

Studies on the Amidoximation of Polyacrylonitrile Films: Influence of Synthesis Conditions

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Received 4 September 2010; accepted 23 October 2010

DOI 10.1002/app.33884

Published online 29 March 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Chemical transformation of acrylic membranes with hydroxylamine hydrochloride (HA) was carried out to introduce amidoxime groups. It was found that the reaction conditions, such as reaction time, HA concentration and temperature influence the amidoxime content, significantly. A sharp enhancement in the amidoximation at 80°C was observed. The FTIR studies showed a signifi-

cant loss of nitrile groups during amidoximation process. Optimum conditions for the amidoximation process were investigated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2705–2709, 2011

Key words: acrylic; hydroxylamine hydrochloride; films; modification; amidoxime

INTRODUCTION

Modification of polymers is a highly interesting domain to introduce desirable properties so that the resulting materials may be used for specific applications. Polyacrylonitrile (PAN) has several desirable properties, such as resistance to organic solvents, good mechanical strength, thermal stability (~ 200 °C), and possesses good insect resistance. However, PAN has few demerits of moderate hydrophilicity, low moisture absorption and the lack of active functionality which limit its usages in certain areas. Several methods have been followed to improve their hydrophilic properties, such as coating, adsorption, surface plasma treatment, surface hydrolysis, surface graft polymerization and chemical modification.^{1–4} Various vinyl and acrylic monomers, have been reported as a comonomer to modify PAN properties.^{5–7} Ulbricht et al.⁴ introduced carboxylic groups by grafting acrylic acid under pure helium plasma, whereas Zhao et al.⁸ used argon plasma for the grafting in PAN.

The copolymerization of acrylic acid with acrylonitrile is an interesting route to develop hydrophilic acrylic copolymers.^{9–11} This may be achieved by various methods, such as solution, emulsion, and suspension polymerization.^{12,13} Among various copolymerization techniques used in the production of PAN copolymers, solution polymerization is one of the

most common ones. Brar and Dutta¹⁴ reported the preparation of acrylonitrile-acrylic acid copolymer by photopolymerization. It has been found that hydrophilic moiety, acrylic acid improves mechanical strength, pervaporation, permeation flux, antifouling behavior, and biocompatibility, which gives the PAN-based copolymer membranes great potential for the treatment of wastewater and production of ultra pure water.^{15–18} The clinical uses of acrylonitrile-acrylic acid copolymer membrane as a base material have been projected in the haemofiltration devices and dialysis.^{15,19} Kim and Kim¹⁵ also reported that with the increase in acrylic acid content, free water increases, which facilitates the nonionic solute permeation through copolymer membrane.

By virtue of the presence of nitrile groups along with the acrylonitrile moiety, it offers multidirectional approaches to modify polymer structure for specific applications. This includes plasma and photo-induced graft copolymerization, enzymatic modification and chemical modification such as hydrolysis and reduction.^{20,21} Hydroxylamine hydrochloride (HA) is an exceptionally nucleophilic amino compound and reacts with nitriles to give amidoxime.²⁰ The chemical treatment with HA is an interesting application for introduction of amidoxime groups along the polymer chain.^{22–25} The introduction of amidoxime is controlled by the reaction conditions to a large extent. The amidoximated material offers enormous potential toward the development of matrix for the separation of toxic metal ions.^{20,24,26} Tendency to form strong metal complexes with metals, attracted us to use this property of amidoxime group for antimicrobial activity.

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Our interest is to develop amidoximated acrylic membranes, which may be subsequently transformed into antimicrobial materials for water disinfection material. Acrylic membranes were prepared by solution polymerization of acrylonitrile and acrylic acid, and the amidoximation was accomplished by reaction of nitrile groups of PAN with HA. In this study, we have investigated the influence of reaction parameters, such as reaction time, temperature, and the HA concentration during the amidoximation process.

EXPERIMENTAL

Materials

Acrylic acid (AA) and acrylonitrile (AN) was purchased from Loba chemie Ltd. India and α -azobisisobutyronitrile (AIBN) from G.S. Chemical Testing Lab and Allied Industries, New Delhi. Toluene and dimethylformamide (DMF) were obtained from Merck India Ltd, Mumbai, while diethyl ether was supplied by Ranbaxy India Ltd. The chemicals were of the minimum assay of 99%. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) pellets was purchased from Merck India Ltd, Mumbai. The chemicals were used without further purification.

