Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 4, No. 3, p. 227-232, 2014
http://www.innspub.net

RESEARCH PAPER OPEN ACCESS

Modification of chitosan radiation-induced graft copolymerization of acrylonitrile onto chitosan

Mohammad Sadeghi*, Esmat Mohammadinasab,Fatemeh Shafiei, Sahar Mirdarikvande, Hossein Sadeghi

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

Article published on March 15, 2014

Key words: Chitosan, acrylonitrile, graft copolymerization, γ-irradiation.

Abstract

The monomer, acrylonitrile, was graft copolymerized onto Chitosan using γ-rays as initiator. The reactions were carried out in a homogenous aqueous medium. After removal of the homopolymer, the graft copolymer was characterized by FTIR ,TGA and DTG spectroscopies. The thermal properties of crude Chitosan and grafted with monomer were also evaluated with a simultaneous thermal analysis system. The synthetic conditions were systematically optimized through studying the influential factors including temperature, concentration of the initiator, acrylonitrile monomer and Chitosan. The graft copolymerization reactions were kinetically investigated using semi-empirical expressions and a suitable rate expression has been derived.

***Corresponding Author:** Mohammad Sadeghi ✉ m-sadeghi@iau-arak.ac.ir

Introduction

Graft copolymerization of hydrophilic vinyl monomers is a well-known technique employed by polymer chemists for significantly modifying the chemical and physical properties of the synthetic or natural starting materials with minimum degradation of the original properties. Graft copolymers are prepared by first generating free radicals on the polysaccharide backbone and then allowing these radicals to serve as macroinitiators for the vinyl monomers(Po,1994).

Radiation grafting technology is well established and accepted by industry((Po ,1994;Zhou *et al.*,2011;Huixia *et al.*,2010). Radiation polymerization, radiation crosslinking and controlled degradation of polymers comprise most of commercial applications of radiation technology.

The chosen polysaccharide for modification, i.e. Chitosan is a linear natural polysaccharide composed of a partially deacetylated material of chitin. It is a basic polymer, having amine side groups(Raghavendra *et al.*,2010; Hoffman,2002). Due to its excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied to fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since chitosan is easily soluble in acidic solutions, crosslinking of chitosan to form a network is the only way to prepare chitosan hydrogels(Zhang *et al*,2007).

Of the monomers grafted, acrylonitrile has been the most frequently used one, mainly due to its highest grafting efficiency, improving the thermal resistance of the graft copolymer and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents. The present report describes graft copolymerization of acrylonitrile onto Chitosan backbone, initiated by γ-rays.

Experimental

Materials

Chitosan (from Fluka, with MW=22742 and degree of deacetylation of 0.7) was used as received**.**Acrylonitrile monomer (Merck) was distilled before use.

Grafting procedure

Graft copolymerization of acrylonitrile onto Chitosan was carried out with γ-rays initiator. In a 100 mL flask, certain amount of Chitosan (0.75-1.50 g) was dissolved in 50 mL of degassed distilled water containing 2 wt% of acetic acid. The flask was placed in a water bath with desired temperature (50 ^{o}C). A given amount of monomer, AN (1.5-4.0 g), was added to the flask and the mixture was stirred for 15 min. The cold mixture was removed into a 250 mL aluminium tube. The inner wall of aluminium tube was covered with aluminium foil. The tube was closed tightly with the foil and paraffin film. The tube was then irradiated under γ-rays according to the desired total doses.

Homopolymer extraction

The graft copolymer was freed from polyacrylonitrile (PAN) homopolymer, by pouring 0.750 g of the product in 50 mL of dimethyl formamide solution. The mixture was stirred gently at room temperature for 48 h. After complete removal of the homopolymer, the copolymer was filtered, washed with ethanol and dried in oven at 50˚C to reach a constant weight.

Instrumental Analysis

The Polysaccharide-*g*-PAN samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer. A simultaneous thermal analyser (STA-625, Reometric Scientific) was used for thermogravimetric analysis (TGA). The thermal analyses were accomplished under purified N_2 gas (flow rate 10 mL/min). The heating rate was 20 ^{o}C/min. Irradiation was carried out using γ-rays from ^{60}Co source, in a Gammacell-220 (Nordion, Canada) with a dose rate of 1.6 kGy/h, in air and at room temperature. The dose rate was determined by the convention al Fricke dosimeter.

