## Preparation of Poly(vinyl alcohol) Grafted with Acrylic Acid/Styrene Binary Monomers for Selective Permeation of Heavy Metals

## H. A. ABD EL-REHIM, EL-SAYED A. HEGAZY, A. M. ALI

National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

Received 6 November 1998; accepted 22 December 1998

ABSTRACT: A study was made to modify water-soluble poly(vinyl alcohol) (PVA) by grafting acrylic acid and styrene (AAc/Sty) comonomers using gamma rays as an initiator. The factors that affect the preparation process and grafting yield were studied and more economical grafts under the most favorable reaction conditions were obtained. It was found that the high degree of grafting in such systems was obtained in the presence of an ethanol-water mixture in which water plays a significant role in enhancing the graft copolymerization. The critical amount of water to afford the maximum grafting yield was evaluated. The effect of the comonomer composition on the grafting yield was also investigated and it was observed that using a mixture of AAc/Sty monomers influences the extent of grafting of each monomer onto the PVA substrate and the phenomenon of synergism occurs during such a reaction. Also, the degree of grafting increases as the content of the solvent decreases in the reaction medium. However, the grafting yield increased as the total dose increased. The graft copolymer was characterized by IR and UV spectroscopic methods. The permeation of heavy metals such as Ni and Co through the grafted membranes was investigated and the efficiency of the separation process was also determined. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 806-815, 1999

**Key words:** poly(vinyl alcohol); graft copolymerization; membrane; separation; selective; permeation

## **INTRODUCTION**

<sup>1</sup>Heavy metal pollution from industrial effluents is an urgent problem of many industrialized cities under the current trends of worldwide environmental regulations. The chemical industry has the obligation to control the wastewater and hazardous wastes that they generate. The electroplating industry produces a great number of metal ions that contaminate industrial effluents. The separation of such metals from each other is one of the principal challenges facing scientists. Also, selective separation of some metals from other components is of practical interest, either with the aim to isolate such elements from natural sources or for the purpose of their separation from industrial effluents or wastewater with respect to the low concentration.<sup>1–5</sup>

Poly(vinyl alcohol) PVA is a well-known membrane material with good film-forming properties, is a highly hydrophilic polymer, and has easy availability. Investigations have been done on its use in the field of separation processes.<sup>6,7</sup> However, such a polymer suffers from poor water resistance and low mechanical strength in aqueous

Correspondence to: H. A. Abd El-Rehim.

Contract grant sponsor: International Atomic Energy Agency (IAEA); contract grant number: 9566/RO (Regular Budget Fund).

Journal of Applied Polymer Science, Vol. 74, 806-815 (1999)

<sup>© 1999</sup> John Wiley & Sons, Inc. CCC 0021-8995/99/040806-10

solutions. Therefore, it has to be turned into a completely insoluble stable material with good mechanical properties. A number of investigations have been reported in the literature to modify PVA by crosslinking with different reagents such as aldehyde,<sup>8</sup> dicarboxylic acid,<sup>9</sup> heat,<sup>10</sup>  $H_3BO_3$ ,<sup>11</sup> and radiation.<sup>12</sup>

Radiation methods have been particularly studied for the production of a large variety of graft copolymers having interesting properties.<sup>13</sup> Extensive work has been performed on methods for optimizing yields when monomers are radiation-grafted to a backbone polymer, especially with a simultaneous technique.<sup>14,15</sup>

The purpose of this investigation was to study and control the insolublization of PVA, thereby creating a permanent gel-layer membranes. Modification by graft copolymerization of acrylic acid/ styrene (AAc/Sty) binary monomers onto PVA film, using gamma rays as an initiator, and the factors that affect such a grafting process are the topic of this study. Also, a trial was made to separate Co and Ni ions from their solutions using dialysis cells containing PVA-g-P(AAc/Sty) membranes.

## **EXPERIMENTAL**

## **Materials**

PVA powder (Hanawa Chemical Pure, Osaka, Japan), DP = 1700, degree of saponification of 98%, was used. Sty GRG (Avondale Laboratories, Oxon, England), purity 99%, and AAc (Merck, Germany), purity 99.9%, were used without further purification. The other chemicals, such as solvents and reagents, were reagent grade and used as received.

