

Radiation-Induced Graft Copolymerization of 2-hydroxyethyl-methacrylate and Styrene onto Polytetrafluoroethylene

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불소수지 필름에 2-Hydroxyethyl methacrylate와 스티렌의 방사선 그래프트 공중합

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Abstract: Graft polymerization of 2-hydroxyethyl methacrylate(HEMA) and styrene, from both their binary and unitary systems, onto polytetrafluoroethylene(PTFE) film was investigated by means of the simultaneous γ -ray induced method. The effect of various parameters such as monomer concentration, dose rate, absorbed dose, HEMA/styrene feed ratios and the type of diluent on the extent of grafting in unitary and binary systems was studied. It was observed that when unitary HEMA was used for grafting, the grafting extent was very slight, whereas when comonomers were used, a good grafting yield could be obtained. Inclusion of sulfuric acid in the monomer solution resulted in enhanced grafting yields.

요 약: 2-hydroxyethyl methacrylate(HEMA)나 스티렌을 단독 혹은 혼합하여 γ -ray를 사용한 동시조사법으로 불소수지 필름에 공중합시켰다. 단량체 농도, 조사속도, 조사량, 용매형태 및 HEMA와 스티렌의 혼합조성비가 방사선 그래프트율에 미치는 영향을 검토하였다. HEMA 단독으로 불소수지 필름에 그래프트시킨 경우의 그래프트율은 아주 적었으나 HEMA와 styrene 혼합물의 그래프트 공중합은 좋은 수율을 나타내었다. 그래프트 용액에 황산을 첨가하면 그래프트율 상승효과가 나타났다.

1. Introduction

Radiation-induced graft copolymerization is a well-known method for modification of chemical and physical properties of polymeric materials, and is of particular interest for achieving specifically desired properties such as dyeability, blood compatibility, membrane quality and immobilization of bioactive materials.

PTFE has attracted much attention for a long time and has gained practical uses because of its good chemical stability and thermal and mechanical properties.

By using the simultaneous or preirradiation grafting method, it was found that PTFE could be grafted with styrene[1-3], 4-vinylpyridine[4], acrylic acid[5, 6] and methyl methacrylate[7].

However, it is generally difficult with PTFE to graft hydrophilic monomers such as HEMA and acrylamide because homopolymer is formed more rapidly than graft copolymer.

One of the methods for minimizing the problem is the addition of metal salts such as Cu^{2+} and Fe^{2+} to the grafting solution[8, 9]. However by this metal ion technique, both grafting and homopolymerization are suppressed to a great extent.

In the present work, the comonomer technique involving styrene was used to graft radiation-sensitive HEMA by the simultaneous irradiation method because, with this technique, radiation conditions can be readily chosen to graft aromatic type monomers such as styrene with little competing homopolymer formation. We examined the effect of grafting parameters such as the type of diluent, dose rate and the composition of monomers in the graft polymerization of HEMA and styrene, from both unitary and binary systems, onto PTFE film. This was carried out by γ -ray irradiation to increase the grafting yield of monomers to the backbone polymer as well as to introduce dual properties such as hydrophilicity and hydrophobicity[10]. The effect of including mineral acid in the monomer solution was also investigated since previous work has shown

that this additive is valuable for accelerating these reactions[11, 12].

2. Experimental

2.1. Material

PTFE films of 0.11mm thickness were used. Styrene was purchased from Monsanto(Australia) Ltd., while HEMA was supplied from Fluka AG. Monomers were purified by column chromatography on alumina, a procedure that has previously been satisfactory for radiation copolymerization[13].

The other chemicals were AR grade and used without further purification.

2.2. Irradiation Procedure

Grafting experiment were performed in pyrex tubes, solvent being added first, followed by monomers to a total volume of 20ml. PTFE strips(30mm \times 50mm) were then fully immersed in the monomer solutions. After irradiation using the Co-60 source at Australian Nuclear Science and Technology Organization, the grafted polymer film was quickly removed from the monomer solution, extracted in benzene and then methanol for 72hr respectively to remove homopolymer. This film was dried at 60°C to constant weight. The percent of grafting was calculated from equation 1.

$$(W_g - W_i) / W_i \times 100 \quad (1)$$

where W_i and W_g represent the weights of the initial and grafted film respectively.