Polymerization

Free radical copolymerization of acrylonitrile and acrylic acid was carried out in a three-neck round bottom flask in toluene as a reaction medium at 60°C in thermostat water bath for 12 h, under nitrogen atmosphere. The monomer concentration was fixed at 20% in toluene. The acrylic acid content in the feed varied from 2–16%. To begin polymerization process, acrylonitrile was added to the flask and purged by nitrogen gas for 1 h. Subsequently, AIBN (0.025 mol % with respect to total monomer concentration) was added to it. Acrylic acid was added dropwise in the reaction mixture and the reaction was allowed to continue for 12 h with continuous nitrogen purging.

The reaction mixture was cooled and then precipitated in excess diethyl ether to get the copolymer. The copolymers were washed three times with excess diethyl ether to remove traces of unreacted monomers and toluene, followed by repeated washing with excess acetone to remove any homopolymer of acrylic acid. The purified copolymer was dried in a vacuum oven at 60°C. Membranes were fabricated by taking 10% copolymer solution in DMF and dried for 6 h in air oven and then for 4 h for complete drying under vacuum.

Hydroxylamine Treatment

The copolymer was treated with HA in aqueous medium. The HA concentration was varied from 1–3%

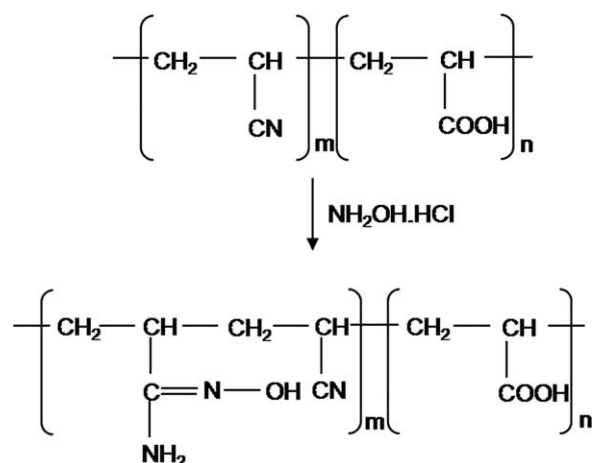


Figure 1 Schematic representation of the amidoximation of acrylic copolymer.

(w/v) and the pH of the solution was adjusted to 7 by neutralizing with sodium hydroxide solution. The reaction temperature was maintained in the range of 50–90°C.

Amidoxime Content Evaluation

The total amidoxime content in hydroxyl amine treated membranes before and after treatment was determined by the acid-base titration. The membranes were placed in 0.1 N HCl solution for 6 h, the membrane was removed, rinsed with deionized water, the remaining solution was titrated with 0.05 N NaOH solution. Phenolphthalein was used as an indicator for titration.

Fourier Transform Infrared Spectroscopy

The amidoximation reaction was investigated via Fourier-transform-infrared spectroscopy (FTIR). Perkin-Elmer FT-IR System Spectrum GX was used to acquire IR spectra of samples. Pellets were prepared by mixing of copolymer samples with FTIR grade potassium bromide (KBr), and grinding the mixture to a fine powder. Spectra were recorded over the 400–4500 cm^{-1} range.

RESULTS AND DISCUSSION

Schematic representation of the amidoximation of acrylic copolymer is presented in Figure 1. In the amidoximation process, a fraction of nitrile groups of copolymer is converted into amidoxime groups. As a result, the acrylic backbone contains amidoxime groups along with the carboxyl and nitrile groups. The variation of amidoxime content with the reaction time at different acrylic acid content in copolymers is presented in Figure 2. The amidoxime

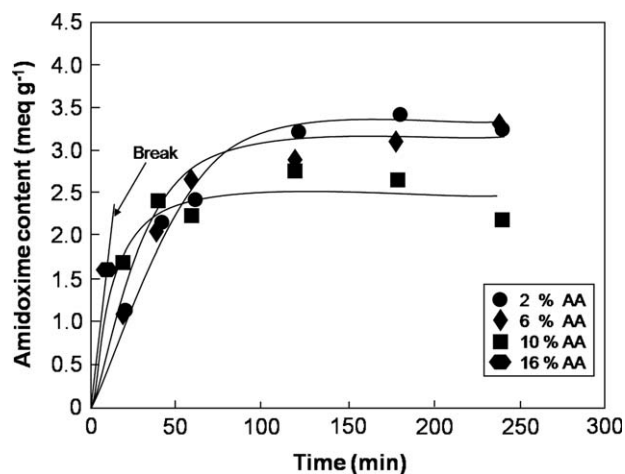


Figure 2 Variation of amidoxime content with the reaction time at different acrylic acid content. Reaction conditions: HA concentration, 3%; reaction medium, water; reaction temperature, 80°C.

content increases with the reaction time and reaches equilibrium value within 2 h. However, at higher acrylic acid concentration, the equilibrium levels off much faster. The reaction with 16% AA leads to very fragile membrane, which breaks into pieces within a few minutes of the reaction time. It seems that with the increase in acrylic acid content, the hydrophilicity of the membrane increases. As a result, the diffusion of HA within the polymer matrix is enhanced. This leads to more rapid conversion of nitrile groups into amidoxime groups. The equilibrium amidoxime content, however, was found to be much lower at high AA content. This may be associated with the lower content of AN moiety available in copolymer for the reaction with HA. Therefore, we confined our studies for 2% AA in the copolymer.