#### **Methods and Apparatus**

#### **Preparation of PVA Films**

A solution of PVA was prepared by dissolving 5 g of PVA, in a conical flask with a standard joint, in 100 mL distilled water at 80°C. The PVA films were cast from a 5 wt % aqueous solution on a glass plate and then subsequently dried in air at room temperature. The film thickness was in the range of  $50-60 \ \mu$ m.

## Graft Copolymerization

Strips of PVA films were weighed and then immersed in the monomer or binary monomer solu-

tion in glass ampules. The direct radiation grafting method was used in an air atmosphere. The glass ampules containing all the reactants and polymer substrates were then subjected to <sup>60</sup>Co gamma rays at dose rate that ranged from 1.1 to 1.2 Gy/s. The grafted films were removed and washed thoroughly with methanol, which is a good solvent for copolymers of AAc and Sty, washed with benzene and with a mixture of benzene/methanol (1:1), and then immersed in a mixture of water/methanol (2:1) to extract the residual monomer or homopolymer which may be accumulated in the grafted films. The films were then dried in a vacuum oven at 50°C. The degree of grafting was determined by the percent increase in weight as follows:

Degree of grafting (%) =  $[(W_g - W_0/W_0)] \times 100$ 

where  $W_0$  and  $W_g$  are the weights of initial and grafted films, respectively.

## Ultraviolet Spectroscopy

Analysis by a UV spectrophotometer was carried out using a Milton Roy Spectronic 1201 in the range from 190 to 900 nm.

#### Infrared Spectroscopy

Analysis by infrared spectroscopy was carried out using a Shimadzu IR 408 in the range from 650 to  $4000 \text{ cm}^{-1}$ .

#### **Dialysis Apparatus and Procedure**

The dialysis permeability measurements were conducted using a diaphragm-type cell. The prepared membrane was placed in between the two compartments. In the left-hand side of the cell, a metal solution was introduced, and in the righthand side, distilled water was introduced. Samples were withdrawn from both sides of the membrane in time periods of 5, 15, 20, ..., and 100 min.

## **Determination of Nickel Ions**

Nickel ions have chromophoric properties and give colored reactions with many reagents. The most important photometric reagents for determining nickel are dioximes, which give specific and sensitive methods.<sup>16</sup>

*Procedure.* Quantitatively transfer the sample solution to a 50-mL volumetric flask and 1 mL of the 1% dimethylglyoxime solution, 2 mL of 4% potassium persulfate solution, and 5 mL of a concentrated  $NH_3$  solution in that order. Dilute the solution with water to the mark, and mix well. After 10 min, measure the absorbance at 445 nm against water.

#### **Determination of Cobalt Ions**

In concentrated solutions of potassium, or ammonium thiocvanate, cobaltous ions produce a blue color, which fades when the solution is diluted with water, owing to dissociation of the complex. The addition of acetone or any other water-miscible organic solvent, which lowers the dielectric constant and thereby suppresses the dissociation of the complex, restores the blue color to the solution.<sup>17</sup> The color intensity depends on the concentration of SCN- and acetone. It was established that in a 50% acetone solution increasing the KSCN concentration above 10% produces no further increase in the color intensity. The acidity of the solution also affects the absorbance and should, therefore, be kept constant (within the limits from 0.1 to 1M HCl in the sample and the reference solutions).

*Procedure.* To the sample solution in a 50-mL volumetric flask containing less than 1 mg of Co, add hydrochloric acid until 0.5M. Add 10 mL of the 50% ammonium thiocyanate solution. If a red color appears (indicative of iron), add a 2% ascorbic acid solution dropwise until decolorization, and then add 1 mL more. Add 25 mL of acetone, and dilute the solution with water to the mark. Measure the absorbance of the blue solution at 620 nm, using water as a reference.

