



EG0000238

T-23

Preparation of Poly(Vinyl Alcohol) Grafted With Acrylic Acid/Styrene Binary Monomers For Selective Permeation of Heavy Metals

El-Sayed A. Hegazy, H. A. Abd El-Rehim, A.M. Ali and H. F. Aly*

*National Center for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt.
Hot Laboratories Center, Atomic Energy Authority, Post No. 13759 Cairo, Egypt.

ABSTRACT

A study has been made to modify water-soluble poly(vinyl alcohol) (PVA), by grafting acrylic acid and styrene (AAc/Sty) binary monomers using gamma rays as 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 of such system was obtained in presence of ethanol-water mixture in which water plays a significant role in enhancing the graft copolymerization. The critical amount of water to afford maximum grafting yield has been evaluated. The effect of comonomer composition on the grafting yield was also investigated and it was observed that using a mixture of AAc/Sty monomers influence the extent of grafting of each monomer onto the PVA substrate and the phenomenon of synergism occurs during such reaction. Also, degree of grafting increases as the content of the solvent decreases in the reaction medium. The permeation of heavy metals such as Ni and Co through the grafted membranes was investigated and efficiency of separation process is also determined.

(Key Words: Poly(vinyl alcohol)/ Graft Copolymerization/ Membrane/ Separation/ Selective/Permeation)

INTRODUCTION

Heavy metal pollution from industrial effluents are urgent problem of many industrialized cities under current trends of worldwide environmental regulations. Chemical industry has the obligation to control the wastewater and hazardous wastes they generate. The electroplating industry produces a great number of metal ions that contaminate the industrial effluents. The separation of such metal from each other is one of the principle challenges facing scientists. Also, Selective separation of some metals from other components is of practical interest, either with the aim to isolate this element from natural sources or for the purpose of its separation from industrial effluents or wastewater with respect to the low concentration⁽¹⁻⁵⁾.

Poly(vinyl alcohol) PVA is a well known membrane material with good film-forming, highly hydrophilic polymer, and easy availability. Investigations have been done for its use in the field of separation processes^(6,7). However, such polymer suffers from poor water resistance and low mechanical strength in aqueous solution. Therefore, it has to be turned into a completely insoluble stable material with good mechanical properties. A number of investigations have been reported in literature to modify PVA by crosslinking with different reagents such as mono- and divalent-ions by aldehyde⁽⁸⁾, dicarboxylic acid⁽⁹⁾, heat⁽¹⁰⁾, H₃Bo₃⁽¹¹⁾ and radiation⁽¹²⁾.

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

The purpose of this investigation is to study and control the insolubilization of PVA, thereby creating a permanent gel layer membranes. Modification by graft copolymerization of AAc/Sty binary monomers onto PVA film using gamma rays as initiator and the factors affect such grafting process are the topic of this study. Also, a trial has been made to separate Co and Ni from their solutions by using dialysis cells containing PVA-g-AAc/Sty membranes.

EXPERIMENTAL

Materials

- Poly(vinyl alcohol) (PVA) powder, Hanawa Chemical Pure, Japan, DP = 1700, degree of saponification of 98 mol %, was used.
- Styrene GRG (Avondale laboratories, England), purity 99% and Acrylic acid (AAc), purity 99.9% (Merck, Germany) 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 5g of PVA in conical flask with standard joint in 100ml distilled water at 80°C. The PVA films were casted from 5wt % aqueous solution on glass plate and then subsequently dried in air at room temperature. Film thickness is in the range of 50- 60 µm.

Graft Copolymerization

Strips of PVA films were weighed and then immersed in the monomer or binary monomers solution in glass ampoules. The direct radiation grafting method was used in air atmosphere. The glass ampoules contain all reactants and polymer substrate were then subjected to ⁶⁰Co gamma rays at dose rate that ranged from 1.1 to 1.2Gy/s. The grafted films were removed and washed thoroughly with methanol which is a good solvent for homopolymers of acrylic acid and styrene, to extract the residual monomer or homopolymer which may be accumulated in the grafted films. The films were then dried in vacuum oven at 50 °C. The degree of grafting was determined by the percent increase in weight as follows: -

$$\text{Degree of Grafting (\%)} = [(W_g - W_0 / W_0)] \times 100$$

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

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, metal solution was introduced and in the right hand side, distilled water was introduced. Sample was withdrawn from both sides of the membrane in time period "5, 15, 20, and 100 min."

Determination of Nickel Ions

Nickel ions have chromophoric properties and give coloured reactions with many reagents. The most important photometric reagents for determining nickel are dioximes, which give specific and fairly sensitive methods⁽¹⁶⁾.

Procedure:

Quantitatively transfer the solution obtained to a 50-ml volumetric flask and 1 ml of the dimethylglyoxime solution, 2 ml of persulphate solution), and 5 ml of conc. NH_3 solution in that order. Dilute the solution with water to the mark, and mix well. After 10 minutes, measure the absorbance at 445 nm against water.

Determination of Cobalt Ions

In concentrated solutions of potassium, ammonium thiocyanate, cobaltous ions produce a blue colour, 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 colour to the solution⁽¹⁷⁾. The colour intensity depends on the concentration of SCN^- and acetone. It has established that in 50% acetone solution increasing the KSCN concentration above 10% produces no further increase in the colour 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 1mg of Co, add hydrochloric acid until 0.5M. Add 10 ml of the thiocyanate solution. If a red colour appears (indicative of iron), the ascorbic acid solution is added dropwise till 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 in the structure of supported materials used. The reaction conditions of the grafting system can be manipulated and a graft copolymer of desired properties may be obtained. The factors studied which affect on the preparation process and grafting yield are; the effect of solvent, comonomer concentration and composition. In the following, the influence of such parameters will be described and discussed.

