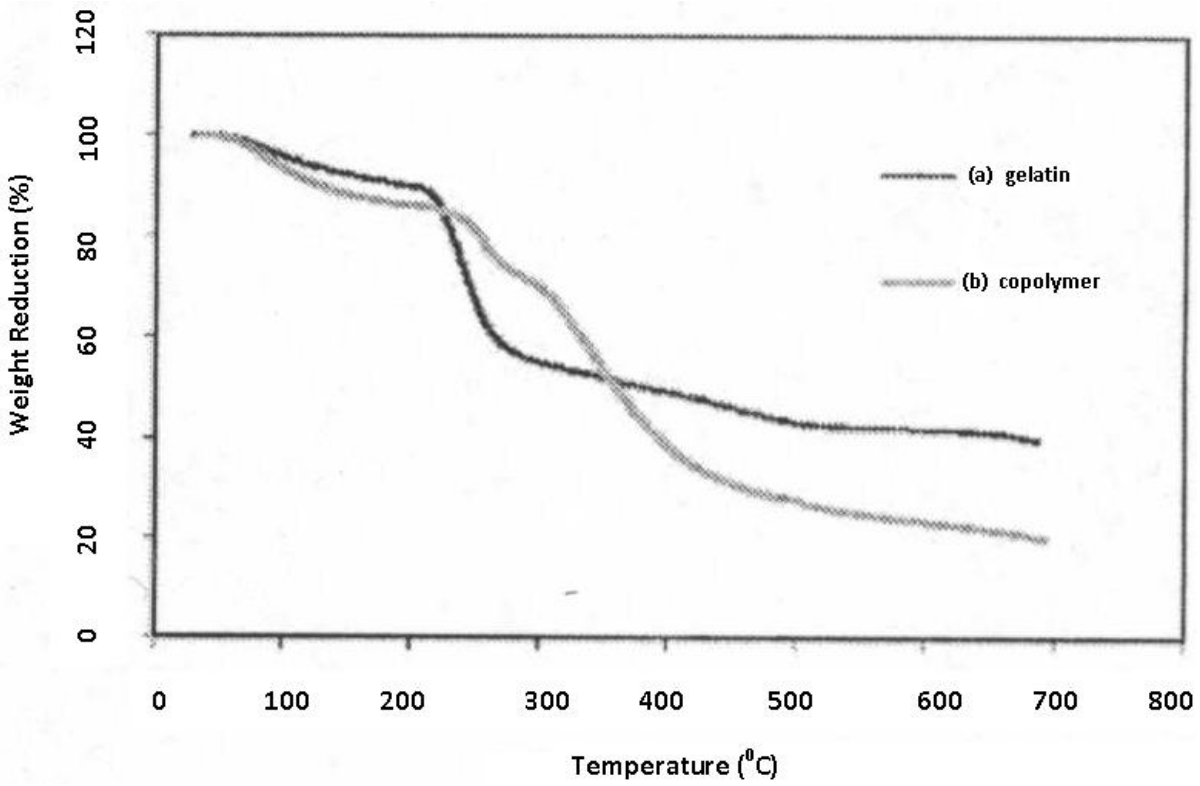


Figure 2. TGA curves of (a) pure gelatin and (b) gelatin-*g*-poly (N-vinyl pyrollidone).

by changing the 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.

The grafting parameters, that is, grafting ratio (Gr%), add-on value (Ad%), and homopolymer content (Hp%), used to characterize the nature of the copolymer are defined and calculated using the following equations (Fanta et al., 1986):

$$Gr\ \% = 100\ (W_2 - W_0) / W_0 \quad (1)$$

$$Ad\ \% = 100\ (W_2 - W_0) / W_2 \quad (2)$$

$$Hp\ \% = 100\ (W_1 - W_2) / W_1 \quad (3)$$

Where W_0, W_1, and W_2 are the weights of the initial substrate, total product (copolymer and homopolymer), and pure graft copolymer (after DMF extraction), respectively.