Evaluation of grafting parameters

The grafting parameters used to characterize the nature of the copolymer are defined with the weight basis expressions as reported by Fanta(Fanta,1973). The percentage of grafting ratio (Gr%) stands for the weight percent of the graft copolymer synthetic part (PAN grafted) formed from initial sodium hyaluronate used.

$$Grafting\ ratio(\%Gr) = \frac{Weight\ of\ grafted\ polymer}{Weight\ of\ substrate} \cdot 100$$

The percentage of grafting efficiency (Ge%) stands for the grafted PAA formed from initial monomer charged.

$$Grafting\ efficiency(\%Ge) = \frac{Weight\ of\ grafted\ polymer}{Weight\ of\ polymer\ formed} \cdot 100$$

The percentage of Add-on (Ad%) is the weight percent of the grafted PAN of the graft copolymer.

$$Add\ on(\%Ad) = \frac{Weight\ of\ grafted\ polymer}{Weight\ of\ graft\ copolymer} \cdot 100$$

The percentage of homopolymer (%Hp) denotes the weight percent of the homopolymer formed from initial monomer charged.

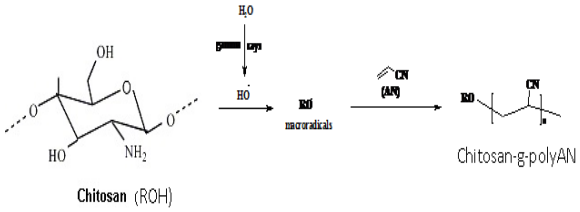
Results and discussion

Graft copolymerization mechanism and FTIR spectroscopy

The simplest method to prove the formation of Chitosan-*g*-PolyAN is based on the solubility difference of the graft copolymer and the homopolymer, PAN. Chitosan and PAN 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 was still remained. A Chitosan /PAN physical mixture was dissolved completely when it was treated in the same was. Therefore, it is obvious that the graft copolymer obtained was not a simple physical mixture, but some chemical bonds must exist between the Chitosan substrate and PAN macromolecules.

Scheme 1

For identification of the copolymer, infrared and TGA and DTG spectroscopies were used. The FTIR spectra of crude chitosan and graft copolymer based on chitosan, chitosan-g-polyAN, are shown in Figure 1. In Figure 1(a) a broad band at 3418 cm^{-1} corresponds to the associated –OH stretching vibrations of the hydroxyl groups, and the peak at 1611 cm^{-1} corresponds to the N-H deformation bending of chitosan. The existence of a sharp intense peak at 2246 cm^{-1} in IR spectra of the graft copolymers is a certain 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 PAN could be extracted nearly completely from a physical mixture of PAN 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(Peppas and Harland,1990; Kost,1995).



Scheme 1. A brief proposed mechanism for γ-rays-induced grafting of poly(AN) onto Chitosan.

Thermal analysis

Thermogravimetric analysis (TGA) was employed to thermally characterize the copolymer in comparison with the intact Chitosan (Figure 2). The thermal stability of the grafted Chitosan is improved as is obvious from the TGA curve.

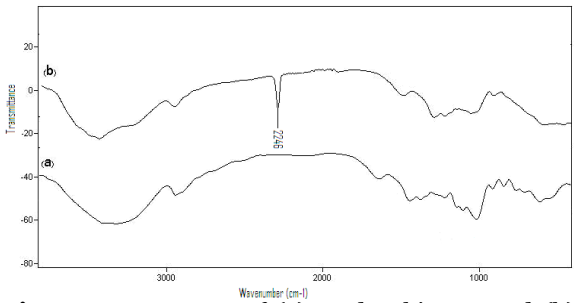


Fig. 1. FTIR spectra of (a) crude Chitosan and (b) homopolymer-free Chitosan -*g*-PolyAN.

Reaction rate

The rates of polymerization (Rp) and graft copolymerization (Rg) may be evaluated as measures of the rate of monomer disappearance by using the following equations:

$$Rp(mol.\ s^{-1}.m^{-1}) = \frac{\text{Weight of total polymer formed}}{\text{Molecular weight of monomer} \times \text{reaction time (s)} \times \text{volume (ml}^{-1})}$$

$$Rg(mol.\ s^{-1}.m^{-1}) = \frac{\text{Weight of grafted polymer}}{\text{Molecular weight of monomer} \times \text{reaction time (s)} \times \text{volume (ml}^{-1})}$$

The calculation of Rp 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 AN and Chitosan(Zhang, *et al.*,2007). Figures 3 and 4 show that the plots of Rp versus the monomer concentration, [AN] and half-order of the polysaccharide concentration, $[Chi]^{1/2}$ are linear. This is in agreement with a modified kinetic scheme already explored for CAN-initiated acrylonitrile grafting onto carboxymethyl cellulose. The statement of rate of polymerization according to the scheme is as follows:

$R_p = k_p (K k_d / k_t)^{1/2} [\ Chi\ ]^{1/2} [AN]$

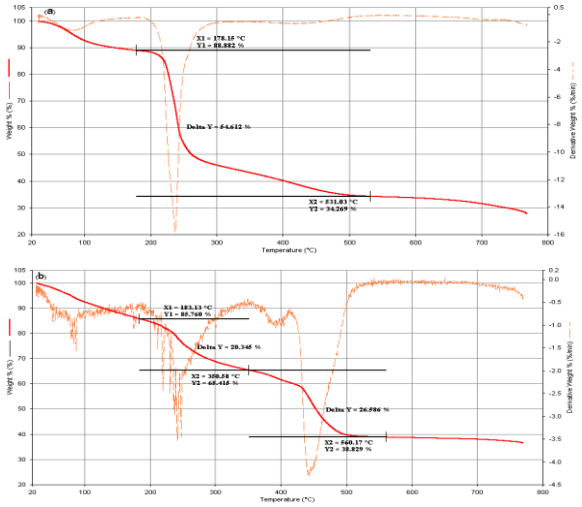


Fig. 2. TGA of crude Chitosan (a) and Chitosan-g-PolyAN (b).

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 radiation-initiated grafting of AN onto Chitosan is also fitted with this kind of rate statement.

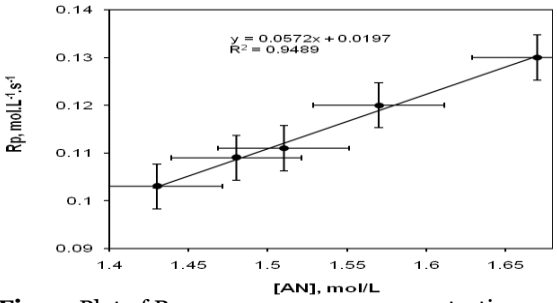


Fig. 3. Plot of Rp versus monomer concentration.

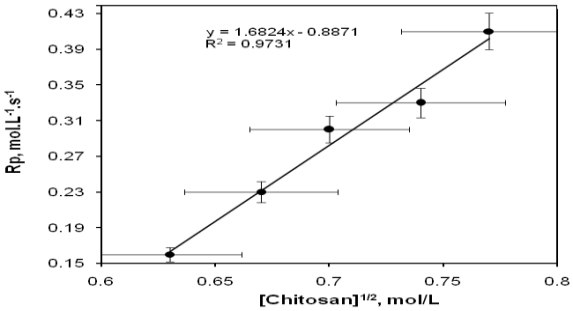


Fig. 4. Plot of Rp versus polysaccharide concentration.

Effect of δ-rays dose

Graft copolymerization was studied at various doses of δ-rays by keeping other reaction conditions constant. As shown in Figure 5, the %Ge and %Gr increase with increasing in the doses of δ-rays and reach at a maximum value. Further increase of doses of δ-rays beyond 60 kGy disfavoured the grafting parameters(Wang and Wang,2010). A relatively high dose of δ-rays may cause a reduction of %Ge and %Gr due to increase in the number of Chitosan free radicals terminated prior to AN addition. Furthermore, homopolymer formation at higher doses of δ-rays which compete with the grafting reaction for available monomer could lead to decrease in the %Ge and %Gr(Hua and Wang,2009).

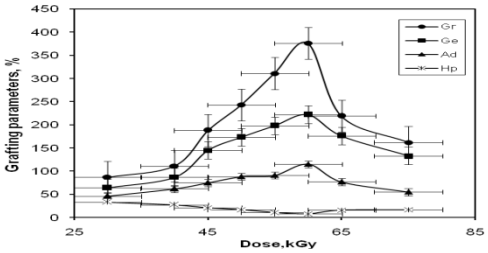


Fig. 5. Grafting parameters as functions of doses of δ-rays.

Effect of polysaccharide concentration

Figure 6 shows the effect of Chitosan concentration on the grafting parameters. With increasing the Chitosan amount, more reactive grafting sites are formed which are favourable for grafting. This can account for initial increment in grafting parameters up to 6.6.0 wt% of Chitosan value. Beyond this amount, the grafting values were diminished. This may be ascribed to the increase in viscosity that restricts the movement of the monomer molecules in a relatively small volume of the reaction mixture of 50 mL, and the termination reaction between macroradical-macroradical and macroradical-primary radicals as well (Chen *et al.*,2009; Wang and Wang,2010).

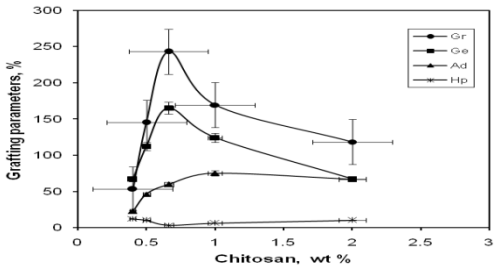


Fig. 6. Effect of polysaccharide concentration on the grafting parameters.