Effect of Solvent

It is well known that solvent plays an important role to enhance the grafting process of a monomer onto a trunk polymer. Irradiation of monomer-solvent mixture often leads to energy transfer 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 is investigated and shown in Table (1). It can be seen that the high degree of grafting obtained when water-solvent mixture are used. The higher degree of grafting of such system was observed in the presence of water-ethanol solvent mixture. The presence of mixed water with any solvent used here resulted in enhancing the grafting yield if compared with that obtained when such solvents were used alone.

Results suggested that solvents influenced grafting yield of AAc/Sty comonomer onto PVA membrane and the enhancement effect is more pronounced with the most polar solvent such as ethanol / H_2O -mixture. Also, results suggested that water plays an important role in such grafting system.

Table (1): Effect of different solvents on the grafting process of (AAc/Sty) binary monomers system (2/1 mole/mole) onto PVA films. Irradiation dose; 10 kGy and comonomer concentration (20 wt. %).

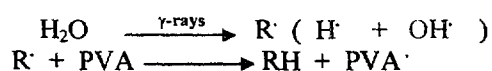
Solvent	Solvent Composition (wt. %)	Degree of Grafting (%)
EtOH/H ₂ O	65/35	290
EtOH	100	60
DMF/H ₂ O	65/35	16
DMF	100	-
Acetone/H ₂ O	65/35	14
Acetone	100	-
DMSO/H ₂ O	65/35	7.5
DMSO	100	3.5

Effect of Water/ Ethanol Mixture Composition On Grafting Yield

As mentioned above, the graft copolymerization of (AAc/Sty) binary monomers mixture, onto PVA films is enhanced in the presence of ethanol/water-mixture as a good diluent for this binary monomers system. The content of water in the solvent mixture is limited depending on the styrene content in the comonomer composition due to its insolubility in water. Therefore, the optimum composition of water/ethanol mixture in the binary monomers, at which the grafting process proceeds successfully is determined and shown in Figs. (1) and (2) for 1/1 and 2/1 (mole/mole) comonomer compositions of (AAc/Sty), respectively. It can be seen that there is a critical amount of water, at which the maximum grafting yield is occurred. The degree of grafting increases as the water content increases to reach its maximum value at water/ethanol composition of (10/90 mole %) and (20/80 mole %) for AAc/Sty compositions of 1/1 and 2/1 (mole/mole), respectively. Thereafter, it gradually decreases as the water content increases in the solvent-mixture. Under such solvent-mixtures, the grafted films were easily removed and extracted from the reaction medium and seem to be smooth, flat and possessed homogeneous grafting.

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 comonomer composition, the higher the water content required for obtaining high degrees of the grafting. This is quit reasonable because AAc is a water-soluble monomer, but Sty is insoluble in water. It seems that in the presence of water, the packing of PVA polymer is loosened through swelling action of water permitting easily penetration of AAc/Sty comonomer that resulted in the enhancement of grafting. Water as a diluent has zero chain transfer constant, therefore, the side reaction involves chain transfer is minimal in water. All these factors combined together made addition of water very important for grafting of AAc/Sty onto PVA.

Results showed also that at optimum condition, the radiolytic fragments of water may activate PVA by abstracting the tertiary hydrogen atom in the following manner:



However, at high water content beyond optimum, radiolysis of additional water produces a number of radical species, which mutually inhibit the growing of grafted chains leading to decrease in percent grafting. Meanwhile, in presence of pure ethanol, various chain transfer and hydrogen abstraction reactions are accelerated resulted in decreasing the grafting yield of such binary monomers mixture onto PVA films.

Effect of Comonomer Concentration

Since the suitable monomer concentration varies from one system to another depending on the polymer substrate, solvent, total dose, comonomer composition,etc. The influence of monomer concentration on the grafting process of AAc/Sty grafting system has been investigated and shown in Fig.(3) using water-ethanol-mixture (20:80) as a diluent. It can be seen that, the degree of grafting increases with comonomer concentration, i.e. 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 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 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 the increased extent of chain propagation resulting in a greater degree of graft add on.

Effect of Commoner Composition

Some attention on enhancing the 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 is investigated at overall commoner concentration of 20 wt. in ethanol / H₂O mixture as diluent and shown in Fig.(4). It is clear that the grafting yield increases with increasing styrene content in the comonomer mixture to reach a maximum percent grafting at (AAc/Sty) of composition (55/45 mole/mole). Thereafter, it decreases with increasing the styrene content. It is also seen that the percent grafting for comonomer mixture is higher than that obtained for the individual grafting of Sty or AAc alone. i.e; there is a synergistic effect in the grafting process of AAc/Sty binary mixture onto PVA film. The presence of Sty and AAc enhanced the extent of grafting for both monomers onto PVA.