## **RESULTS AND DISCUSSION**

Graft copolymerization of a mixture of vinyl monomers is important since different types of polymer chains containing various functional groups can be introduced into the structure of the supported materials used. The reaction conditions of the grafting system can be manipulated and a graft copolymer of desired properties might be obtained. The factors studied which affect the preparation process and grafting yield are the solvent and the total dose, the comonomer concentration, and the composition. In the following,

Table I	Effect of Different Solvents on the
Grafting	<b>Process of AAc/Sty Binary Monomer</b>
System (	2/1 mol/mol) onto PVA Films

Solvent Composition (wt %)	Degree of Grafting (%)
65/35	290
100	60
65/35	16
100	_
65/35	14
100	_
65/35	7.5
100	3.5
	Solvent Composition (wt %) 65/35 100 65/35 100 65/35 100 65/35 100

Irradiation dose: 10 kGy; comonomer concentration: 20 wt %.

the influence of such parameters will be described and discussed.

#### **Effect of Solvent**

It is well known that a solvent plays an important role in enhancing the grafting process of a monomer onto a trunk polymer. Irradiation of a monomer-solvent mixture often leads to an energytransfer process; this introduces additional complications in the reaction kinetics. In this connection, the effect of different solvents on the graft copolymerization of AAc/Sty binary monomers onto PVA films was investigated and is shown in Table I. It can be seen that a high degree of grafting is obtained when a water-solvent mixture is used. The higher degree of grafting of such a system was observed in the presence of a waterethanol solvent mixture. The presence of mixed water with any solvent used here resulted in enhancement of the grafting yield as compared to that obtained when such solvents were used alone.

The results suggest that the solvents influenced the grafting yield of the AAc/Sty comonomer onto the PVA membrane and the enhancement effect is more pronounced with the most polar solvent such as an ethanol/water mixture. In addition, the results suggested that water plays an important role in such a grafting system.

## Effect of Water/Ethanol Mixture Composition on Grafting Yield

As mentioned above, the graft copolymerization of AAc/Sty binary monomer mixtures onto PVA



**Figure 1** Effect of solvent composition on the grafting of AAc/Sty binary monomers of composition 1/1 mol/mol onto PVA films. Comonomer concentration: 20 wt %; irradiation dose: 5 kGy.

films is enhanced in the presence of an ethanol/ water-mixture as a good diluent for this binary monomer system. The content of water in the solvent mixture is limited depending on the Sty content in the comonomer composition due to its insolubility in water. Therefore, the optimum composition of a water/ethanol mixture in the binary monomers, at which the grafting process proceeds successfully, is determined and is shown in Figures 1 and 2 for 1/1 and 2/1 mol/mol comonomer compositions of AAc/Sty, respectively. It can be seen that there is a critical amount of water at which the maximum grafting yield can be obtained. The degree of grafting increases as the water content increases, reaching its maximum value at a water/ethanol composition of 10/90 and 20/80 mol % for AAc/Sty compositions of 1/1 and 2/1 mol/mol, respectively. Thereafter, it gradually decreases as the water content increases in the solvent mixture. With such solvent mixtures, the grafted films were easily removed and extracted from the reaction medium and seemed to be smooth and flat and possessed homogeneous grafting.

The results showed that the presence of water is essential for enhancing the grafting process. The results also suggest that the higher the AAc content in the comonomer composition, the higher the water content required for obtaining high degrees of grafting. This is quite reasonable because AAc is a water-soluble monomer, but Sty is insoluble in water. In the presence of water, the packing of a PVA polymer is loosened through the swelling action of water, permitting easy penetration of the AAc/Sty comonomer, which resulted in the enhancement of grafting. Water as a diluent has a zero-chain transfer constant; therefore, the side reaction that involves chain transfer is minimal in water. All these factors combined together made the addition of water very important for the grafting of AAc/Sty onto PVA.

The results showed also that at optimum conditions the radiolytic fragments of water may activate PVA by abstracting the tertiary hydrogen atom in the following manner:

$$H_2O \xrightarrow{\gamma \text{-rays}} \mathbb{R}^{\bullet}(\mathbb{H}^{\bullet} + O\mathbb{H}^{\bullet})$$
$$\mathbb{R}^{\bullet} + \mathbb{P}VA \to \mathbb{R}\mathbb{H} + \mathbb{P}VA^{\bullet}$$

However, at a high water content beyond the optimum, radiolysis of additional water produces a number of radical species, which mutually inhibit the growing of grafted chains, leading to a decrease in the percent grafting. Meanwhile, in the



**Figure 2** Effect of solvent composition on the grafting of AAc/Sty binary monomers of composition 2/1 mol/mol onto PVA films. Comonomer concentration: 20 wt %; irradiation dose: 10kGy.



