

《Original》

Preparation of Permselective Membrane by Means of a Radiation-Induced Grafting

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방사선 그래프트에 의한 반투막 제조연구

공영근 · 장훈선 · *이종광 · **최재호

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Abstract

By controlling both the means of grafting and the cast-solution components, no degradation and dimensional change of radiation-induced graft polymerization were found.

The electric resistance of styrene-cellulose acetate grafts increases with increasing styrene content, while those for the hydrophilic monomers show no marked effect.

In comparison with the grafted cellulose acetate membrane by simultaneous irradiation method, the appearance of the grafted membrane by post-polymerization method was not markedly changed irrespective of the percent of grafting and radiation dose of electron beam or γ -ray.

The combination of crosslinking agents such as divinyl benzene (DB) or trimethyl propane triacrylate (TMPT) in the VP:St:BPO system leads to gradual increase of the percent of grafting.

The activation energy for grafting of St:VP:BPO solution onto cellulose acetate membrane was determined to be about 21.8 Kcal/mole over the range of 55°-80°C. The initial rate of grafting (in %/hr) is proportional to the power 0.76 for dose intensities.

요 약

Grafting과 주형용액 성분의 조절에 의한 붕괴반응과 방사선에 의한 graft 중합의 공간적 변화는 발견되지 않았다. 스티렌-셀룰로즈 아세테이트 grafts의 내전성능은 스티렌 함량이 증가할수록 증가한 반면 친수성 단량체에 관한 grafts는 확실한 효과를 나타내지 않았다.

동시 조사법에 의해 graft된 셀룰로즈 아세테이트막과 비교해 보면 전조사법에 의해 graft된 막은 γ 선 또는 전자선의 방사선선량과 graft %에 관계없이 거의 변하지 않았다.

VP:St: BPO 시스템내 디비닐벤젠 (DB) 또는 트리메틸프로판트리아크레이트(TMPT) 같은 가교제의 혼합으로 점차 graft %는 증가되었다. 셀룰로즈 아세테이트막에 대한 St:VP:BPO 용액의 grafting에 관한 활성화 에너지는 55°-80°C에서 약 21.8Kcal/mole이었다. Grafting의 초기속도 (%/hr)는 선량강도의 0.76 승에 비례하였다.

1. Introduction

Graft copolymerization¹⁻⁵⁾ is an attractive means for modifying base polymers, because grafting results frequently in the superposition of properties relating to backbone and pendant chains, and is of particular interest for the synthesis of mechanically stabilized cellulose acetate membranes. Radiation grafting is one of the most promising methods because of large transmittance of ionizing radiation into substrate polymer, readily creating active sites for initiation of grafting.

Membranes formed from secondary cellulose acetate have been the most successful for the reverse osmosis method of water desalination. However, the pressures used for seawater desalination (about 1500 psi) lead to the gradual compaction of the expanded Loeb type membrane structures⁶⁾ with a consequent decrease of the product flux rate and apparent salt rejection. The effects of styrene or styrene-mixture grafting to cellulose acetate were studied as a possible technique for mechanically stabilizing cellulose acetate membrane.

Hydrophobic monomers such as 4-vinyl pyridine or styrene were chosen because of their inherently low creep and insensitivity to water. By controlling the monomer composition, total dose and dose rate, considerably predictable grafts were prepared.

Most works were done by irradiation of the intense electron beams, while partly Co-60 Gamma irradiated results were also prepared for comparison.

2. Experimental

2-1. Materials

Reagent grade acrylic acid, 4-vinyl pyridine (VP) and divinyl benzene were purified by

vacuum distillation.^{7,8)} Traces of impurities left in commercial styrene monomer (St) such as alkyl benzenes and peroxides were removed by vacuum distillation in stream of nitrogen before use.⁹⁾

Benzoyl peroxide (BPO) was dissolved in chloroform and then precipitated with excess methanol.

Reagent grade acrylamide was used without post treatment. Pyridine, acetone, benzene, hydrochloric acid, TMPT and magnesium perchlorate were GR grade and were not purified.