Effect of ammonium persulfate concentration

The effect of concentration of APS on graft polymerization was studied by changing its concentration from 0.0012 to 0.012 mol/L (Figure 3). It was observed that the grafting parameters of Gr% and Ad% are increased versus increasing the APS concentration from 0.01 up to 0.006 mol/L and then, they are decreased considerably with a further increase in the amount of APS. The maximum of Gr (88.70%) and Ad (67.35%) are obtained at APS 0.006 mol/L. It is obvious that at this concentration of APS, minimum percent of homopolymer (Ad 15.80%) are obtained. The number of active free radicals on the gelatin backbone is increased in terms of the initiator levels lower than 0.006 mol/L. This accounts for the initial increment in grafting percent up to a certain amount of APS. The Gr% and Ad% decrease after the maximum may be attributed to increased number of produced radicals led to terminating step via bimolecular collision resulting in enhanced crosslink density (Zhang and Tan, 2000).

An additional reason for decreasing of Gr% and Ad% can be related to decreasing molecular weight (MW) of the grafted poly(N-vinyl pyrrolidone) at high levels of APS concentration. Since MW inversely depends on initiator concentration, (I), higher (I) results in lower MW and, in turn, lower grafting percent of the copolymer (Zohuriaan et al., 2005). On the other hand, free radical degradation of gelatin substrate is also possible at high APS levels. A similar observation is recently reported by Hsu et al.

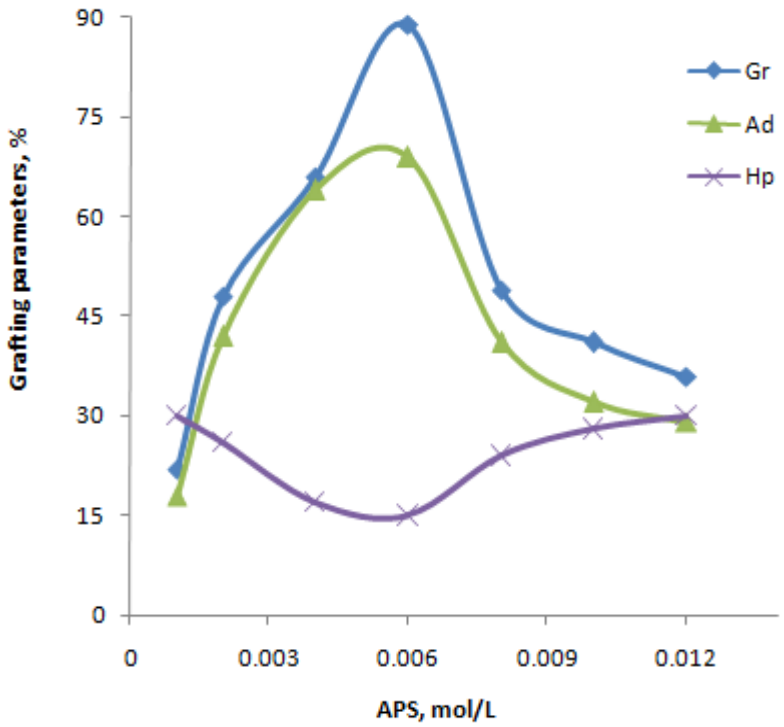


Figure 3. Effect of initiator concentration on the grafting parameters. Reaction conditions: gelatin 1.2 wt%, NVP 1.30 mol.L^{-1}, temperature 50˚C, time 90 min.

(2002) in the case of degradation of chitosan with potassium persulfate (Figure 3).

Effect of reaction temperature

To study the influence of the reaction bath temperature on the grafting parameters, the grafting of N-vinyl pyrollidone onto gelatin was carried out at seven temperatures ranging from 40 to 100^{o}C (Zohuriaan et al., 2005). The results are given in Figure 4. The grafting parameters, Gr% and Ad%, are increased with increasing the temperature from 40 to 60^{o}C, and then decreased. At 70^{o}C, maximum grafting (Gr 136.80%), highest add-on value (Ad 83.62%), and minimum homopolymer content (Hp 9.50%) was obtained. Improvement of grafting up to 60^{o}C can be attributed to the following factors: 1) increased number of free radicals formed on the gelatin backbone, 2) increased propagation of the graft copolymerization onto gelatin, 3) enhanced diffusion of monomer and initiator into and onto backbone structure, and 4) increased in mobility of the monomer molecules and their higher collision probability with the backbone macro radicals (Tan et al., 1998). However, grafting parameters of Gr% and Ad% were decreased as the bath temperature was raised beyond 60^{o}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-gelatin, oxidative degradation of gelatin chains by sulfate radical-anions and decomposition of APS to give O_2 (a radical scavenger), which reacts with primary free radicals (Equations 4 and 5), (Hsu et al., 2002), are presumably another reason for reduced amount of grafting beyond 60^{o}C:

$$SO_4^{-\cdot} + H_2O \longrightarrow HSO_4^{-} + HO^{-} \quad (4)$$

$$2\,HO^{-} \longrightarrow H_2O_2 \longrightarrow H_2O + 1/2O_2 \quad (5)$$

The rates of graft copolymerization (R_g) may be evaluated as measures of the rate of monomer disappearance by using the following equations (Fanta et al., 1986):

$$Rg\left(mol.\ s^{-1}.m^{-3}\right) = \frac{Weight\ of\ grafted\ \ polymer}{Molecular\ weight\ of\ monomer \times [rection\ time\ (s)] \times volume\ (m^3)} \quad (6)$$

The calculation of Rg values may be of significant importance in confirming a proposed reaction mechanism and kinetics. Therefore, we investigated the relationship between the rate of graft copolymerization and concentration of NVP and APS. Results show that the

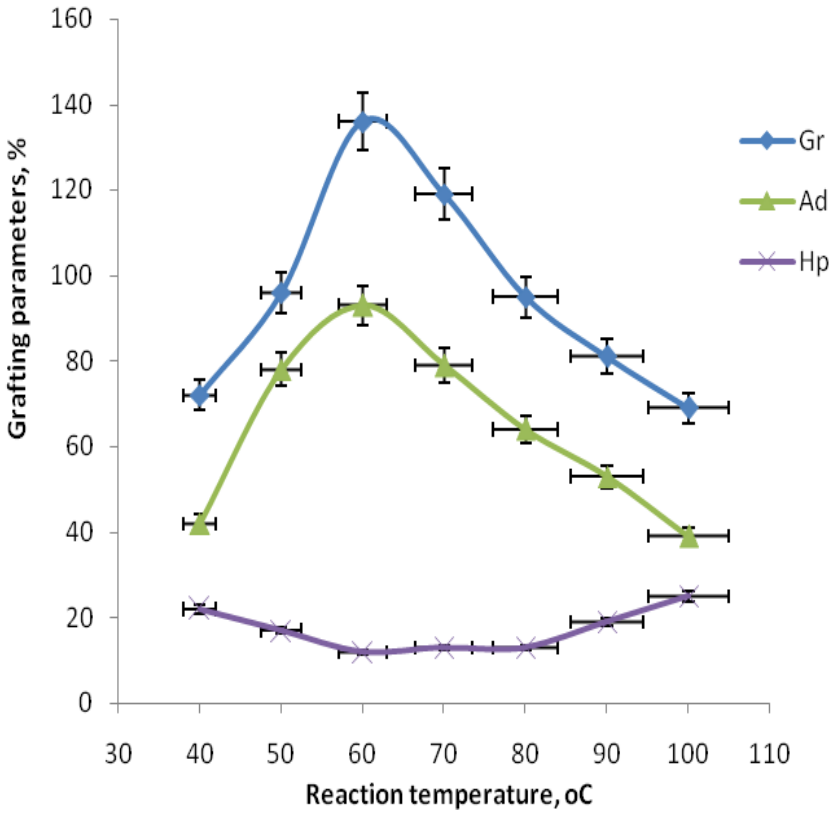


Figure 4. Effect of temperature on the grafting parameters. Reaction conditions: gelatin 1.2 wt%, NVP 1.30 mol.L^{-1}, APS 0.006 mol.L^{-1}, time 90 min.