Results suggested that the styrene is a retarding agent by dissipation of the radiation energy forming a stable exciting state that prevents the free radical formation responsible for the initiation of grafting sites. Therefore, the feed solution containing excess of styrene hinders the grafting yield of the comonomer onto polymeric substrate. However, AAc has a higher G(R[•])-Value than that of styrene⁽¹⁸⁾. This resulted in homopolymer formation, which also retard the grafting process. The presence of styrene in feed solution containing AAc prevents the later to homopolymerize, however the later activated the styrene units to graft with onto PVA substrate. This resulted in obtaining higher degree of grafting if compared with that obtained for individual grafting of acrylic acid and styrene. Again synergistic effect can be attributed to the great amount of complex mobility of AAc/Sty in feed solution which retarding the rate of homopolymerization due to the retarding effect of styrene units. When one monomer molecule diffuses inside the film structure, it automatically carried 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.

Separation of Ni⁺² from Solution that Containing Co⁺²

It is well known that it is not so easy to separate Co⁺² from Ni⁺² metal from their feed solutions because Co⁺² and Ni⁺² has the same atomic weight and atomic radii and also they having the same valence. Therefore, a trial has been made to separate the two metals from their solution by using dialysis cell containing PVA-g-P(AAc/Sty) membranes.

Fig. (5) shows the transportation process of Ni⁺² and Co⁺² through PVA grafted membrane. It can be seen that, under such experimental conditions, Ni⁺² only is transported via the membrane and moved into the received solution. However, Co⁺² is not transported but it 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 received solution is occurred after ~20 min.

Results suggested that the PVA-g-P(AAc/Sty) membrane is selective towards the chelation of Co^{+2} and allow to permit Ni^{+2} to transport through membrane to reach the received solution. This means that the Co^{+2} has high ability to complex with -COOH and -OH groups of grafted membranes rather than Ni^{+2} . The induction period may be attributed to that the Ni^{+2} and Co^{+2} at the beginning of the transportation process chelate with functional groups of membranes. After short time, the unstable Ni^{+2} complex replaced by stable Co^{+2} one, resulting in transporting of Ni^{+2} into the received solution.

Effect of Degree of Grafting

Fig. (6) shows the effect of grafting yield on the transportation process of Co^{+2} and Ni^{+2} through PVA-g-P(AAc/Sty) membrane. It is obvious that the concentration of transported Ni^{+2} ions increases with time and it gives a curvature relationship at longer time above ~60min. This behavior is observed for all membranes that having different degrees of grafting. However, the rate and concentration of transported Ni^{+2} increases as the degree of grafting decreases. Meanwhile, the Co^{+2} does not transported but it is chelated by the membrane.

Results suggested that at higher grafting yield the content of crosslinked network structure is greater than that at lower grafting yield, which restricts the diffusion of metal through such network structure. Also the content of hydrophobic of grafted polystyrene increases as the grafting yield increases. As a consequence, the diffusion of water through membrane decreased resulting in retarding the diffusion of Ni^{+2} through the membrane. Therefore, at higher grafting yield, the rate and the amount of transported Ni^{+2} metal decreased and a much longer time is needed for its transportation.

Effect of pH

Fig. (7) represents the transportation of Ni through the membrane at different pH's of feed or received solutions. It can be seen that the change in pH for received or feed solution resulted in non-remarkable change in the amount of Ni transported throughout PVA-g-P(AAc/Sty) membrane. This means that the change in pH in such system does not affect the transportation of Ni or enhance the transportation of Co.

Effect of Ni Concentration on Its Transportation Throughout Membrane

It is expected that the transportation of metal ions throughout the membrane is affected by the concentration of metal in its feed solution. Fig. (8) shows that as the Ni^{+2} concentration increases in the feed solution, the amount and rate of transported Ni^{+2} increases in the received compartment.

Results suggested that the reduction of Ni^{+2} amount in feed solution does not affect its transportation through membranes. Also, the transportation of Co^{+2} is not enhanced by reducing the amount of Ni^{+2} in feed solution.

CONCLUSION

PVA membranes were modified by radiation-induced graft copolymerization of acrylic acid/styrene (AAc/Sty) binary monomers system. The insolubility of PVA is achieved beside the introduction of reactive groups capable for separation processes. The optimum conditions at which such grafting reactions can give more economical grafts were determined. Separation of Ni from solution that containing cobalt was also studied. Nickel only is transported via the grafted membranes and moved into the received one. The rate and concentration of transported nickel increases as the degree of grafting decreases. Also, the change in pH for received or feed solution did not affect into the amount of nickel transported throughout the membrane. Reducing the amount of nickel in feed

solution does not enhance the transportation of cobalt. Cobalt is not transported but it is expected to be chelated with the membrane functional groups. The prepared PVA-g-P(AAc/Sty) membranes showed a great promise in the practical use in the field of metal separation processes.