**Figure 3** Effect of AAc/Sty concentration of composition 2/1 mol/mol on the degree of grafting onto PVA films. EtOH/H<sub>2</sub>O mixture composition: 75/25 wt %; irradiation dose: 5 kGy.

presence of pure ethanol, various chain-transfer and hydrogen-abstraction reactions were accelerated, which resulted in a decrease of the grafting yield of such binary monomer mixtures onto PVA films.

#### Effect of Comonomer Concentration

The suitable monomer concentration varies from one system to another depending on the polymer substrate, solvent, total dose, comonomer composition, etc. The influence of the monomer concentration on the grafting process of the AAc/Sty grafting system was investigated and is shown in Figure 3 using a water-ethanol mixture (20 : 80) as a diluent. It can be seen that the degree of grafting increases with the comonomer concentration, that is, it increases as the content of the solvent decreases in the reaction medium.

These results can be explained by taking into account the diffusion coefficient of both binary monomers and its variation in various solvent contents. In general, at a high comonomer concentration, a great number of molecules are available to react with the free radical formed in the backbone of the polymer chains. Alternatively, it also favors the production of a large number of growing chains, which increases the possibility of H abstraction via chain transfer to give rise to the substrate macroradicals. This leads to an increased extent of chain propagation, resulting in a greater degree of graft add-on.

#### **Effect of Comonomer Composition**

Some of the attention paid to enhancing grafting efficiencies has involved the use of mixed monomer systems, particularly with regard to synergistic effects, leading to more efficient grafting processes. Therefore, the grafting of AAc/Sty binary monomers of various relative compositions was investigated at an overall comonomer concentration of 20 wt % in an ethanol/water mixture as a diluent and is shown in Figure 4. It is clear that the grafting yield increases with increasing Sty content in the comonomer mixture, to reach a maximum percent grafting at an AAc/Sty composition of 55/45 mol/mol. Thereafter, it decreases with increasing Sty content. It is also seen that the percent grafting for the comonomer mixture is higher than that obtained for the individual grafting of Sty or Aac, that is, there is a synergistic effect in the grafting process of an AAc/Sty binary mixture onto PVA film. The presence of Sty and AAc enhanced the extent of grafting for both monomers onto PVA.

The results suggest that Sty is a retarding agent by dissipation of the radiation energy form-



**Figure 4** Effect of AAc/Sty comonomer composition on the degree of grafting onto PVA films. Comonomer concentration: 20 wt %; EtOH/H<sub>2</sub>O mixture composition: 75/25 wt %; irradiation dose; 5 kGy.

ing a stable exciting state that prevents the freeradical formation responsible for the initiation of grafting sites. Therefore, the feed solution containing an excess of Sty hinders the grafting yield of the comonomer onto the polymeric substrate. However, AAc has a higher G(R) value than that of Sty.<sup>18</sup> This resulted in homopolymer formation, which also retards the grafting process. In the feed solutions containing both monomers, the presence of Sty prevents AAc from homopolymerizing; however, the latter activates the Sty monomer to graft onto the PVA substrate. This results in obtaining a higher degree of grafting if compared with that obtained for the individual grafting of AAc or Sty. Again, a synergistic effect can be attributed to the great amount of the complex mobility of AAc/Sty in a feed solution, which retards the rate of homopolymerization due to the retarding effect of the Sty ring. When one monomer molecule diffuses inside the film structure, it automatically carries the other monomer molecules present in the complex, thus increasing the monomer concentration in the film phase, a very favorable situation for higher grafting copolymer formulation.

#### **Effect of Irradiation Dose**

The irradiation dose is an important factor in any radiation grafting system. In the direct radiation method, the total dose determines the number of grafting sites. Therefore, the effect of the dose on the grafting process in such a system was investigated and is shown in Figure 5. It is obvious that the grafting yield initially increases rapidly with an irradiation dose up to 15 kGy; thereafter, it tends to level off at higher irradiation doses.