plots of Rg versus the monomer concentration, [NVP] and half-order of the initiator concentration, $[APS]^{1/2}$ are linear. This is in agreement with a modified kinetic scheme already explored for ceric-initiated acrylonitrile grafting onto carboxymethyl cellulose (Zohuriaan et al., 2005). The statement of rate of polymerization according to the scheme is as follows:

$$R_g = k_p (K k_d / k_t)^{1/2} [APS]^{1/2} [NVP]$$

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

Overall activation energy of grafting (E_a) may also be estimated from the temperature data through plotting $\ln R_g$ versus 1/T ($^oK^{-1}$) for the initial portion of the data of the temperature series given in above text. The slope of this Arrhenius plot (Figure 5) resulted in a rough estimation of E_a of grafting using the relationship slope = $-E_a/R$; where R is the universal gas constant. Therefore, Ea for the graft copolymerization was found to be 36.60 kJ/mol (8.75 kcal/mol).

Effect of N-vinyl pyrollidone concentration

The effect of N-vinyl pyrollidone amount on the grafting reaction was studied at various concentrations of NVP while other influential factors were unchanged. The grafting parameter variations are changed by the amount of charged monomer. The results are given in Figure 6. The grafting extent that is to say, both %Ge and %Gr are significantly increased due to more availability of monomer for grafting. However, beyond a certain Gr% and Ad% value, at NVP 0.7 mol/l the trend is inversed. The conversion and the Add-on are decreased, and homopolymer content is increased noticeably from 14.3 to 32.8%. Thus, N-vinyl pyrrolidone in an amount of NVP 0.7 mol/lit 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.

Effect of gelatin concentration

Related to the grafting dependence on gelatin amount is summarized in Figure 7. Maximum grafting and add-on percent and the lowest homopolymer formation were

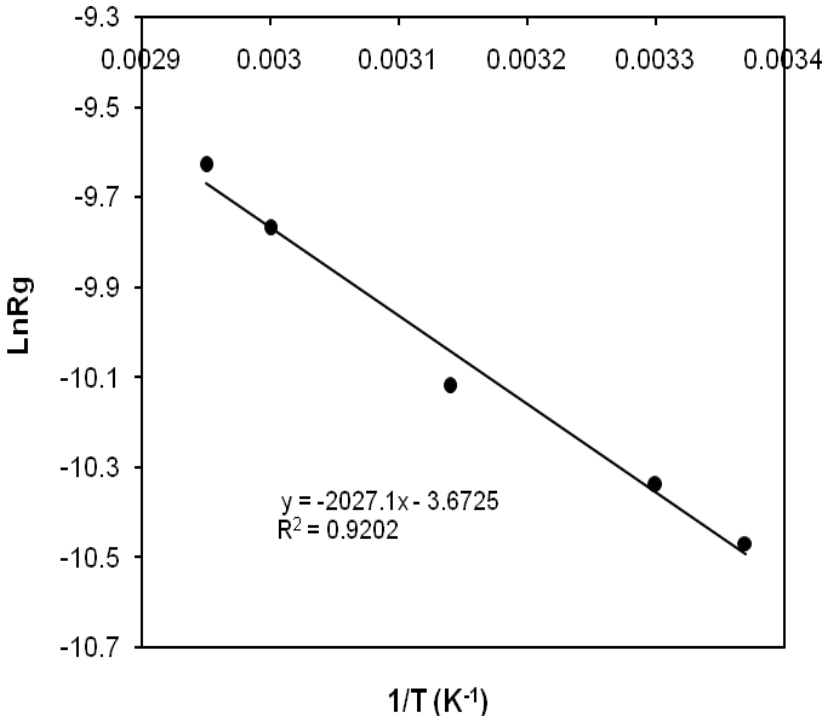


Figure 5. Plot of lnR_g versus 1/T for estimating the activation energy of the graft polymerization reaction.