2.3. Measurement of Water Content

Water content of grafted PTFE was measured as follows. The film was immersed into distilled water for 20 hours at room temperature. It was then removed, and the excess water remaining on the surface of the film was removed by filter paper and weighed quickly. Water content was calculated from equation 2.

$$\text{Water content \%} = (W_w - W_g) / W_g \times 100 \quad (2)$$

where W_g and W_w represent the weights of dry and wet films respectively.

2. 4. Characterization

The composition of PTFE film grafted with a mixture of two monomers was determined by FT-IR Spectroscopy using a calibration curve, which was made at 1600cm^{-1} of PTFE films grafted with styrene alone.

3. Results and Discussion

Teflon is very inert towards most organic chemicals, and this polymer does not swell in any known organic solvent. Therefore, it is hard for monomers to penetrate into this polymer.

To obtain high grafting efficiency, particularly by the simultaneous irradiation, the monomer must be close to the active center created in the polymer backbone[14].

The possibility of this occurring is enhanced if the monomer can diffuse into the polymer, therefore, a suitable solvent which makes this feasible is often used.

Table 1 shows the grafting percent of HEMA/styrene(1/1 by volume) comonomer to PTFE obtained in the presence of various solvents. It was found that tetrahydrofuran(THF) and methanol were good solvents for grafting of PTFE. A high grafting percent was also obtained with ethanol

Table 1. Effect of Solvent on Graft Percent of HEMA/Styrene^a onto PTFE by γ -Ray Irradiation^b

Solvent	Graft percent	Total dose(Mrad)
MeOH	6.45	1
EtOH	6.35	1
EtOH : H ₂ O(1:1)	7.84(solid)	1
DMF	4.28	1
THF	7.0	1
Acetone	6.29	1

^aHEMA : Styrene volume ratio, 1:1

monomers concentration 60vol%

^bDose rate : 0.0538 Mrad/hr, Total dose : 1Mrad

/water(1/1) solvent, but monomer solution was solidified after irradiation.

Infrared spectra of PTFE films grafted with HEMA and styrene are shown in Fig. 1. Peaks d and g are HEMA characteristic bands, whilst peaks a, b, c, e and f are characteristic bands of styrene.

Effect of absorbed dose on the grafting percent of HEMA/styrene(1/1 by volume) onto PTFE in the presence of various solvents is shown in Fig. 2. In all solvents, grafting yields increased with absorbed dose. However, at any irradiation time, grafting percent was shown to be higher in THF or methanol than in DMF.

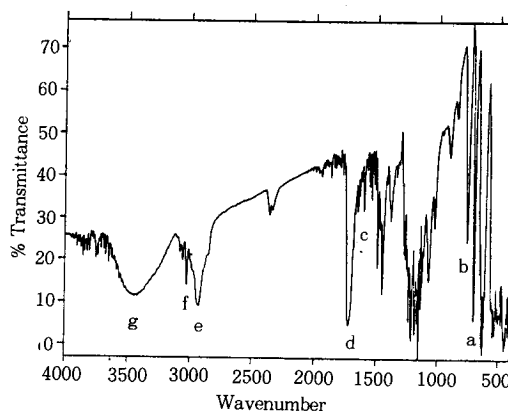


Fig. 1. FTIR spectra of PTFE film grafted with comonomer(HEMA/styrene) : feed ratio (HEMA/styrene)=1/1, graft percent=6.3.

The presence of solvent can lead to graft copolymer possessing unique properties. Components in graft solution which wet and swell backbone polymers generally assist grafting[11]. The surface free energy of PTFE(19dyne/cm) is one of the lowest of any known solid material and, as a result, few liquids spread on the material. Studies of the wetting of various liquids on surface of PTFE have shown a linear increase in the cosine of the contact angle (improved wetting) as the surface tension of the liquid is decreased[15]. The high graft yield in the presence of THF and Alcohol can be attributed to the low surface tensions of those solvents, which may significantly improve the wetting of monomer