2-2. Irradiation

Irradiation was done by electron beams from electron accelerator (300KeV, 25mA) located at the Korea Advanced Energy Research Institute.

Dose rate of electron beams was in the range of 1.6-10 Mrad/sec. and radiation dose was measured with CTA (Cellulose Triacetate) film as standard.

Also, irradiation was carried out at room temperature at dose rate of 2.42×10^5 rad/hr in Gammacell Co-60 source.

Chemical dosimetry utilizing the oxidation of ferrous sulfate was used as the method of measurement of radiation intensity of 10,000 Ci-Gamma irradiation facility.

2-3. Preparation of Sample

Cellulose acetate membranes (100 μ m thickness) prepared by Millipore Intertech Inc. (MF-Millipore, AAO) were used as received.

Other membranes were prepared by casting an acetone solution of cellulose acetate chips on glass. Membranes were fabricated for synthesizing cellulose acetate membranes with improved resistance to compact according to techniques described in recent years.^{10,11)} However, the radiation dose used for preirradiation leads to gradual acid-evolution of added hydrochloric acid-components with a consequent degradation and dimensional change of the graft membrane.

And so the method described by Loeb and Manjikian¹⁰⁾ was modified by controlling the

casting-solution components. The newly adapted components of casting solution were as follows:

Components	% by Wt.
Cellulose acetate	24.0
Acetone	69.0
Water	6.0
Magnesium perchlorate	1.0

2-4. Graft Copolymerization

Membranes prepared by Millipore Intertech Inc. were immersed in a styrene-solvent mixture, an acrylic acid-solvent mixture or an acrylamide-solvent mixture at 25°C for an hour. After swelling, the membranes were wiped with filter paper to remove excess monomer solution on the surface of the membrane. The impregnated membranes were placed in vinyl bags (0.05mm thickness), followed with nitrogen stream (5 cm³/sec) and then sealed. The samples were irradiated with electron beams in nitrogen. In the case of the irradiation of γ -rays, casted cellulose acetate membranes were immersed in a monomer mixture and then were irradiated with γ -rays in nitrogen.

After irradiation, acrylic acid and acrylamide-graft copolymers were immersed in warm water at 30-40°C for 4-5 hrs and dried in a vacuum oven at 30°C.

Homopolystyrene was removed from styrene-graft copolymers by washing with benzene.

The homogeneous grafting of cellulose acetate membranes was carried out by post-polymerization¹²⁾ of electron beam-irradiated membrane which was cocatalyzed with radical initiator (BPO). The membranes were irradiated in air to promote the formation of active peroxide groups.

The irradiated membranes were grafted at temperature range between 55° and 80°C, especially at 60°C with diluted monomer mixtures. After polymerization, homopolymers formed on the surface of cellulose acetate membrane were

extracted from graft copolymers by washing with benzene. The percent of graft was calculated from the increase in weight after irradiation, extraction and drying.

2-5. Water Absorption

After immersion of membranes in distilled water for more than 24 hrs at room temp., the weight fraction of water in the membrane was determined by weighing samples of the wet membranes wiped with filter paper to remove excess water on the surface of the membrane.

$$\text{Water absorption \%} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

2-6. Tensile Strength

To examine tensile properties, the sample membranes were cut into strips of 2cm × 8cm. Tensile strength was measured with an Instron using 100 mm/min. rate of cross head speed.

2-7. Electric Resistance¹³⁾

The grafted membrane was immersed in 0.5 N NaCl solution for an hour prior to the measurement of electric resistance. The membrane, swollen with 0.5 N NaCl solution, was cut into a disk and mounted between the platinum electrodes in the electrolytic cell.

The overall electric resistance between the electrodes was measured at 25°C using a 3476B digital multimeter.