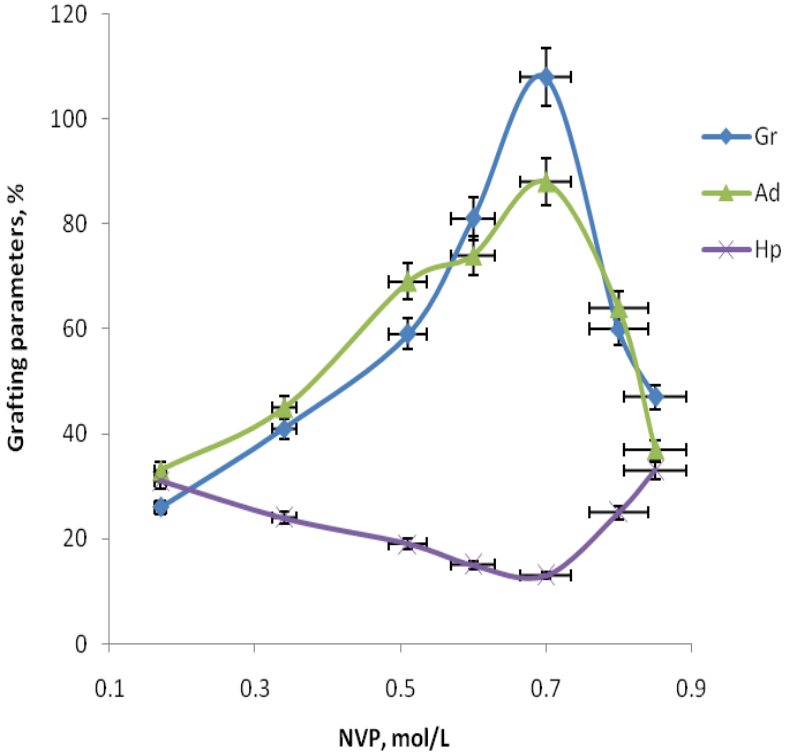


Figure 6. Effect of the monomer concentration on the grafting parameters. Reaction conditions: gelatin 1.2 wt%, APS 0.006 $mol.L^{-1}$, temperature 60°C, time 90 min.

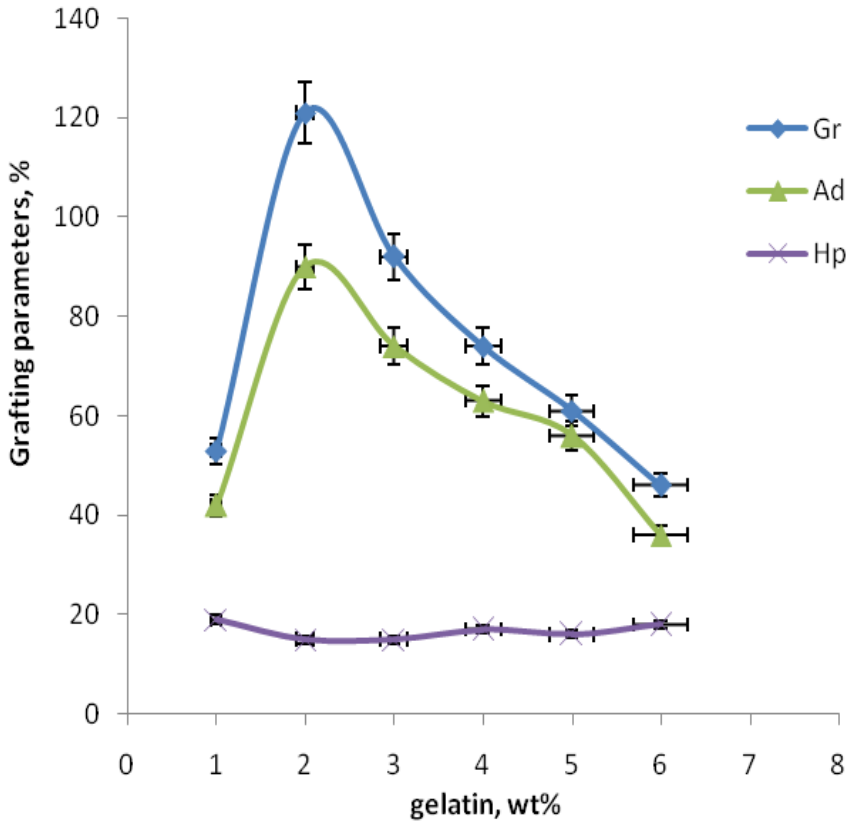


Figure 7. Grafting parameters as functions of gelatin concentration. Reaction conditions: NVP 0.7 mol.L^{-1}, APS 0.006 mol.L^{-1}, T 60°C, time 90 min.