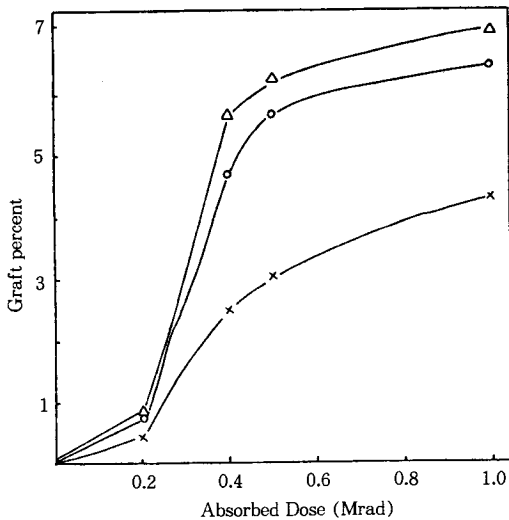


Fig. 2. Effect of absorbed dose on the grafting percent of HEMA/styrene onto PTFE in the presence of various solvents: HEMA : styrene volume ratio 1:1, monomer concentration 60vol.% : (Δ)THF, (\circ)MeOH, (\times)DMF.

toward PTFE.

From the results of Fig. 2, initial grafting increased slowly with increasing irradiation dose up to 0.2 Mrad, then increased quickly to 0.6 Mrad where it gradually levelled off. The induction periods of 0~0.2 Mrad which were observed in these grafting reactions can be attributed to two factors (i) Residual oxygen in the system and (ii) Initial grafting involves styrene to PTFE, however as grafting proceeds, the PTFE becomes styrenated and subsequent grafting is styrenated PTFE which is more facile since the sites involved are most probably pregrafted styrene.

Table 2 shows the effect of dose rate on grafting of HEMA/styrene(1/1 by volume) onto PTFE by γ -ray irradiation using methanol. The grafting yield decreased with increasing dose rate at a dose of 1 Mrad. However, the grafting yield increased with increasing of concentration of comonomers. In order to account for a grafting process causing high grafting yield at low dose rate in PTFE at constant

Table 2. Effect of Dose Rate on the Grafting of HEMA/Styrene^a onto PTFE by γ -Ray Irradiation Using Methanol^b

Monomer concentration	Graft percent		
	Dose rate, 0.0538Mrad/hr	Dose rate, 0.217Mrad/hr	Dose rate, 0.79Mrad/hr
20	1.17	0.43	0.1
30	3.23	0.36	0.1
40	5.14	0.83	0.1
50	5.91	1.25	0.45
60	6.45	1.94	0.9
70	8.45	2.39	0.9

^aHEMA : Styrene volume ratio = 1:1

^bAbsorbed dose : 1 Mrad

absorbed dose which does not swell in monomer, one must assume that grafting occurs stepwise and that the grafted zone moves gradually inwards into the depth of the PTFE film as the reaction proceeds. Initially, the grafted layer swells to some extent in styrene. It follows that provided the rate of polymerization is not too high with respect to the rate of diffusion of the monomer, monomer will diffuse through the superficially grafted layer during irradiation and thus become grafted onto a deeper, ungrafted polymer zone. It is assumed that when the rate of polymerization is too high, the monomer is polymerized before it can diffuse into the film and, under such conditions, the graft copolymerization is necessarily limited to surface layer.

Ishigaki et al.[16] studied the grafting of acrylic acid onto PTFE by simultaneous grafting and found that the grafting occurs by gradual diffusion of the monomer through the successive grafted layers which swell in the radiation medium using the interference microscopy of the grafted film. They suggested that the nongrafted layer remains in the middle part of the film at the lower percent of grafting and then disappears as the grafting proceeds.

For grafting of styrene and methylmethacrylate onto PTFE, Chapiro[17] found that the grafting is carried out under well-defined conditions in which the graft copolymer swells, the grafting can proceed progressively into the PTFE matrix and finally a

homogeneous graft copolymer is obtained.

Table 3 shows the effect of monomers concentration on the graft percent from a unitary system of HEMA and styrene, or a binary mixture of HEMA and styrene in the presence of methanol diluent. It was found that grafting of unitary HEMA was very slight and the surface of the grafted film was rough, while the grafting process could not proceed beyond 40% monomer concentration due to the severe solidification of HEMA. In the other hand, degree of grafting in styrene increased with increasing monomer concentration without a Trommsdorff peak. In the case of the HEMA/styrene(1/1 by volume) comonomer system, grafting yield also increased continuously with increasing HEMA/styrene concentration.