REFERENCES

1. E.A. Hegazy, H.A. Abd El-Rehim, N.A. Khalifa, and A. El-Hag Ali, IAEA-SM-50, Presented at international symposium on Radiation Technology, Zakopane, Poland, 8-12 Sept. (1997).
2. E.A. Hegazy, H.A. Abd El-Rehim, N.A. Khalifa, S.M. Atwa, H.A. Shawky, *Polymer International*, 42, 321, (1997).
3. W. Lin, and Y. Hsieh, *J. Polym. Sci., Part (A): Polym. Chem.*, 35, 631, (1997).
4. D. Poore, R. Benson, and D. Matin, *J. Environ. Sci. Health*, A31(9), 2167, (1996).
5. G.C. Pizarro, O. G. Marambio, B.L. Rivas, and K.E. Geckeller, *J. Macromol. Sci., Pure Appl. Chem.*, 34(8), 1983, (1997).
6. F.T. Burczak, and Y. Ikada, *Proc. Japan. Academy. Series (B).*, 75(5), 83 (1991).
7. V. Shantora, and R.y.M. Huang, *J. Appl. Polym. Sci.*, 26, 3223 (1981).
8. K. Koyama, T. Nishi, and M. Nishimura, *J. Appl. Polym. Sci.*, 27, 2845 (1982).
9. S. Peter, and R. Stefan, *Pro. Int. Symp. Fresh Water from the Sea.*, Vol. 2, E. Delyannis, Athens., 197, (1980).
10. M.G. Katz, and T. Wydeven, *J. Appl. Polym. Sci.*, 27, 79 (1982).
11. S. Peter N. Hese, and R. Stefan, *Desalination.*, 16, 161 (1976).
12. M.G. Katz, and T. Wydeven, *J. Appl. Polym. Sci.*, 26, 2935 (1981).
13. H.A. Abd El-Rehim, A.M. Ali, H.G. Nowier, E.A. Hegazy, H.F. Aly., *Proceedings of the Sixth Conference Nuclear Sciences and Applications*, V.3, 227, Cairo, Egypt (15-20 March 1996).
14. E.A. Hegazy, N.H. Taher, and A.R. Ebaid, *J. Appl. Polym. Sci.*, 41, 2637 (1990).
15. E.A. Hegazy, H.A. Abd El-Rehim, N.A. Khalifa, and A. El-Hag Ali, *J. Radiat. Phys. Chem.* In press
16. W.Z. Nielsh, *Anal. Chem.*, 140, 267, (1953)
17. P.W. West, and C.G. Vries, *Anal. Chem.*, 23, 334, (1951).
18. A. Chapiro, *Radiation Chemistry of Polymeric System*, Wiley Interscience, New york (1962).

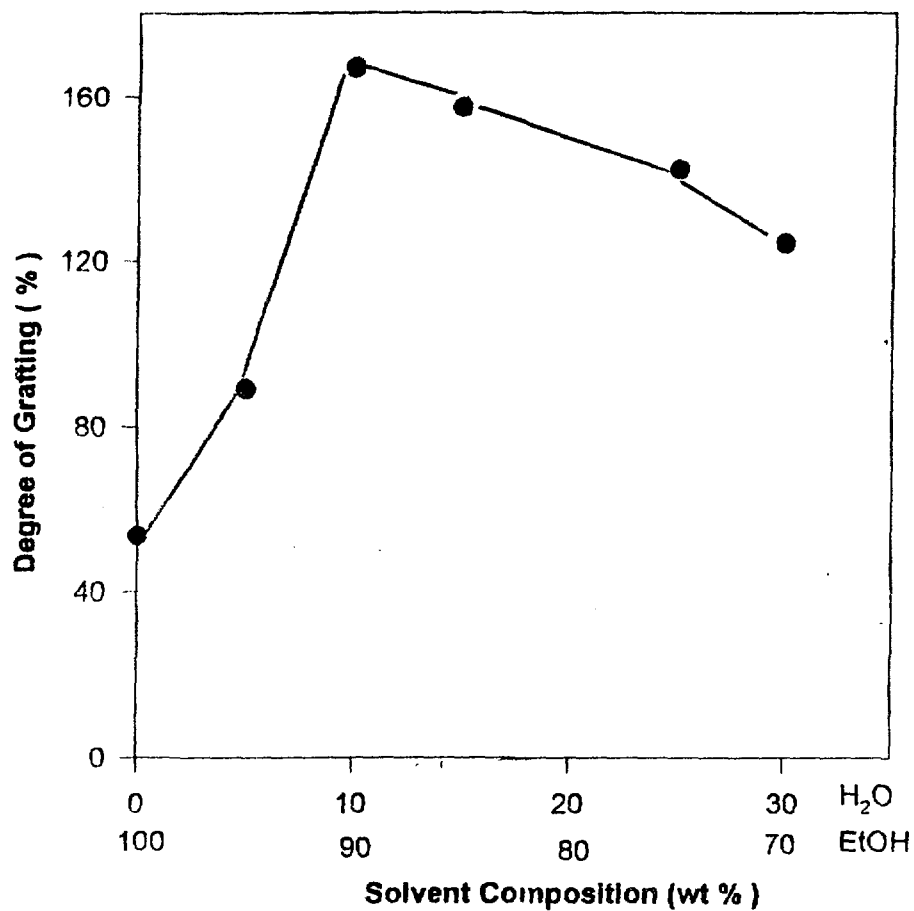


Fig. (1): Effect of solvent composition on the grafting of (AAc/Sty) monomers of composition (1/1 mole/mole) onto PVA films. Comonomer concentration; 20 wt% and irradiation dose; 5 kGy.