observed at 2.0 wt% of gelatin, while other reactants including, monomers, initiator, and temperature were kept constant. Beyond this value, both grafting percent and add-on values are considerably reduced. This behavior is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (until 2.0 wt% gelatin). However, upon further increase in the substrate concentration, increase in the reaction medium viscosity restricts the movements of macroradicals leading to decreased grafting percent and add-on values (Zhang et al., 2000). It may also be attributed to deactivation of the macroradical growing chains (for example, by transfer reactions, combination and/or interaction with the primary radicals) soon after their formation (Pourjavadi et al., 2002; Ibrahim et al., 2002).

Effect of reaction time

Figure 8 shows the effect of reaction time on the grafting parameters. It is clear from this figure that reaction time increases with %Gr and %Ad gradually. The decrease in the %Gr and %Ad with time could be attributed to decrease in concentrations of initiator and the monomer as well as a reduction in the number of free radicals accessible for grafting as reaction proceeds (Ibrahim et al., 2002).

Conclusion

For modified gelatin, N-vinyl pyrollidone monomer can be easily graft copolymerized onto gelatin using APS as an initiator in aqueous medium under an inert atmosphere. In order to prove that the monomer was grafted, solubility test, FTIR spectroscopy, and TGA analysis were used. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, N-vinyl pyrollidone and the substrate gelatin. The effect of the individual factors was investigated by calculating the grafting parameters, that is, grafting percent (Gr), add-on value and homopolymer content (Hp). The reaction conditions were attempted to optimize for obtaining graft copolymers with higher grafting parameters. So, the reaction conditions for achieving the maximum %Gr (136.80) and %Ad (83.62) were found to be as follows; gelatin 2.0 wt%, NVP 0.7 mol/L, APS 0.006 mol/L, reaction bath temperature 60oC, reaction time 120 min.