The results show that the concentration of free radicals, formed in the polymer and the comonomer binary system, increases with irradiation dose. This resulted in an increase in the percentage of grafted chains and their length. By prolonging the irradiation time, the lack of monomer molecules together with AAc/Sty chain cleavage can also be responsible for the plateau trend observed above 15 kGy irradiation. Such a trend is due to the diffusion of the monomer into the films and competes with its polymerization, and as the rate of polymerization increases, a situation is reached at which the reaction medium becomes dependent on the monomer. Also, at high doses, the recombination of free radicals is enhanced and results in a leveling off of the grafting process.



**Figure 5** Effect of irradiation dose on the degree of grafting of AAc/Sty onto PVA films. Comonomer concentration: 20 wt %; EtOH/H2O mixture composition: 75/25 wt %.

# Effect of AAc or Sty Content in Feed Solution on Poly(AAc/Sty) Ratio of Graft Chains

The influence of comonomer composition on the ratio of AAc/Sty and its content in the graft copolymer was investigated using UV spectroscopy. Figure 6(a,b) shows UV spectra of the PVAgrafted films prepared at comonomer feed solutions of compositions of 0: 100 and 50: 50 AAc/ Sty, respectively. It is obvious that the characteristic bands  $(\lambda_{max})$  of the Sty unit for PVA-g-Sty appear at 269 and 280 nm. However, the intensity of these bands decreases and another new band appears at  $\lambda_{max} = 290$  nm for film prepared at comonomer feed solutions of a composition of 50/50 AAc/Sty. The spectrum of the PVA-grafted film from a feed solution of 30 : 70 AAc/Sty shows characteristics bands of the Sty unit [Fig. 6(c)]. Meanwhile, such bands disappeared in films prepared from a feed solution of a 70 : 30 AAc/Sty comonomer composition [Fig. 6(d)].

The results show that the comonomer composition plays a role in controlling the AAc/Sty ratio of the graft chains, especially at the beginning of the grafting process. As the content of Sty increases in the feed solution, the poly(Sty) content increases in the graft copolymer chains; the richer the Sty content in the feed solution, the higher the content of Sty units in the grafted chains obtained and vice versa.



**Figure 6** UV spectra of (A) PVA-g-Sty having degree of grafting of 35%, (B) PVA-g-PAAc/Sty having degree of grafting of 24% from feed solution of composition 1/2 mol/mol AAc/Sty, (C) PVA-g-PAAc/Sty having degree of grafting of 25% from feed solution of composition 3/1 mol/mol AAc/Sty, and (D) PVA-g-PAAc/Sty having degree of grafting of 34% from feed solution of composition 1/1 mol/mol AAc/Sty.

#### IR Spectra of Grafted and Ungrafted Films

IR analysis was done for the grafted and original PVA films to confirm the formation of the graft copolymer and to obtain knowledge about their structures. Figure (7) shows the spectra of the original PVA and PVA-g-P(AAc/Sty) films. For PVA films, the characteristic band for hydroxyl groups of PVA and a carbonyl group band of residual poly(vinyl acetate) appears at 3200–4000 and ~1720 cm<sup>-1</sup>, respectively [Fig 7(A)]. For PVA-g-P(AAc/Sty) films, the characteristic bands of the PVA substrate and AAc/Sty graft chains

clearly appear [Fig. 7(B)]. In addition, the distinguishing band for carbonyl groups of AAc appears at 1710 cm<sup>-1</sup>, of higher intensity than that of PVA, and the C—H characteristic band of the Sty ring at 700 cm<sup>-1</sup> was observed.

## Separation of Ni<sup>+2</sup> from Solution Containing Co<sup>+2</sup>

It is well known that it is not so easy to separate  $\text{Co}^{+2}$  from  $\text{Ni}^{+2}$  metal from their feed solutions because  $\text{Co}^{+2}$  and  $\text{Ni}^{+2}$  have the same atomic weight and atomic radii and also they have the



Figure 7 IR spectra of (A) original PVA and (B) PVA-g-AAc/Sty having degree of grafting of 16%.

same valence. Therefore, a trial was made to separate the two metals from a solution by using a dialysis cell containing PVA-g-P(AAc/Sty) membranes.