Table 3. Grafting Percent of HEMA/Styrene onto PTFE in the Presence of MeOH Using γ -Ray^a

Monomer concentration	Graft percent		
	HEMA	St	Mixture (HEMA:St, 1:1)
10	0.29	0.51	0.06
20	0.46	1.08	1.17
30	0.52	3.98	3.23
40	—	4.61	5.14
50	—	5.83	5.91
60	—	9.56	6.45
70	—	10.36	8.45

^aDose rate = 0.0538Mrad/hr
 Absorbed dose = 1Mrad

The results in Table 4 show the effect of monomer concentration on the grafting percent from a unitary system of HEMA and styrene or a binary mixture of HEMA and styrene in the presence of THF diluent. THF was found to be generally a more efficient solvent for radiation grafting of styrene or HEMA/styrene comonomer, when compared with methanol. In styrene, the Trommsdorff effect was observed at 60% monomer concentration whereas it occurred at 40% in HEMA/styrene(1/1 by volume). Grafting of unitary HEMA to PTFE in THF as well as methanol was poor.

Table 4. Grafting Percent of HEMA/Styrene onto PTFE in the Presence of THF Using γ -Ray^a

Monomer concentration	Graft percent		
	HEMA	St	Mixture (HEMA:St, 1:1)
10	0.32	0.76	0.54
20	0.33	1.82	3.8
30	0.49	7.2	7.56
40	—	12.4	8.87
50	—	14.8	8.06
60	—	23.17	7.0
70	—	20.95	6.5

^aDose rate = 0.0538Mrad/hr
 Absorbed dose = 1Mrad

Mixtures of HEMA and styrene of various compositions in the presence of methanol and THF were used for grafting to PTFE films in comonomer concentration 30vol.% and 60vol.% respectively (Fig. 3, 4). It was found that total grafting yield increased with increasing the composition of styrene and the concentration of comonomers generally. This result can be attributed to the fact that styrenated PTFE can be swelled more easily in THF than methanol with increasing the composition of styrene[11].

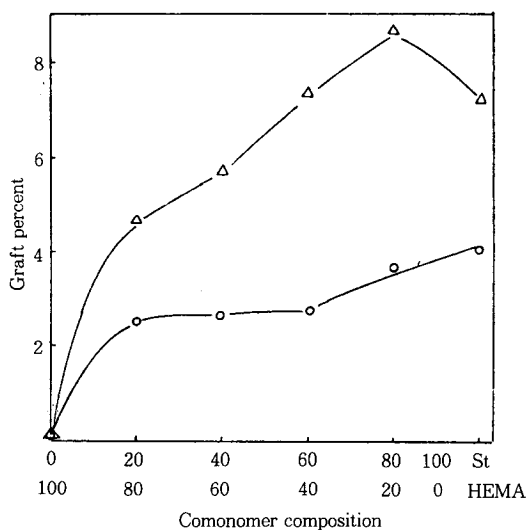


Fig. 3. Effect of solvent on the grafting of styrene/HEMA comonomer to PTFE in comonomer concentration 30vol.% : (Δ) THF, (\circ) MeOH.

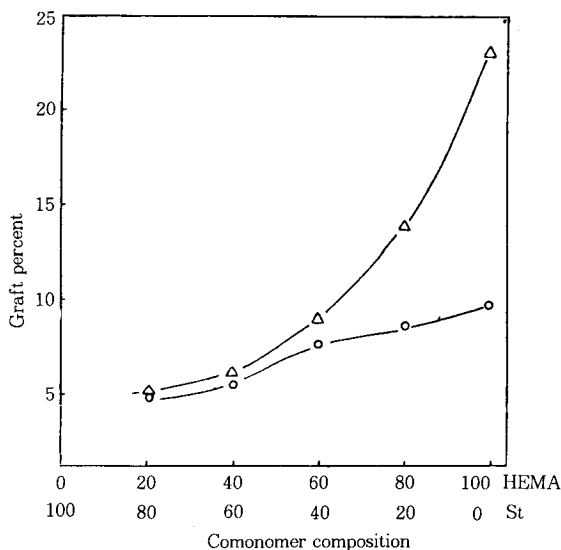


Fig. 4. Effect of solvent on the grafting of styrene/HEMA comonomer to PTFE in comonomer concentration 60vol.% : (Δ) THF, (○) MeOH.