Effect of monomer concentration

The effect of AN concentration on the grafting parameters is presented in Figure 7. In the initial stages, though both %Ge and %Gr rise with increase in AN concentration, but beyond certain concentration of monomer, 0.6 mol/L, the grafting parameters decrease. The initial increase in grafting parameters could be associated with the greater availability of monomer molecules in the vicinity of Chitosan macroradicals. The decrease of %Gr and %Ge with further increase in the AN concentration may be explained as follows: (a) preferential homopolymerization over graft copolymerization, (b) increasing the viscosity of reaction medium, which hinders the movement of free radicals, and (c) increase in the chance of chain transfer to monomer molecules(Wang *et al.*,2009; Zheng and Wang,2009).

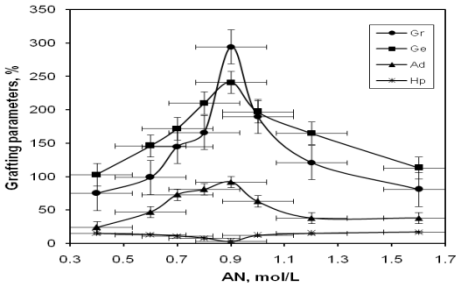


Fig. 7. Effect of the monomer concentration on the grafting parameters.

Conclusion

The polysaccharide, Chitosan was graft copolymerized with synthetic monomer, acrylonitrile, using δ-rays as efficient free radical initiators. In order to prove that monomer molecules were grafted, FTIR ,TGA and DTG spectroscopies were used. The relation between the rate of polymerization (Rp) and the concentrations of reactants was also investigated. Overall, the grafted polysaccharide may be a candidate for manufacture of moulded plastics, ion exchange resins, and plastic films and in cosmetics. On the other hand, since non-biodegradable plastic waste is known as an ecological threat, such natural polymer-based plastics in fact, are the need of time. Hence, improving the thermal stability of the polysaccharides would make them better suited for, for instance, moulded articles.

References

Po R. 1994.Water-absorbent Polymers, A Patent Survey. Journal of *Macromolecular Science*, Reviews in Macromolecular Chemistry and Physics. **C34,** 607-662.

Zhou HY, Zhang YP, Zhang WF, Chen XG. 2011.Biocompatibility and characteristics of injectable chitosan-based thermosensitive hydrogel for drug delivery. *Carbohydrate Polymers* **83,** 1643–1651.

Huixia SH, Wang W, Wang A. 2010. Controlled release of ofloxacin from chitosan-montmorillonite hydrogel. Applied Clay Science **50,** 112 –117.

Raghavendra V, Kulkarni V, Mutalik S, Setty

M, Sa B. 2010. Interpenetrating network hydrogel membranes of sodium alginate and poly(vinyl alcohol) for controlled release of prazosin hydrochloride through skin. International Journal of *Biological* Macromolecules **47,** 520–527.

Hoffman AS. 2002. Hydrogel for biomedical applications. Advanced Drug Delivery Reviews **43,** 3–12.

Zhang JP, Wang Q, Wang AQ. 2007. Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composites. *Carbohydrate Polymers* **68,** 367–374.

Fanta GF. 1973. *Block and Graft Copolymerization*, R. J. Cerasa (Ed.), Wiley, London .

Peppas LB, Harland RS. 1990.Absorbent Polymer Technology, Amsterdam: Elsevier, 233–247 p.

Kost J ,1995, Encyclopedia of Controlled Drug Delivery, New York: Wiley, 119–142 p.

Zhang JP, Wang Q, Wang AQ. 2007. Synthesis and characterization of chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composites. *Carbohydrate Polymers* **68,** 367–374.

Hua S, Wang A. 2009. Synthesis, characterization and swelling behaviors of sodium alginate-g-poly(acrylic acid)/sodium humate superabsorbent. *Carbohydrate Polymers* **75,** 79-84.

Wang Y, Lapitsky Y, Kang CE, Shoiche MS. 2009. Accelerated release of a sparingly soluble drug from an injectable hyaluronan-methylcellulose hydrogel. Journal of *Controlled Release* **140,** 218-223.

Zheng Y, Wang A . 2009. Evaluation of ammonium removal using a chitosan-g-poly (acrylic acid)/rectorite hydrogel composite. Journal of *Hazardous* Materials **171,** 671-677.

ChenY, LiuY F, TanH M, Jiang JX. 2009. Synthesis and characterization of a novel superabsorbent polymer of N,O-carboxymethyl chitosan graft copolymerized with vinyl monomers. *Carbohydrate Polymers* **75,** 287-292.

Wang WB, Wang AQ. 2010,Synthesis and swelling properties of pH-sensitive semi-IPN superabsorbent hydrogels based on sodium alginate-g-poly(sodium acrylate) and polyvinylpyrrolidone. *Carbohydrate Polymers* **80,** 1028-1036.

Wang WB, Wang AQ. 2010.Nanocomposite of carboxymethyl cellulose and attapulgite as a novel pH-sensitive superabsorbent: Synthesis, characterization and properties. Carbohydrate Polymers **82,** 83-91.