Figure (8) shows the transportation process of  $Ni^{+2}$  and  $Co^{+2}$  through a PVA-grafted membrane. It can be seen that, under such experimental conditions,  $Ni^{+2}$  only is transported via the membrane and moved into the receiving solution. However,  $Co^{+2}$  is not transported but seems to be chelated with the membrane functional groups. The transportation process of  $Ni^{+2}$  through the prepared grafted membrane shows an inductive period and the transfer into the receiving solution occurred after ~20 min.

The results suggest that PVA-g-P(AAc/Sty) has a high affinity to chelate with Co and allows Ni<sup>+2</sup> to transport through to reach the receiving solution. This means that the Co<sup>+2</sup> has a high ability to complex with the —COOH and —OH groups of grafted membranes rather than Ni<sup>+2</sup>. The induction period may be attributed to both the Ni<sup>+2</sup> and Co<sup>+2</sup> (at the beginning of the transportation process) chelating with functional groups of the membranes. After a short time, the unstable Ni<sup>+2</sup> complex breaks down unlike the stable Co<sup>+2</sup> one, resulting in the transporting of Ni<sup>+2</sup> into the receiving solution.

## Effect of Degree of Grafting

Figure (9) shows the effect of grafting yield on the transportation process of  $\mathrm{Co}^{+2}$  and  $\mathrm{Ni}^{+2}$  through

the PVA-g-P(AAc/Sty) membrane. It is obvious that the concentration of transported Ni<sup>+2</sup> ions increases with time and it gives a nonlinear relationship at longer times above  $\sim 60$  min. This behavior is observed for all membranes having different degrees of grafting. However, the rate and concentration of transported Ni<sup>+2</sup> increases as the degree of grafting decreases. Meanwhile,



**Figure 8** Transportation of  $Ni^{+2}$  from solution containing Co<sup>+2</sup> through PVA-g-PAAc/Sty membrane having degree of grafting of 79%. pH of feed solution/ receiving solution: 5.4/6.7; Ni/Co composition: 1/1 ppm/ ppm.



**Figure 9** Effect of grafting yield on separation process of Ni<sup>+2</sup> from Co<sup>+2</sup> through PVA-g-PAAc/Sty membrane. Degree of grafting %: (**I**) 79; (**O**) 100; Ni/Co composition: 1/1 ppm/ppm; pH of feed solution/received solution: 5.4/6.7.

the  $\operatorname{Co}^{+2}$  does not transport but is chelated by the membrane.

The results suggest that, at a higher grafting yield, the content of the crosslinked network structure is greater than that at a lower grafting yield, which restricts the diffusion of metal through such a network structure. In addition, the content of hydrophobic-grafted Sty units increases as the grafting yield increases. As a consequence, the diffusion of water through the membrane decreased, resulting in retarding the diffusion of Ni<sup>+2</sup> through the membrane. Therefore, at a higher grafting yield, the rate and the amount of transported Ni<sup>+2</sup> metal decreases and a much longer time is needed for its transportation.

#### Effect of pH

Figure 10 represents the transportation of Ni through the membrane at different pH's of the feed or receiving solutions. It can be seen that the change in pH for the receiving or feed solution resulted in a minor change for the Ni ion transported throughout the PVA-g-P(AAc/Sty) membrane. This means that the change in pH in such a system does not affect the transportation of Ni or enhance the transportation of the Co ion.

## Effect of Ni Concentration on Its Transportation Throughout the Membrane

It is expected that the transportation of metal ions throughout the membrane would be affected by the concentration of metal in its feed solution. Figure 11 shows that as the Ni<sup>+2</sup> concentration increases in the feed solution the amount and rate of transported Ni<sup>+2</sup> increases in the receiving compartment. In addition, reducing the amount of Ni<sup>+2</sup> in the feed solution does not enhance the transportation of Co<sup>+2</sup>. The results suggest that the reduction of the Ni<sup>+2</sup> amount in the feed solution does not affect its transportation through the membranes.