The degree of grafting in comonomer concentration 30 vol.% in the presence of THF as diluent increased with increasing concentration of styrene in comonomer up to composition of (80/20) vol.% of styrene/HEMA comonomer (Fig. 3).

Results in Table 5 show the effect of H_2SO_4 on the total grafting percent of HEMA/styrene with respect to various comonomer compositions. In this result, H_2SO_4 showed an increase in total grafting

Table 5. Effect of H_2SO_4 on the Grafting Percent of HEMA/Styrene^a onto PTFE in the Presence of MeOH

Feed ratio(volume) HEMA : Styrene	Graft percent	
	N.A ^b	H_2SO_4 ^c
5 : 0	—	—
4 : 1	5.0	6.19
3 : 2	5.77	7.33
2 : 3	7.43	8.82
1 : 4	8.45	10.53
0 : 5	9.56	12.55

^aHEMA/styrene concentration 60 vol.%

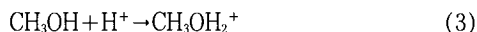
^bN.A : No additive

^c H_2SO_4 : 0.2M

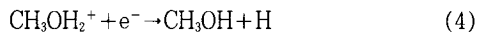
yield which was independent of any feed ratio of monomers. The effect of H_2SO_4 on the grafting yield may be explained by the following mechanism.

The significance of the role of hydrogen atoms in radiation grafting becomes more evident when acid is used as additive. Acid, at the level used, should not markedly effect the precipitation of the grafted polymer chains or the swelling of PTFE. Thus the effect of acid would appear to be due to a radiation chemistry phenomena consistent with the observation by Baxendale and Mellows[18] that addition of acid to methanol increases $G(H_2)$ appreciably.

The precursors of the extra hydrogen were suggested to be hydrogen atoms and electrons, and both species are known to be readily scavenged by styrene monomer. In the presence of acid, protonation of methanol occurs to give $CH_3OH_2^+$.



This reaction is followed by electron capture



The radiolytically produced hydrogen atoms (equation 4) abstract hydrogen atoms from trunk polymer (P) yielding additional grafting sites.

Fig. 5 shows the effect of monomer composition in the binary monomer mixture on the grafting of the two monomers in the mixed graft.

Reactivity ratios under different grafting conditions were calculated from experimental data using the Fineman-Ross method[19].

$$\frac{F}{f} (f - 1) = r_1 \frac{F_2}{f} - r_2 \quad (6)$$

where $F = M_1/M_2$, $f = m_1/m_2$, M_1 and M_2 refer to the compositions of styrene and HEMA in the feed respectively, and m_1 and m_2 to the compositions of styrene and HEMA in polymer respectively. The reactivity values ($r_1 = 0.45$, $r_2 = 0.7$) found at 60 vol.% monomer concentration in the presence of methanol were almost identical to those published by Niwa [20] ($r_1 = 0.45$, $r_2 = 0.54$). The influence of the type

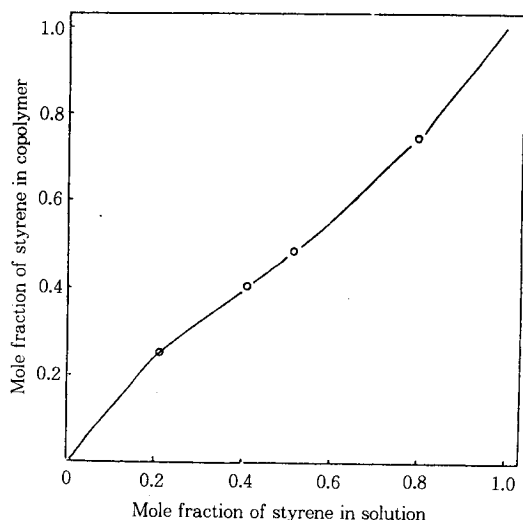


Fig. 5. Effect of monomer composition(HEMA/styrene) in solution on monomer composition in copolymer : monomer concentration 60vol.%, Diluent(MeOH).

of diluent and the presence of H_2SO_4 did not affect reactivity ratios significantly.