3. Results and Discussion

3-1. Grafting of Monomer Mixture by Impregnation Method^{14,15)}

The yield of grafting to cellulose acetate is shown as a function of the total dose for the 90:10 styrene-pyridine, 20:80 acrylic acid-water and 10:30 acrylamide-water solution in Tables 1, 2 and 3, respectively. In all cases grafting yield increases with radiation dose, but as expected, grafting yield of styrene is less than that of hydrophilic acrylic acid and acrylamide. In spite of the same conditions of sample pre-

Table 1. Grafting of Styrene onto Cellulose Acetate Membrane* by Impregnation Method.

Impregnation: 25°C, 1hr; styrene-pyridine (90:10; by Vol.) solution.

Irradiation: Electron beams

Dose rate 3.02×10^6 rad/sec.

Sample No.	Total dose (rad)	Graft yield (%)	Water absorption (%)	Electric resistance (M Ω cm)
Orig.	0	0	255	0.016
1	0.5×10^6	0.8	192	1.05
2	1.0×10^6	2.1	119	6.4
3	2.0×10^6	3.9	74	7.09
4	4.0×10^6	6.3	69	12.2
5	6.0×10^6	8.4	64	20

*Cellulose acetate membrane: Prepared by Millipore Intertech Inc., MF-Millipore (AA) with 100 μ m thickness.

Table 2. Grafting of Acrylic Acid onto Cellulose Acetate Membrane* by Impregnation Method.

Impregnation: 25°C, 24hr; acrylic acid-H₂O (20: 80, by Vol.) solution containing Mohr's salt (3×10^{-3} mole/l).

Irradiation: Electron beams.

Dose rate: 3.02×10^6 rad/sec.

Sample No.	Total dose (rad)	Graft yield (%)	Water absorption (%)	Electric resistance (Ω -cm) $\times 10^{-6}$
Orig.	0	0	255	0.016
1	0.5×10^6	2.2	265	0.26
2	1.0×10^6	6.0	288	0.79
3	2.0×10^6	18.6	274	0.85
4	4.0×10^6	32.5	253	0.86
5	6.0×10^6	34.0	239	0.97

*Cellulose acetate membrane: Prepared by Millipore Intertech Inc., MF-Millipore (AA) with 100 μ m thickness

paration in Tables 1 and 4, there is a remarkable difference in grafting yield. This may be caused mainly by the different diffusion controlled monomer concentration available in the active sites at the different time of irradiation and dose rate.

The water absorption of the grafted membranes are also shown in Tables 1, 2, 3 and 4.

Table 3. Grafting of Acrylamide onto Cellulose Acetate Membrane* by Impregnation Method.

Impregnation: 25°C, 24hr; acrylamide-H₂O (10:30, by wt.) solution.

Irradiation: Electron beams.

Dose rate: 3.02×10^6 rad/hr.

Sample No.	Total dose (rad)	Graft yield (%)	Water absorption (%)	Electric resistance (Ω -cm) $\times 10^{-6}$
Orig.	0.5×10^6	0	255	0.016
1	0.5×10^6	0.9	266	0.014
2	1.0×10^6	2.8	274	0.018
3	2.0×10^6	13.6	270	0.017
4	4.0×10^6	31.0	261	0.018
5	6.0×10^6	75.0	186	0.099

*Cellulose acetate membrane: Prepared by Millipore Intertech Inc., MF-Millipore (AA) with 100 μ m thickness.

The water absorption was found to decrease with an increasing percent in grafting styrene, while it seems to have a maximum water absorption 288% and 274% for acrylic acid and acrylamide, respectively.

Each Table shows the relationship between the electric resistance and the percent of grafting of the membranes obtained at different monomer selection. For styrene it increases rapidly with grafting percent while those for the hydrophilic monomers show not significant effect.

The tensile strength data of styrene-cellulose acetate graft are presented in Table 4. It clearly shows that the tensile strength is increased with increasing grafting and suggests that styrene may be an effective monomer to improve the compaction resistance of cellulose acetate membranes.

3-2 Effect of Catalyst

To investigate the effect of catalyst on the grafting the monomer mixture (4-vinyl pyridine-styrene) onto cellulose acetate membrane, a mixture of 4-vinyl pyridine (VP)—styrene (St)—benzoyl peroxide (BPO) was used.