## **CONCLUSIONS**

PVA membranes were modified by radiationinduced graft copolymerization of an AAc/Sty binary monomer system. The insolubility of PVA is achieved by the introduction of reactive groups having the capability for separation processes. The optimum conditions, at which such grafting reactions can give more economical grafts, were determined. Separation of Ni from a solution containing Co ions was also studied.



**Figure 10** Effect of pH change on transportation process of Ni<sup>+2</sup> or Co<sup>+2</sup> through PVA-g-PAAc/Sty membrane having degree of grafting of 79%. pH of feed solution/receiving solution:  $(\blacklozenge, \blacktriangle)$  2.29/6.7;  $(\diamondsuit, \bigcirc)$  5.4/6.7;  $(\diamondsuit, \bigtriangledown)$  5.95/2.2;  $(\diamondsuit, \blacksquare)$  8.5/6.7. Ni/Co composition: 1/1 ppm/ppm.



Figure 11 Effect of Ni concentration on the transportation process through PVA-g-PAAc/Sty membrane having degree of graftingof 79% at Ni/Co composition of (●) 1/1ppm/ppm and (■) 1/4ppm/ppm; pH of feed solution/receiving solution: 5.4/6.7.

Nickel ions moved from the feed solution via the grafted membranes and were transported into the receiving one. However, cobalt ions did not transport but were expected to be chelated with the membrane functional groups. The rate and concentration of transported nickel ions increases as the degree of grafting decreases. Also, the change in pH for the receiving or feed solution did not affect the amount of nickel ions transported throughout the membrane. Reducing the amount of nickel in the feed solution did not enhance the transportation of cobalt ions. The prepared PVA-g-P(AAc/Sty) membranes show great promise for practical use in the field of metal-separation processes.

## REFERENCES

- Hegazy, E. A.; Abd El-Rehim, H. A.; Khalifa, N. A.; El-Hag Ali, A. IAEA-SM-50, presented at the International Symposium on Radiation Technology, Zakopane, Poland, Sept. 8–12, 1997.
- Hegazy, E. A.; Abd El-Rehim, H. A.; Khalifa, N. A.; Atwa, S. M.; Shawky, H. A. Polym Int 1997, 42, 321.
- Lin, W.; Hsieh, Y. J Polym Sci Part A Polym Chem 1997, 35, 631.
- Poore, D.; Benson, R.; Matin, D. J Environ Sci Health A 1996, 31, 2167.
- Pizarro, G. C.; Marambio, O. G.; Rivas, B. L.; Geckeller, K. E. J Macromol Sci Pure Appl Chem 1997, 34, 1983.
- Burczak, F. T.; Ikada, Y. Proc Jpn Acad Ser B 1991, 75(5), 83.
- Shantora, V.; Huang, R. Y. M. J Appl Polym Sci 1981, 26, 3223.
- Koyama, K.; Nishi, T.; Nishimura, M. J Appl Polym Sci 1982, 27, 2845.
- Peter, S.; Stefan, R. In Proceedings of the International Symposium of Fresh Water from the Sea; E. Delyannis, Ed.; Athens, 1980; Vol. 2, p 197.
- Katz, M. G.; Wydeven, T. J Appl Polym Sci 1982, 27, 79.
- Peter, S.; Hese, N.; Stefan, R. Desalination 1976, 16, 161.
- Katz, M. G.; Wydeven, T. J Appl Polym. Sci 1981, 26, 2935.
- Abd El-Rehim, H. A.; Ali, A. M.; Nowier, H. G.; Hegazy, E. A.; Aly, H. F. In Proceedings of the Sixth Conference on Nuclear Sciences and Applications, Cairo, Egypt, March 15–20, 1996; Vol. 3, p 227.
- Hegazy, E. A.; Taher, N. H.; Ebaid, A. R. J Appl Polym Sci 1990, 41, 2637.
- 15. Hegazy, E. A.; Abd El-Rehim, H. A.; Khalifa, N. A.; El-Hag Ali, A. J Radiat Phys Chem, in press.
- 16. Nielsh, W. Z. Anal Chem 1953, 140, 267.
- 17. West, P. W.; Vries, C. G. Anal Chem 1951, 23, 334.
- Chapiro, A. Radiation Chemistry of Polymeric System; Wiley-Interscience: New York, 1962.