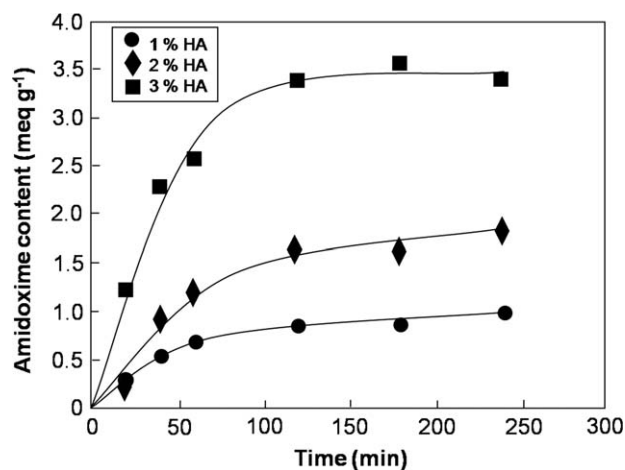


Figure 3 Variation of amidoxime content with the reaction time at different HA concentrations. Reaction conditions: reaction temperature, 80°C; reaction medium, water.

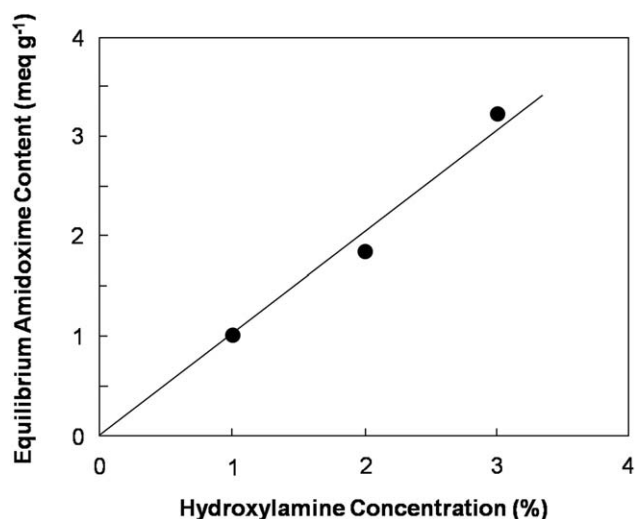


Figure 4 Variation of equilibrium amidoxime content with the HA concentration. Reaction conditions: reaction temperature, 80°C; reaction medium, water.

The amidoximation process has been found to be significantly affected by the reaction conditions, such as reaction time, hydroxyl amine concentration, and reaction temperature. The variation of amidoxime content with the reaction time at different HA concentration is presented in Figure 3. The amidoxime content increases linearly for 1 h and then tends to level off, reaching saturation within 2 h of reactions time. The amidoxime content reaches almost maximum within 3 h. The results are also in good agreement with the studies of Shoushtari et al.²⁷ Equilibrium amidoxime content increases linearly with the increase in HA concentration (Fig. 4). On the other hand, Lin et al.²² have carried out the HA treatment in a much higher range of 25–100 g/L and it was observed that amidoxime content increases slowly up to 50 g/L and subsequently accelerates. Our studies with HA content with 30 g/L concentration are in line with their observations. The log-log plot of rate of reaction with HA molar concentration is presented in Figure 5. The order of reaction for the amidoximation process was obtained from the slope of the plot and was found to be 1.1 indicating the first-order kinetics in this reaction.

The variation of the amidoxime content with the reaction time at different temperatures is presented in the Figure 6. It is interesting to see that for low temperatures, the amidoxime content increases all along 4 h of the reaction time. However, at the temperature of 80°C or more, the amidoxime content levels off at 1 h. These results indicate that at low temperatures the reaction is slow and may lead to higher amidoxime content if it is continued beyond 4 h. At high temperatures, it is faster reaction may be due to the faster diffusion of HA within the film and reaches equilibrium very fast.