In this case, radiation grafting of VP-St so-

Table 4. Grafting of Styrene onto Cellulose Acetate Membrane* Impregnated with a Mixture of Styrene-pyridine (90:10, by Vol.)Irradiation: Co-60 γ -rays. Dose rate: 2.42×10^5 rad/hr

Sample No.	Total dose (rad)	Graft yield (%)	Water absorption (%)	Electric resistance (Ω -cm) $\times 10^{-6}$	Tensile strength (g/cm ²)
Orig.	0	0	10.7	1.06	1,180
1	0.5×10^6	3.3	6.0	6.9	1,210
2	1.0×10^6	6.4	2.7	13.2	1,230
3	2.0×10^6	16.7	9.2	20	1,290
4	4.0×10^6	25.2	1.7	20	1,320
5	6.0×10^6	34.4	4.8	20	1,400

*Cellulose acetate membrane: Prepared by casting an acetone solution of the cellulose acetate chips on glass.

Table 5. Grafting of Monomer Mixture onto Cellulose Acetate Membrane Prepared by Casting Technique.

Impregnation: 25°C, 30 min.; VP-St solution.

Irradiation: Electron beams.

Dose rate: 3.02×10^6 rad/sec.

Sample No.	Total dose (rad)	Monomer composition VP: St (by Vol.)	Graft (%)
1	4×10^6	1 : 99	0.2
2	4×10^6	2.5 : 97.5	0.4
3	4×10^6	5 : 95	0.7
4	4×10^6	10 : 90	1.2
5	4×10^6	15 : 85	2.3
6	4×10^6	20 : 80	4.5
7	4×10^6	30 : 70	5.7

lution or VP-St-BPO (0.02%, by wt.) solution onto cellulose acetate membrane was carried out with an impregnation method using electron beams from an electron accelerator.

The effect of catalyst on grafting of two VP-St solution systems onto cellulose acetate membrane is shown in Table 5 and 6.

Table 5 shows that in the absence of catalyst the percent of grafting was increased with the concentration in the mixture of VP-St.

It is seen from Table 5 that VP plays a role as an effective swelling agent rather than comonomer in this system.

It is supposed that the swelling of cellulose acetate membrane is caused mainly by sorption of VP, and consequently the amorphous regions loosen and become accessible to monomer and result in increased grafting yields.

When benzoyl peroxide as a catalyst was added in the monomer mixture, the grafting percent at a given radiation dose was increased considerably as shown in Table 6.

Table 6. Effect of Catalyst on Grafting of Monomer Mixture onto Cellulose Acetate Membrane Prepared by Casting Technique.

Impregnation: 25°C, 30min.; VP-St-BPO solution.

Irradiation: Electron beams Total dose: 4×10^6 rad

Sample No.	Monomer composition VP(ml):St(ml):BPO(wt. %)	Graft (%)	Water absorption (%)	Electric resistance (Ω -cm) $\times 10^{-6}$
1	1 : 99 : 0.02	0.4	9.7	2.3
2	2.5 : 97.5 : 0.02	1.2	8.5	8.7
3	5 : 95 : 0.02	2.8	6.9	15.2
4	10 : 90 : 0.02	5.2	5.4	>20
5	15 : 85 : 0.02	8.4	2.8	>20
6	20 : 80 : 0.02	11.3	4.1	>20
7	30 : 70 : 0.02	18.9	3.2	>20

It is thought that the dense radical sites are generated in base polymer (cellulose acetate membrane) by means of the radiation-induced degradation of catalyst and the graft copolymerization proceeds with monomers within the life time of radicals.

The water absorption of the grafted membrane was found to decrease with an increasing grafting percent for VP-St-BPO system.

The relationship between the electric resistance¹³⁾ and the grafting percent in VP-St-BPO solutions is also shown in Table 6.

The electric resistance is found to increase with the grafting % in Table 6. It suggests that VP and St monomer may be an effective comonomer for improving the compaction resistance of cellulose acetate membrane.