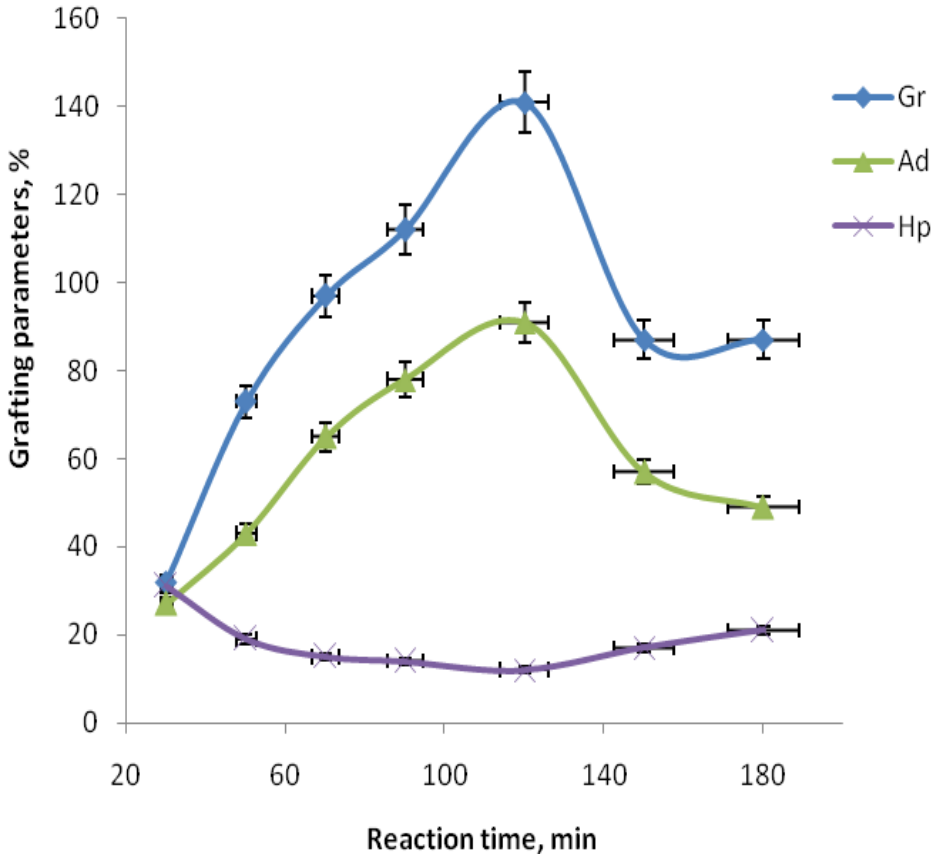


Figure 8. Effect of reaction time on the grafting parameters. Reaction conditions: gelatin 2.0 wt%, NVP 0.70 mol.L^{-1}, APS 0.006 mol.L^{-1}, temperature 60˚C.

Empirical polymerization rate also showed a first-order dependence on the monomer concentration and a half-order dependence on the initiator concentration. According to the slope of LnRg versus 1/T, the overall activation energy for graft copolymerization reaction was estimated to be 36.60 kJ/mol (8.75 kcal/mol).

REFERENCES

Athawale VD, Rathi SC (1997). Role and Relevance of Polarity and Solubility of Vinyl Monomers in Graft Polymerization onto Starch. React. Func. Polym., 34: 11-17.

Athawale VD, Rathi SC (1999). Graft Polymerization: Starch as a Model Substrate. J. Macromol. Sci.-Rev. Macromol. Chem. Phys., C39(3): 445-480.

Cook SE, Park IK, Kim EM, Jeong H, Park TG, Jaie Y, Akaikea T, Cho CS (2005). Galactosylated Polyethylenimine-g-Poly(Vinyl Pyrrolidone) as a Hepatocyte-Targeting Gene Carrier. J. Control. Rel., 105: 151-163.

Deshmukh SR, Sudhakar K, Singh RP (1991). Drag-Reduction Efficiency, Shear Stability, and Biodegradation Resistance of Carboxymethyl Cellulose-Based and Starch-Based Graft Copolymers. J. Appl. Polym. Sci., 43: 1091-1101.

Fanta GF, Doane WM (1986). Grafted Starches. In Modified Starches: Properties and Uses; Wurzburg, O.B., Ed.; CRC Press: Boca Raton (Florida), pp.149-178.

Galvão Barros GA, Caldeira Brant AJ, Catalani LH (2011). Hydrogels from Chitosan and a Novel Copolymer Poly(N-Vinyl-2-Pyrrolidone-Co-Acrolein). Mater. Sci. Appl., 2: 1058-1069.

Heinze T, Liebert T (2001). Unconventional Methods in Cellulose Functionalization. Prog. Polym. Sci. 26: 1689-1762.

Hsu SC, Don TM, Chiu WY (2002). Free Radical Degradation of Chitosan with Potassium Persulfate. Polym. Degrad. Stab., 75: 73-82.

Ibrahim MM, Flefel EM, El-Zawawy WK (2002). Cellulose Membranes Grafted with Vinyl Monomers in Homogeneous System. J. Appl. Polym. Sci., 84: 2629-2638.

Kahya S, Şanlı O, İbrahim Ünal H, Camurlu P (2009). A Novel Copolymer: Starch-g-Polyvinylpyrrolidone. Starch-Stärke, 61: 267-274.

Leza ML, Casinos I, Guzman GM (1990). Graft Copolymerization of 4-Vinylpyridine onto Cellulosics: Effects of Stirring and Inorganic Salts. Brit. Polym. J., 23: 341-346.

Maiti S, Ranjit S, Sa B (2010). Polysaccharide-Based Graft Copolymers in Controlled Drug Delivery. Int. J. Pharm. Tech. Res., 2: 1350-1358.

Mishra MM, Sand A, Mishra DK, Yadav M, Behari K (2010). Free Radical Graft Copolymerization of N-Vinyl-2-Pyrrolidone onto k-Carrageenan in Aqueous Media and Applications. Carbohyd. Polym., 82: 424-431.