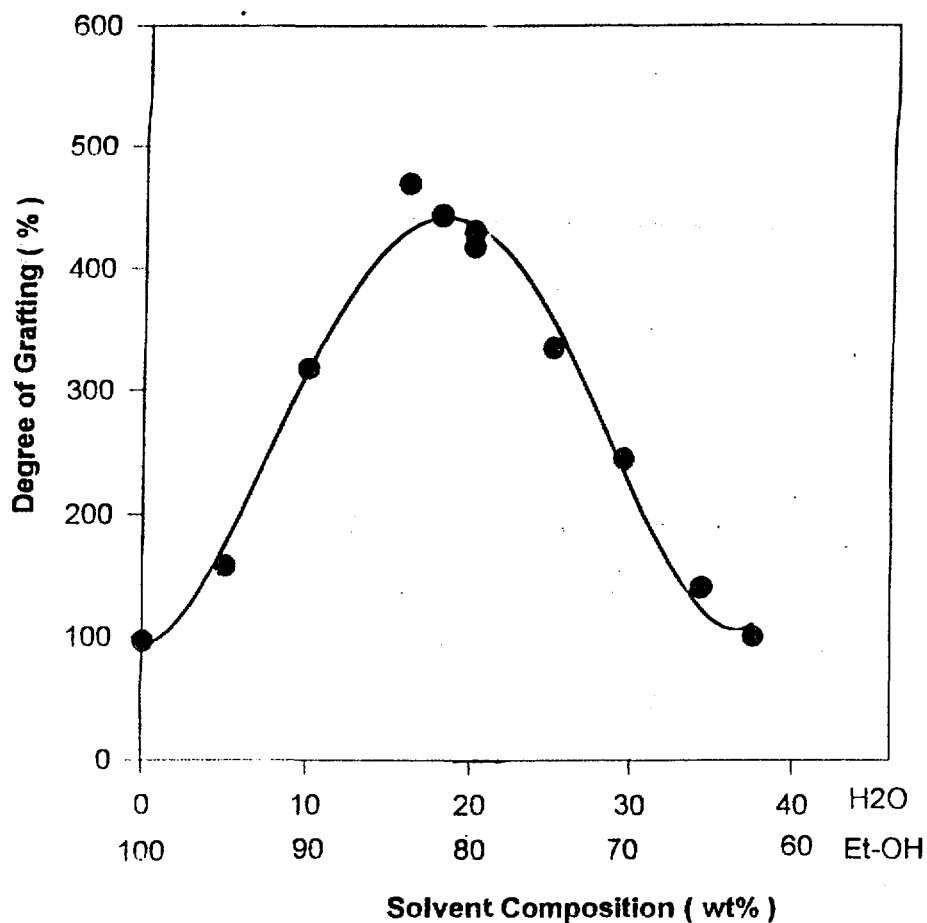


Fig. (2): Effect of solvent composition on the grafting of (AAc/Sty) binary monomers of composition (2/1 mole/mole) onto PVA films. Comonomer concentration; 20 wt% and irradiation dose; 10 kGy.