3-3. Effect of Radiation Dose

The effect of radiation dose on grafting of VP-St mixture with impregnating solution containing 0.02% BPO as catalyst is shown in Table 7. It is shown from Table 7 that the percent grafting was increased with increasing radiation dose.

It can be said that an effective way of increasing the graft yield is also to irradiate the reaction system with electron beams in the range of the nondegradation of cellulose acetate sub-

Table 7. Effect of Radiation Dose on Grafting of Monomer Mixture onto Cellulose acetate Membrane Prepared by Casting Technique.

Impregnation: 25°C, 30 min.; VP-St-BPO solution.

Irradiation: Electron beams

Dose rate: 3.02×10^6 rad/sec.

Sample No.	Radiation dose (rad)	Monomer composition VP(ml):St(ml):BPO (wt. %)	Graft (%)
1	0.5×10^6	10 : 90 : 0.02	1.4
2	1.0×10^6	10 : 90 : 0.02	2.2
3	2.0×10^6	10 : 90 : 0.02	3.6
4	4.0×10^6	10 : 90 : 0.02	6.2
5	6.0×10^6	10 : 90 : 0.02	8.5
6	8.0×10^6	10 : 90 : 0.02	11.9

strate.

3-4. Effect of Crosslinking Agent

Crosslinking was obtained by adding the crosslinking agent such as divinyl benzene to the monomer mixture.

It is shown in Table 8 that although the grafting yield was not high, the yield was increased with divinyl benzene concentration in a constant composition of VP-St solution.

This is attributed to the effect of crosslinking in grafted zone, since the grafting on cellulose acetate membrane begins at the surface and then proceeds progressively into the matrix by the diffusion of the monomer mixture through the grafted zone.¹⁶⁾

Table 8. Effect of Crosslinking Agent (divinyl benzene) on Grafting of Monomer Mixture onto Cellulose Acetate Membrane Prepared by Casting Technique.

Impregnation: 25°C, 30 min.; VP-St-divinyl benzene solution.

Irradiation: Electron beams

Dose rate: 3.02×10^6 rad/sec.

Sample No.	Total dose (rad)	Monomer composition VP:St:divinylbenzene:BPO (wt. %)	Graft (%)
1	4×10^6	10 : 80 : 2.5 : 0.02	2.5
2	4×10^6	10 : 80 : 5.0 : 0.02	4.6
3	4×10^6	10 : 80 : 10 : 0.02	5.6
4	4×10^6	10 : 80 : 15 : 0.02	6.8
5	4×10^6	10 : 80 : 17.5 : 0.02	8.2
6	4×10^6	10 : 80 : 20 : 0.02	9.1

3-5. Effect of Post-polymerization¹⁷⁾

To obtain the homogeneous grafting on the surface of cellulose acetate membranes, the grafting of a monomer mixture was carried out by post-polymerization of either γ -irradiated membrane (3.8×10^6 rad) or electron beams-irradiated membrane (4.0×10^6 rad).

In both cases, the membranes were irradiated in air to promote the formation of active peroxide groups. The γ -irradiated membranes and the electron beams-irradiated membranes (Table 9) were all grafted at 60°C with the mixture of VP-St-BPO (0.02%, by wt.).

Table 9. Grafting of Monomer Mixture onto Cellulose Acetate Membrane by Post-polymerization Method.Radiation dose: γ -rays (3.8×10^6 rad) and electron beams (4.0×10^6 rad)

Monomer mixture: VP-St-BPO solution

Reaction temp.: 60°C

Sample No.	Monomer composition VP(ml): St(ml):BPO (wt. %)	Post- polymerization time(min.)	Graft (%) by γ -ray	Graft (%) by electron beam
1	10 : 90 : 0.02	60	12.5	5.3
2	10 : 90 : 0.02	60	14.0	5.9
3	10 : 90 : 0.02	120	30.6	12.8
4	10 : 90 : 0.02	120	32.8	11.5
5	10 : 90 : 0.02	180	42.9	17.8
6	10 : 90 : 0.02	180	45.3	18.2
7	10 : 90 : 0.02	240	59.6	25.2
8	10 : 90 : 0.02	240	55.7	24.7

In comparison with the original membrane, the appearance of the grafted membrane was not markedly changed irrespective of the percent of grafting and radiation dose of γ -rays or electron beams. However, the grafted membrane by simultaneous irradiation method underwent dimensional changes upon grafting.