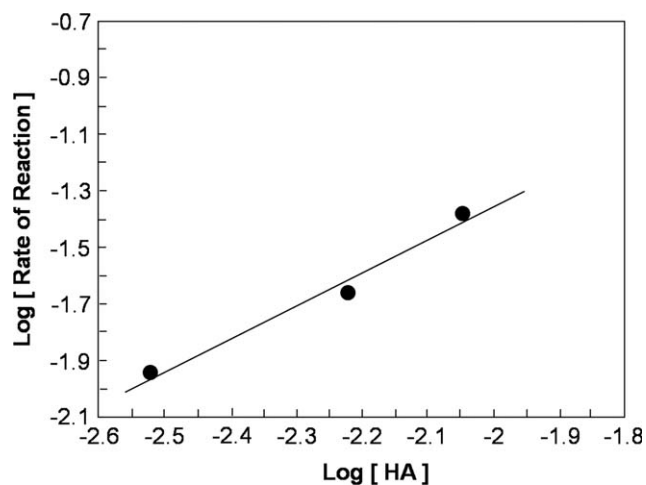


Figure 5 Log-log plot of rate of reaction with the HA concentration.

It is interesting to see the reaction trends and the amidoxime contents are almost identical for the temperature 80 and 90°C. Almost similar results were observed by Shoushtari et al.²⁷ Authors observed that amidoxime content increases up to 70°C, beyond which the amidoxime content becomes almost constant at 60 min.

The amidoxime content (at 4 h) and initial rate of reaction for all the temperatures are plotted against reaction temperature is in Figure 7. The trends in amidoxime content variation are divided onto distinct part. The amidoxime content increases slowly up to 60°C beyond which it tends to. The rate of reaction also increases up to 60°C after which it increases fast. It seems that some structural changes takes place at the temperature of 60°C which makes the structure amenable to the amenable process. There is strong correlation between amidoxime content and glass transition temperature of the copoly-

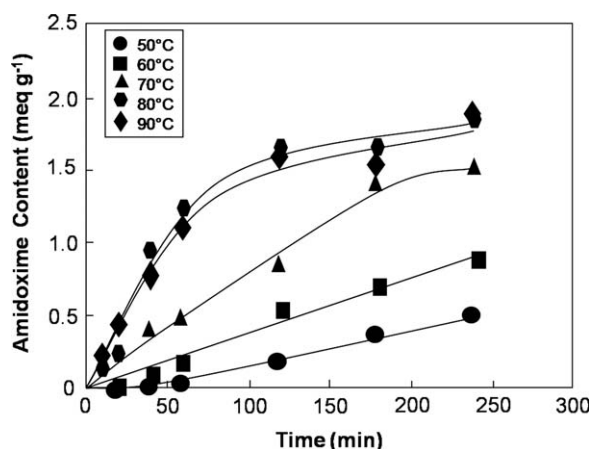


Figure 6 Variation of amidoxime content with the reaction time at different reaction temperatures, Reaction conditions: HA concentration, 2%; reaction medium, water.

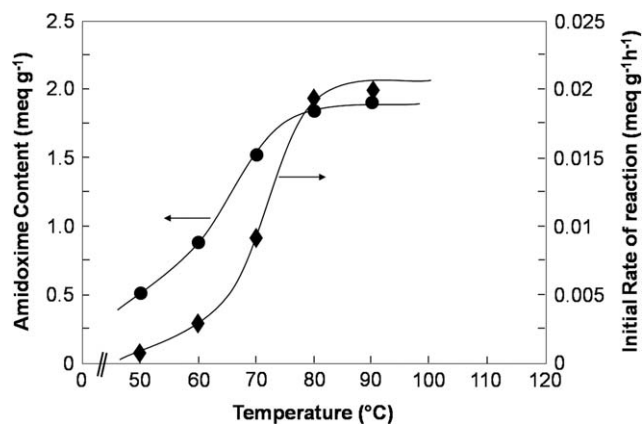


Figure 7 Variation of limiting amidoxime content and initial rate of reaction with the reaction temperature. Reaction conditions: as in Figure 6

mer $\sim 70^\circ\text{C}$. Below 70°C , the mobility of chains is much lower, as result the diffusion of HA within the film matrix is restricted thereby slowing down the amidoximation process. As the temperature moves to 70°C , the transition to rubbery stage leads to significant enhancement in HA diffusion which leads to higher rate of nitrile transformation. Our studies are in agreement with the results of Lin et al.²² where sharp transition at 70°C was attributed to the enhanced diffusion and destruction of crystallinity of the fiber.