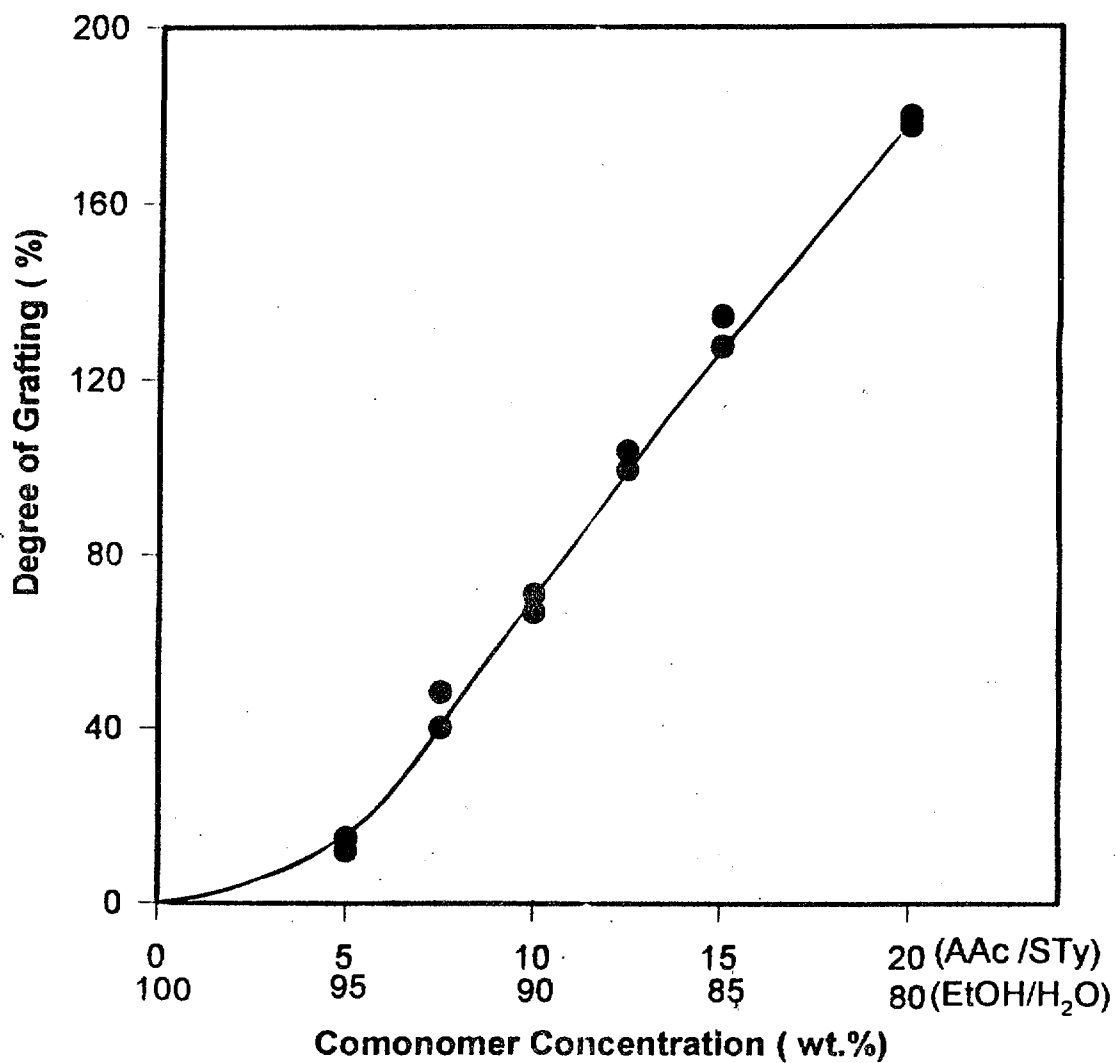


Fig. (3): Effect of (AAc/Sty) concentration of composition (2/1 mole/mole) on the grafting yield onto PVA films. EtOH/H₂O-mixture composition; (75/25 wt.%) and irradiation dose; 5 kGy.

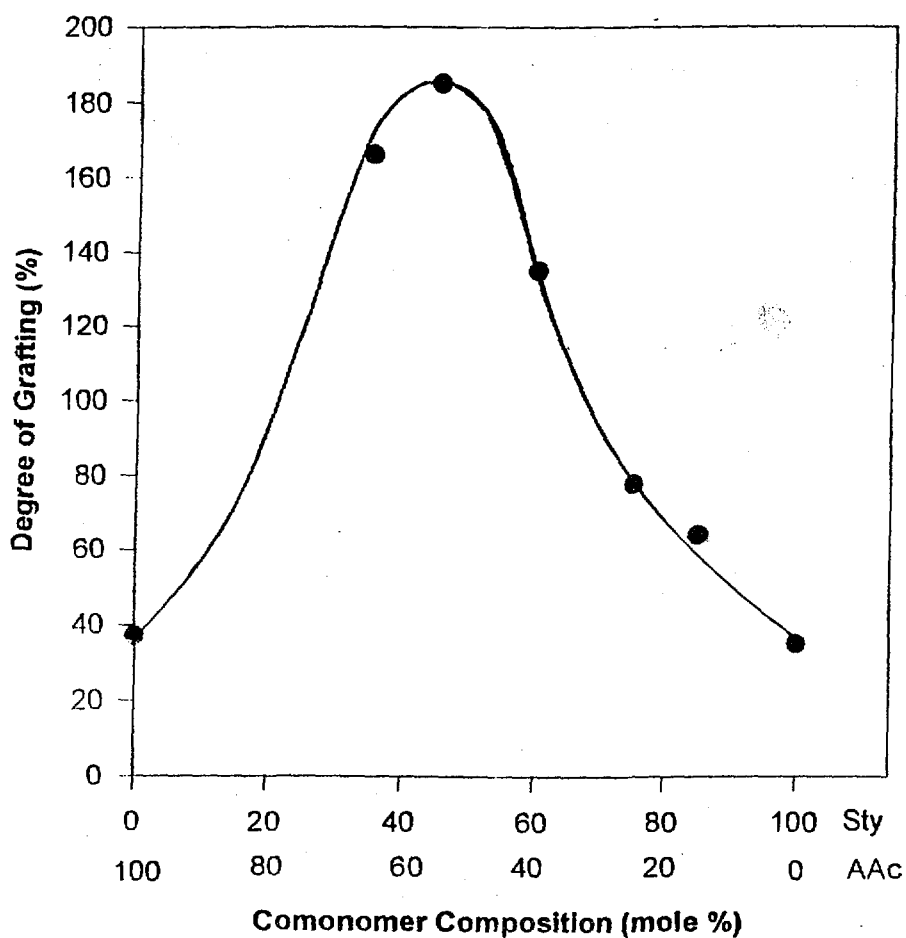


Fig. (4): Effect of AAc/Sty comonomer composition on the grafting yield onto PVA films. Comonomer concentration; 20wt%, EtOH/H₂O-mixture; (75/25 wt.%) and irradiation dose; 5 kGy.