Narayan R, Biermann CJ, Hunt MO, Horn DP (1989). Cellulose Graft Copolymers for Potential Adhesive Applications, Am. Chem. Soc., chap. 24: 337.

Nayak BR, Biswal DR, Karmakar NC, Singh RP (2002). Grafted Hydroxypropyl Guar Gum: Development, Characterization and Application as Flocculating Agent. Bull. Mater. Sci., 25: 537-540.

Okieimen FE (2003). Preparation, Characterization and Properties of Cellulose-Polyacrylamide Graft Copolymers. J. Appl. Polym. Sci., 89:

913-923.
Okieimen FE, Ogbeifun DE (1996). Graft Copolymerizations of Modified Cellulose: Grafting of Methyl Acrylate, Ethyl Acrylate and Ethyl Methacrylate on Carboxymethyl Cellulose. Eur. Polym. J., 3(3): 311-315.
Pourjavadi A, Zohuriaan-Mehr MJ (2002). Modification of Carbohydrate Polymers via Grafting in Air. 1. Ceric-Induced Synthesis of Starch-g-Polyacrylonitrile in Presence and Absence of Oxygen. Starch/Starke. 54: 140-147.
Sadeghi M, Hosseinzadeh H (2010a). Studies on graft copolymerization of 2-hydroxyethylmethacrylate onto kappa-carrageenan initiated by ceric ammonium nitrate, J. Chil. Chem. Soc., 55: 283.
Sadeghi M, Hosseinzadeh H (2010b). Synthesis and super-swelling behavior of a novel low salt-sensitive protein-based superabsorbent hydrogel: collagen-g-poly(AMPS), Turk. J. Chem., 34: 739-752.
Sandle NK, Verma OPS (1987). Varma, I.K. Thermal Characterization of Starch-g-Acrylonitrile Copolymers. Thermochim. Acta, 115: 189-198.
Srivastava A, Behari K (2006). Synthesis and Characterization of Graft Copolymer (Guar Gum–g–N-Vinyl-2-Pyrrolidone) and Investigation of Metal Ion Sorption and Swelling Behavior. J. Appl. Polym. Sci., 100: 2480-2489.
Tan Y, Zhang L, Li Z (1998). Synthesis and Characterization of New Amphoteric Graft Copolymer of Sodium Carboxymethylcellulose with Acrylamide and Dimethylaminoethyl Methacrylate. J. Appl. Polym. Sci., 69: 879-885.
Yazdani-Pedram M, Retuert J (1997). Homogeneous Grafting Reaction of Vinyl Pyrrolidone onto Chitosan. J. Appl. Polym. Sci., 63: 1321-1326.
Yiğitoğlu M, Işıklan N, Özmen R (2007). Graft Copolymerization of N-Vinyl-2-Pyrrolidone onto Sodium Carboxymethylcellulose with Azobisisobutyronitrile as the Initiator. J. App. Polym. Sci., 104: 936-943.
Zhang Y, Lam YM (2005). Poly(Ethylene Oxide)-b-(Poly Propyleneoxide)-b-Poly(Ethyleneoxide)-g-(Poly Vinyl Pyrrolidone): Synthesis and Characterization. J. Colloid. Interface Sci., 285: 80-85.
Zhang LM, Tan YB (2000). Graft Copolymerization of 2-(Dimethylamino)ethyl Methacrylate onto Carboxymethylated Cellulose. Macromol. Mater. Eng., 280/281: 59-65.
Zhang J, Zhang LM, Li ZM (2000). Synthesis and Aqueous Solution Properties of Hydrophobically Modified Graft Copolymer of Sodium Carboxymethyl Cellulose with Acrylamide and Dimethyloctyl(2-methacryloxyethyl)ammonium Bromide. J. Appl. Polym. Sci., 78 :537-542.
Zohuriaan MJ, Pourjavadi A, Sadeghi M (2005). Modified CMC. 1. Optimized Synthesis of Carboxymethylcellulose-g-Polyacrylonitrile, Iran. Polym. J., 14 (2): 131-138.