The newly adapted components of casting solution were as follows:

Components	%
Cellulose acetate	24
Acetone	69
Water	6.0
Magnesium perchlorate	1.0

3-6. Effects of Catalyst and Crosslinking Agents in Post-polymerization

To investigate the effects of catalyst and crosslinking agents on the grafting of the monomer mixture onto cellulose acetate membrane by post-polymerization, four kinds of monomer mixture composition were used.

The yields of graft copolymers are shown as function of polymerization time for VP:St, VP:St:BPO, VP:St:DB:BPO and VP:St:DB:TMPT:BPO systems in Table 10.

As can be seen from Table 10, polymerization was very much accelerated by the use of catalyst (BPO) and the graft reaction by post-polymerization is mainly controlled by the activation of catalyst with radicals formed in cellulose acetate membrane during irradiation.

In the case of the VP:St system in the absence of catalyst, the percent of grafting was only about 1.6% when the polymerization time is 60 min. With the VP:St:BPO system, however, the percent of grafting was increased to 14.6% for the same polymerization time.

The combination of crosslinking agent such as divinyl benzene(DB) or trimethyl propane triacrylate (TMPT) in the VP:St:BPO system leads to gradual increase of the percent of grafting.

It was found that all of the grafted cellulose

Table 10. Grafting of Monomer Mixtures onto Cellulose Acetate Membranes by Post-polymerization.

Radiation dose: Electron beams (2.4 Mrads)

Reaction temp.: 60°C

Monomer composition	Reaction time (min.)	Graft				
		Apparent graft, %				
		15	30	60	90	120
VP-St(10ml : 90ml)		0	0	1.6	2.4	4.2
VP-St-BPO(10ml:90ml:0.02g)		4.2	8.6	14.6	26.2	32.0
VP-St-DB-BPO(10ml:80ml:10ml:0.02g)		4.3	9.6	18.1	24.6	34.0
VP-St-DB-TMPT-BPO(10ml:79ml:10ml:1ml:0.02g)		5.6	10.4	22.5	32.1	45.7

acetate membranes didn't undergo dimensional changes upon grafting.

3-7. Effect of Radiation Dose in Post-polymerization

The effect of radiation dose on grafting of the VP:St:BPO system by post-polymerization is shown in Table 11. It can be seen that the percent of grafting was increased with increasing radiation dose and polymerization time.

In comparison with the grafted cellulose acetate membrane by impregnation method, the appearance of the grafted membrane by post-polymerization was not nearly changed irrespective of the percent of grafting and radiation dose of electron beam.

Table 11. Effect of Radiation Dose on Grafting of Monomer Mixture onto Cellulose Acetate Membrane by Post-polymerization.

Radiation: Electron beams
Dose rate: 3.8×10^6 rad/sec.
Monomer composition: VP-St-BPO(10ml:90ml:0.02g)
Reaction temp.: $60 \pm 0.1^\circ\text{C}$

Radiation dose	Graft				
	Apparent graft, %				
Rection time(min.)	15	30	60	90	120
1.2×10^6	2.3	6.6	12.2	18.7	22.9
2.4×10^6	4.7	8.2	14.6	26.4	34.0
4.8×10^6	6.2	10.4	19.5	34.8	54.2
9.6×10^6	12.8	25.5	42.3	63.7	90.8

It was also found that the percent of grafting was considerably higher than that obtained by simultaneous irradiation method.

3-8. Effect of Initiator Concentration in Post-polymerization

Table 12 shows the relationship between the concentration of catalyst and the grafting percent of the membrane obtained at constant dose rate. When benzoyl peroxide was added in monomer mixture, the percent of grafting at a given radiation dose was increased considerably as shown in Table 12.