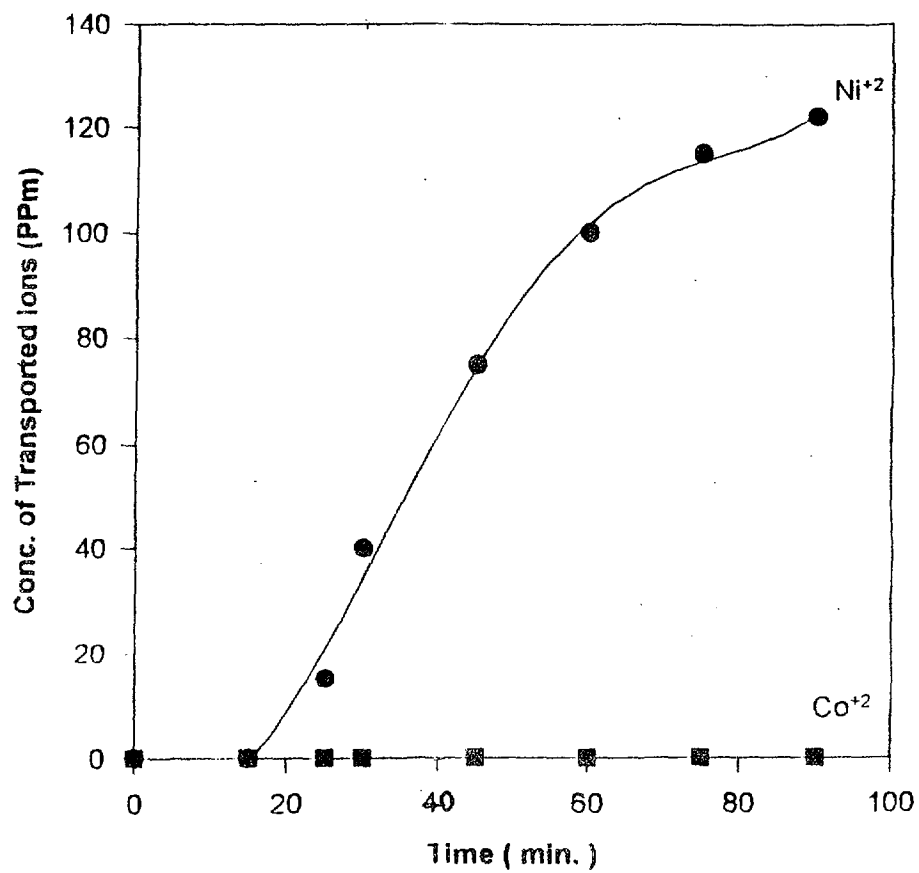


Fig. (5): Transportation of Ni^{+2} from solution containing Co^{+2} through PVA-g-P(AAc/Sty) membrane having degree of grafting 79%. PH (feed solution/ received solution) = (5.40/ 6.70). Ni/Co Composition (1/1 PPM/PPm).

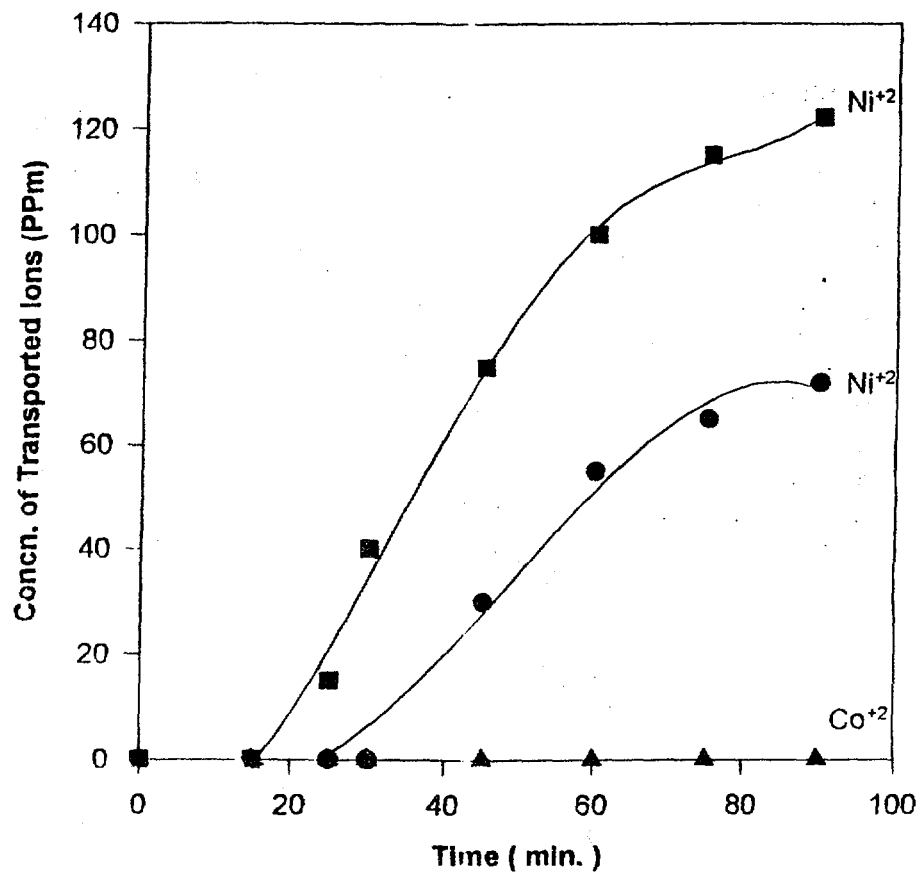


Fig. (6): Effect of grafting yield on separation process of Ni²⁺ from Co²⁺ through PVA-g-P(AAc/Sty) membranes. Degree of grafting (%): (■) 79 and (●) 100. Ni/Co composition (1/1) (PPm/PPm) PH of (feed solution/ received solution) = (5.4/6.7)