The data in Table 6 show the comparison between grafting yield and water content for various HEMA/styrene compositions. The extent of water absorption increased with increasing grafting yield and HEMA composition in the feed. the water contents of these grafts are parameters of interest since they are believed to influence biological interactions with these materials[21, 22].

Table 6. Graft Percent and Water Content for HEMA/ Styrene Comonomers Grafted on PTFE^a

Feed ratio (volume) HEMA:Styrene	MeOH		THF	
	Graft percent	Water content(%)	Graft percent	Water content(%)
5 : 0	—	—	—	—
4 : 1	5.0	3.2	5.73	3.5
3 : 2	5.77	2.1	6.67	2.36
2 : 3	7.43	1.85	8.03	1.89
1 : 4	8.45	0.62	13.71	1.5
0 : 5	9.56	0.4	23.17	1.34

^aHEMA/styrene concentration: 60 vol.%

4. Conclusions

The main conclusions to be drawn from the above experiments are as follows. Monomer concentration, the composition of binary mixture, the presence of H_2SO_4 and solvent type were found to have influence on the grafting yield. The grafting percent of HEMA/styrene comonomer onto PTFE in the presence of various solvents was shown to be higher in THF than in other solvents.

The degree of grafting of unitary HEMA was poor. The grafting process could not proceed in more than 40% monomer concentration due to the homopolymerization of HEMA. HEMA/styrene comonomer permitted reasonable grafting yield with little homopolymer contamination. It was also found that the total grafting yield in the binary mixture of HEMA and styrene increased with increasing the composition of styrene and the concentration of comonomers generally.

The extent water absorption increased with increasing grafting yield and HEMA composition in the feed.

References

1. A. Chapiro, *J. Polym. Sci.*, **34**, 481(1959).
2. A. Chapiro and A. Matsumoto, *J. Polym. Sci.*, **57**, 743(1962).
3. J. Dobo, A. Somogyi and T. Czvikovszky, *J. Polym. Sci.*, Part C, **4**, 1173(1964).
4. P. Aptel, J. Cuny, J. Jozefowicz, G. Morel and J. Neel, *J. Appl. Polym. Sci.*, **16**, 1061
5. A. Chapiro and P. Seidler, *Eur. Polym. J.*, **1**, 189 (1965).
6. I. Ishigaki, N. Kamiya, T. Sugo and S. Machi, *Polym. J.*, **10**, 513(1978).
7. A. Chapiro, *J. Polym. Sci.*, **34**, 481(1959).
8. M. B. Huglin and B. L. Johnson, *J. Polym. Sci.*, Part A-1, **7**, 1379(1969).
9. T. O'Neill, *J. Polym. Sci.*, Part A-1, **10**, 569 (1972).
10. D. Cohn, A. S. Hoffman and B. D. Ratner, *J.*

- Appl. Polym. Sci.*, **29**, 2645(1984).
11. J. L. Garnett, *Radiat. Phys. Chem.*, **14**, 79 (1979).
 12. J. L. Garnett and J. D. Leeder, *ACS Symp. Series*, **49**, 197(1977).
 13. J. L. Garnett and R. S. Kenyon, *J. Polym. Sci., Polym. Lett. Ed.* **15**, 421(1977).
 14. W. J. Burlant and A. S. Hoffman, *Block and Graft Polymer*, Reinhold, New York.
 15. N. L. Jarvis and W. A. Zisman, NRL Report 6324 Naval Research Laboratory, Washington, D.C., (1964).
 16. I. Ishigaki et al., *Polym. J.*, **10**, 513(1978).
 17. A. Chapiro, *J. Polym. Sci.*, **34**, 481(1959).
 18. J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720(1961).
 19. M. Fineman and L. D. Ross, *J. Polym. Sci.*, **5**, 269(1950).
 20. M. Niwa, S. Iida and Y. Nakazato, *Kobunshi Ronbunshu*, **32**, 189(1975).
 21. A. S. Hoffman, *J. Biomed. Mater. Res. Symp.*, **5** (Part 1), 77(1974).
 22. S. D. Bruck, *J. Biomed. Mat. Res*, **7**, 387(1973).