It is thought that the combination of the

Table 12. Effect of Initiator Concentration on Grafting of Monomer Mixture onto Cellulose Acetate Membrane by Post-polymerization.

Radiation: Electron beams
Reaction time: 60 min.
Reaction temp.: $60 \pm 0.1^\circ\text{C}$

Radiation dose (rad)	Monomer composition VP(ml):St(ml):BPO(g)	Graft (%)
4.2×10^6	10 : 90 : 0	0
4.2×10^6	10 : 90 : 0.01	1.2
4.2×10^6	10 : 90 : 0.02	16.2
4.2×10^6	10 : 90 : 0.04	30.4
4.2×10^6	10 : 90 : 0.08	49.2
4.2×10^6	10 : 90 : 0.10	53.0
4.2×10^6	10 : 90 : 0.20	73.8

dense radical sites generated in the base polymer by means of preirradiation and the radicals generated on the surface of the base polymer by thermal-induced degradation of catalyst leads to acceleration of the grafting within the life time of radicals.

3-9. Activation Energy and Relationship between Grafting Rate and Dose Rate

The results of the temperature effect on grafting of monomer mixture onto cellulose acetate membrane by post-polymerization are shown in Fig. 1.

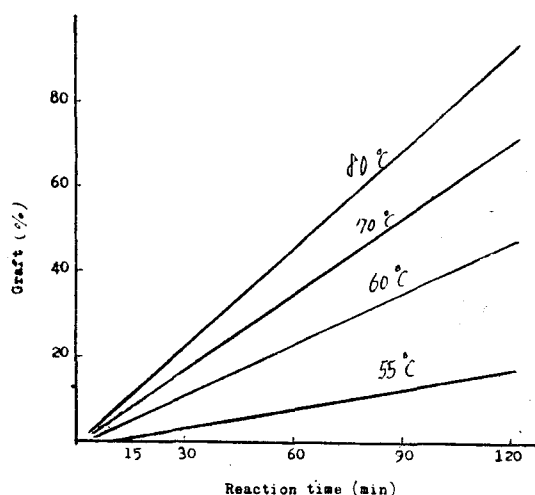


Fig. 1. Relationship of grafting time and graft % at various temp. by post-polymerization.

As shown in Fig. 1, the grafting percent of VP:St:BPO solution onto cellulose acetate membrane was significantly altered in the reaction temp. over the range of $55^{\circ}\sim 80^{\circ}\text{C}$.

Arrhenius plot of initial rate of grafting R_p (in %/hr), calculated on the basis of the least square method, versus temp. gives a straight line whose slope is a basis of determining the activation energy (Fig. 2). The activation energy for grafting of VP:St:BPO solution onto cellulose acetate membrane was determined to be about 21.8Kcal/mole over the range of $55^{\circ}\sim 80^{\circ}\text{C}$.

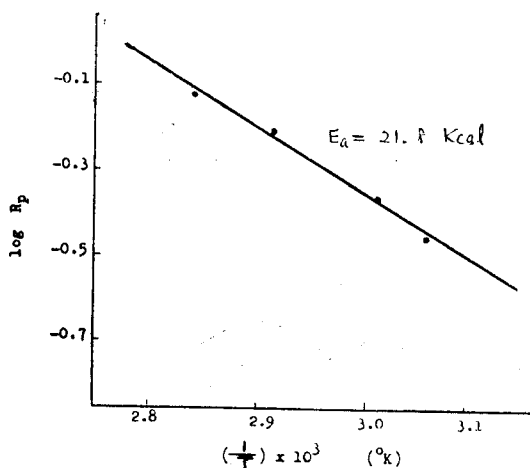


Fig. 2. Determination of Activation Energy (E_a) for the Grafting of VP-St-BPO Solution Onto Cellulose Acetate Membrane by Post-polymerization.

It is supposed from the result that the grafting time of monomer mixture depends upon the activation energy, the value in activation energy being lower the shorter the induction period.

The studies reported here involved the homogeneous grafting and the investigation of reasonable and reproducible conditions by newly adapted means of grafting on casting membrane with the least reduced dimensional changes.