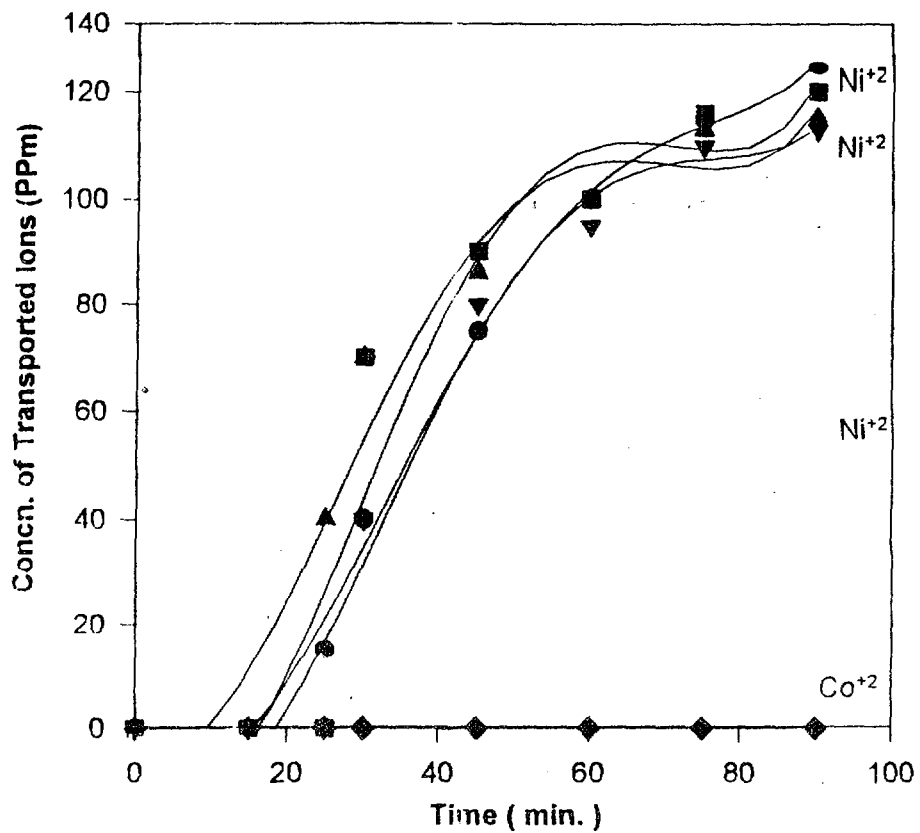


Fig. (7): Effect of pH change on transportation process of Ni^{+2} or Co^{+2} through PVA-g-P(AAc/Sty) membrane having degree of grafting 79%. PH of (feed solution/ received solution); ($\blacktriangle, \blacktriangle$) 2.29/ 6.70, (\blacklozenge, \bullet) 5.40/6.70, ($\blacklozenge, \blacktriangledown$), 5.95/2.20 and ($\blacklozenge, \blacksquare$) 8.50/6.70. Ni/Co composition (1/1) (PPm/PPm).

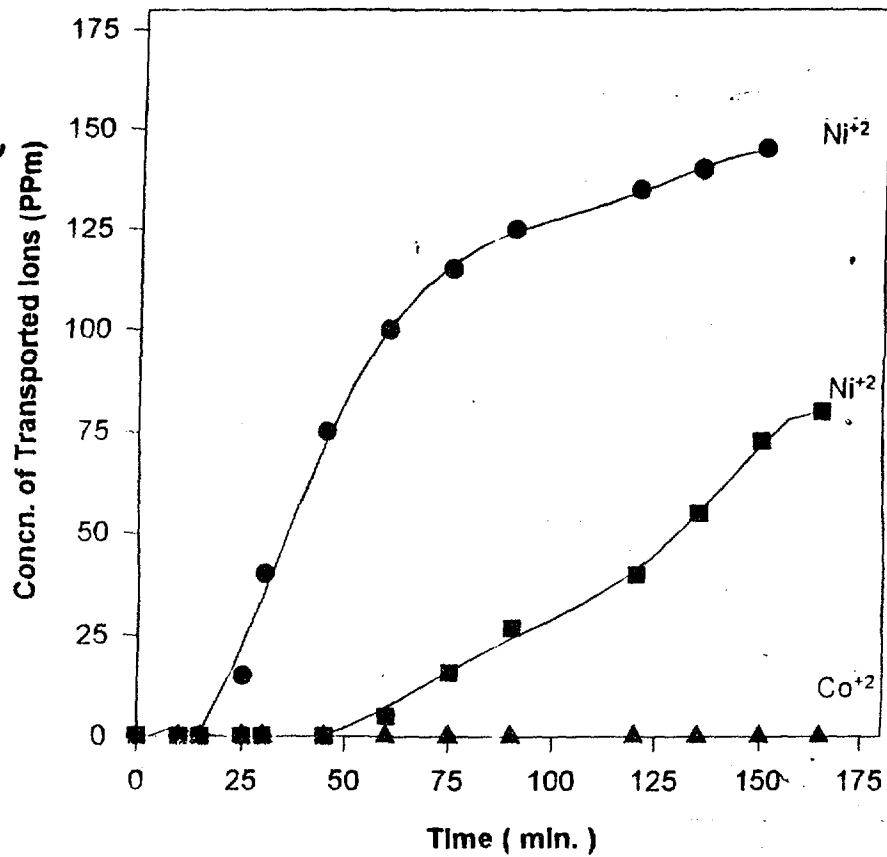


Fig (8): Effect of Ni concentration on the transportation process through PVA-g-P(AAc/Sty) membrane having degree of grafting 79%, at different Ni/Co compositions; (● , 1/1) and (■ , 1/4) (PPm/PPm). PH of (feed solution/received solution) = (5.40/ 6.7)