The Arrhenius plot of the initial rate of reaction-versus $1/T$ from 50 to 80°C , as presented in Figure 8 is linear. The activation energy obtained from the slope of the plot is 102.0 kJ/mol. The transformation of nitrile into amidoxime was ascertained by FTIR. The FTIR spectra of virgin and amidoximated acrylic copolymer with 3.4 meq g^{-1} amidoxime content is presented in Figure 9. The peak at 3414 cm^{-1} shows the characteristic peak of O-H of COOH, 2943 cm^{-1}

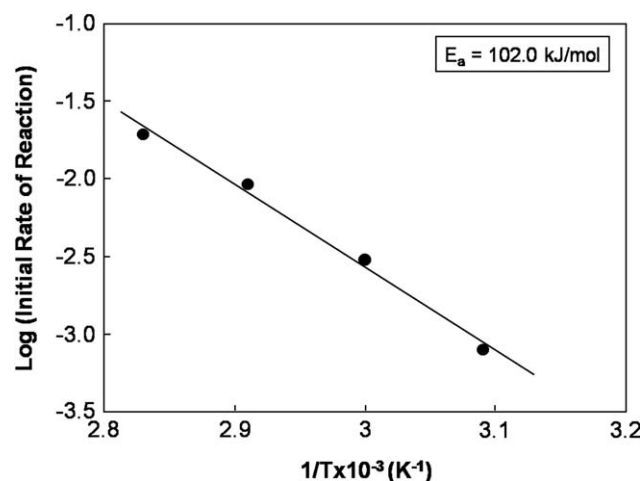


Figure 8 Arrhenius plot of rate of reaction vs. $1/T$. Reaction conditions.

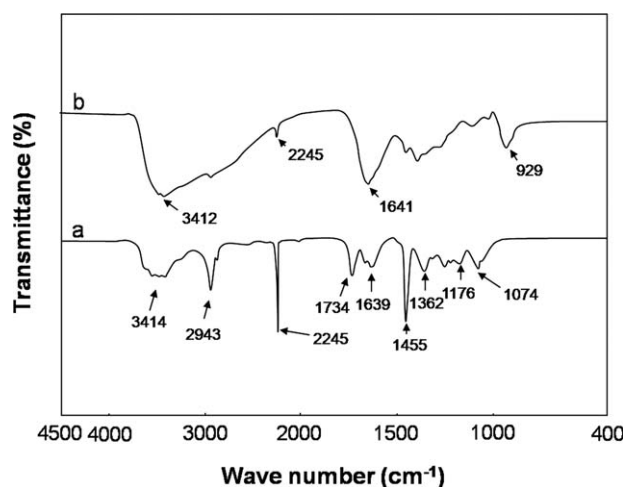


Figure 9 FTIR spectra of acrylic copolymers (a) virgin copolymer (b) amidoxime content 3.4 meq g⁻¹

corresponds to —CH stretching and the peak at 2245 cm^{-1} represents $\text{—C}\equiv\text{N}$ stretching vibration. A peak at 1734 cm^{-1} representing to stretching of —C=O of carboxyl group is observed due to the addition of small amount of acrylic acid during the polymerization. The peak at 1639 cm^{-1} represents for stretching vibration of COO^- group, peak at 1455 cm^{-1} represents for CH_2 stretching, peaks at 1176 cm^{-1} and 1074 cm^{-1} represents $\text{—C}\equiv\text{N}$ stretching and bending, respectively.

As a result of amidoximation, the most obvious change is in the significant loss of peak at around 2245 cm^{-1} , which corresponds to nitrile groups of AN. This indicates that nitrile groups decrease during amidoximation. Another favorable change is newly formed band belonging to the N—O stretching vibration of amidoxime at around 929 cm^{-1} . In virgin copolymer, the peak at 1639 cm^{-1} is due to stretching vibration of COO^- group.^{11,28} As the amidoximation reaction proceeds, a new peak of —C=N— group of amidoxime generates in this region. With the increase in amidoxime content, —C=N— group of amidoxime increases. Such increase is so intense that it overpowers the band of —C=O of carboxyl group and COO^- . Similar behavior has been observed by Liu et al.²³

CONCLUSION

The acrylic polymer may be amidoximated by treating with HA. Amidoxime content is governed by the reaction parameters, such as reaction temperature, time of reaction and HA concentration. It was interesting to see that at higher acrylic acid concentration, amidoxime content initially increased, but reached equilibrium very fast. With increase in hydroxyla-

mine concentration, amidoxime content increased. It was also evident that at a reaction temperature of 80°C and more the glass transition temperature induced diffusion, of HA is enhanced. The amidoxime content increased, significantly. The FTIR showed very precise transformation of AN into amidoxime groups. We concluded the optimum conditions to get optimum amidoxime content are 2% acrylic acid, 3% hydroxyl amine, at 80°C temperature for 3 h of reaction time.

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