The intensity dependence of grafting was investigated for the dose rate range, $8.7 \times 10^4 \sim 7.8 \times 10^5$ rad/hr. The results are shown in Figs. 3 and 4.

It is shown in Fig. 3 that the percent of

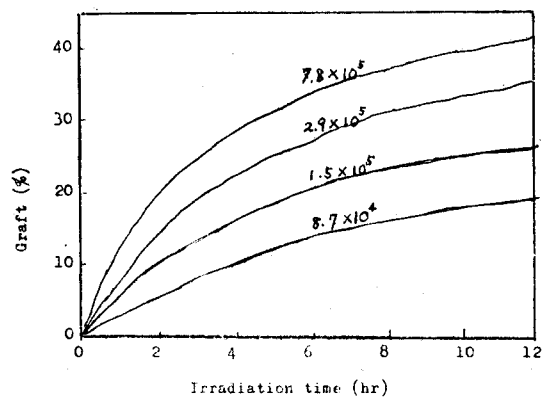


Fig. 3. Grafting of VP:St:BPO(10ml:90ml:0.04g) Mixture Onto Cellulose Acetate Membrane by Co-60 γ -ray.

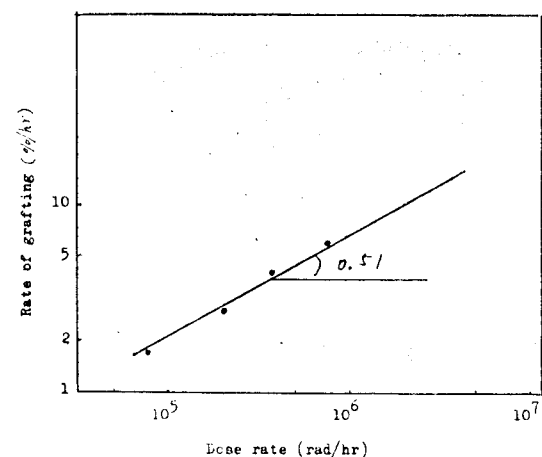


Fig. 4. Influence of Dose Rate on the Grafting of VP:St:BPO (10ml:90ml:0.04g) mixture Onto Cellulose Acetate Membrane by Co-60 γ -ray.

grafting is increased with increasing dose rate. The log-log plot of the initial rate versus intensity gives a straight line whose slope is the intensity exponent (Fig. 4). Fig. 4 gives intensity exponent value to be 0.51. Thus the initial rate of grafting (in %/hr) is proportional to the power 0.76 for dose intensities.

4. Conclusion

The kinetics of styrene grafting to homogeneous cellulose acetate membrane is rate controlled

by monomer diffusion to growth sites. By controlling the ratio of styrene to VP and controlling the means of irradiation predictably reproducible graft can be prepared.

The water absorption of the grafted membrane was found to decrease with an increasing percent in grafting for styrene, while it is modified for hydrophilic acrylic acid and acrylamide. The electric resistance of styrene-cellulose acetate grafts increases with increasing styrene content, while those for the hydrophilic monomers show no marked effect. These data are interpreted to suggest that styrene grafting may be an effective tool for improving the compaction resistance of cellulose acetate membrane.

It is thought that the graft reaction by post-polymerization is mainly controlled by the activation of catalyst with radicals formed in cellulose acetate membrane during irradiation.

In comparison with the grafted cellulose acetate membrane by the impregnation method, the appearance of the grafted membrane by post-polymerization was not nearly changed irrespective of the percent of grafting and radiation dose of γ -ray or electron beam.

It was also found that the percent of grafting was considerably higher than that obtained by simultaneous irradiation method. The activation energy for grafting of VP:St:BPO solution onto cellulose acetate membrane was determined to be about 21.8 Kcal/mole over the range of 55° ~80°C. The initial rate of grafting (in %/hr) is proportional to the power 0.76 for dose intensities.

By controlling the means of grafting and the casting-solution components, no degradation and dimensional change of radiation-induced graft polymerization was found.

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