

용매존재하에서 폴리에틸렌 필름에 Vinyl Benzyl Trimethyl Ammonium Chloride(VBTAC)와 Hydroxyethyl Methacrylate의 방사선 그래프트 중합

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Radiation-Induced Co-Grafting of Vinyl Benzyl Trimethyl Ammonium Chloride and Hydroxyethyl Methacrylate onto Polyethylene in the Presence of Solvents

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요 약 : 여러가지의 용매존재하에서 전조사방법으로 vinyl benzyl trimethyl ammonium chloride(VB-TAC)와 hydroxyethyl methacrylate(HEMA)를 혼합하여 폴리에틸렌 필름에 방사선 그래프트시켰다. 용매의 방사선 그래프트율에 미치는 효과에 대하여 조사하였다. 총 그래프트율과 그래프트 공중합체 중의 VBTAC/HEMA 조성은 사용한 용매의 종류에 크게 의존하였다. VBTAC/HEMA 혼합 단량체의 그래프트율은 테트라 하이드로퓨란/메탄올 혼합용매를 사용할 때 가장 높았다. 용매로서 증류수를 사용하였을 경우 공중합체의 VBTAC 함량은 유기용매를 사용하였을 때보다 증류수 존재하에서 이온화된 vinyl benzyl trimethyl ammonium ions의 강한 정전기적 반발력이 작용하게 되어 그래프트율이 낮아졌다.

Abstract : By pre-irradiation grafting technique the high density polyethylene film was graft-copolymerized with the binary mixture of vinyl benzyl trimethyl ammonium chloride(VBTAC) and hydroxyethyl methacrylate(HEMA) in the presence of various solvents. The effect of solvent on the degree of grafting was examined. The total degree of grafting and the composition of VBTAC/HEMA in the grafted copolymer depended on the solvent or the mixture of solvents used. It was found that the degree of grafting of the binary mixture of VBTAC and HEMA was higher in the co-solvent of tetrahydrofuran and methanol than those in other solvents. As the reaction time was increased, the composition of VBTAC in the grafted copolymer was increased gradually. The copolymer obtained in water was much lower on VBTAC than the copolymer obtained in organic solvents owing to the repulsion between highly ionized cationic vinyl benzyl trimethyl ammonium ions.

INTRODUCTION

Radiation-induced graft copolymerization is one of the valuable techniques to impart membrane properties onto various commercial polymers since it is possible to make uniform active sites for initiating grafting throughout the polymer substrates. Thus, if the diffusion of monomer into polymer is large enough to come to the inside of matrix, homogeneous and uniform grafting can be carried out throughout the whole polymer matrix. Ion exchange membrane synthesized by grafting acrylic acid onto the polyethylene film using pre-irradiation method is commercially useful for a battery separator.¹⁻²

In the present study, an attempt was made to synthesize strong anion exchange membrane which is important for electrodialysis. It has been reported that an indirect method to introduce anion exchange group such as quaternary amine could be carried out by grafting of styrene onto polymer matrix, followed by chloromethylation and amination with tertiary amine.³ The present article involves an attempt to examine the effect of solvent in the graft copolymerization of binary mixture of vinyl benzyl trimethyl ammonium chloride (VBTAC) and 2-hydroxyethyl methacrylate (HEMA) onto the polyethylene film. It has been reported that the use of solvent in the grafting media influences the radiation induced-graft polymerization.⁴⁻⁷ Odian et al.⁸⁻⁹ reported the acceleration of radiation-induced graft polymerization by solvent in the systems of polyethylene-styrene and nylon-styrene. Wilson¹⁰ developed a new theoretical approach to the rate of radiation of vinyl monomer on the polymer matrix based on Hildebrand solubility parameter. The use of suitable solvent has a pronounced accelerating effect on the grafting yield, but the effect of solvent on the grafting yield may depend on the grafting system, the type of monomer and polymer substrates.

EXPERIMENT

Material. Commercial high density polyethylene films of 25 μm , 50 μm and 75 μm (Asahi Chemicals Co. Ltd.) were used as polymer substrate. Unless otherwise indicated, the polyethylene films of 25 μm was used. VBTAC (Semi Chemical Co. Ltd.) and HEMA (Kishida Chemical Co. Ltd.) were used without further treatment. Other chemicals were reagent grade.

Grafting Procedure. Irradiation was carried out by the electron beam accelerator (Dynamitron IEA 300-25-2, Radiation Dynamics, Ltd.) operating at beam of energy of 1.5 MeV and current of 1 mA in the circumstance of nitrogen gas. The irradiated films were immersed in the monomer solution which was prepared from 30 wt. % (VBTAC/HEMA = 1/1 wt. ratio)/L and various solvents, and then deaerated by bubbling nitrogen gas. After grafting reaction, the grafted films were removed from the monomer solution in glass ampoules and washed with methanol several times to remove monomer and homopolymer which can be formed during the grafting reaction. The films were then dried in vacuum until a constant weight was reached and weighed. The degree of grafting (%) was determined by the increase in weight based on the original film weight as followings.

$$\text{Degree of grafting (\%)} = \frac{W_g - W_o}{W_o} \times 100$$

where W_g and W_o are the weight of the grafted and the original films, respectively.

Swelling was determined by the increase in weight between the original film and the swelled film. The weight of the film swelled with monomer/solvent was measured after quickly blotting the films between filter papers. Percent swelling was calculated as followings.

$$\text{Swelling (\%)} = \frac{W_s - W_o}{W_o} \times 100$$

where W_s and W_o are the weight of the swelled film and the original film, respectively. The extent

of VBTAC grafted onto the polyethylene substrates was determined by measuring salt-splitting capacity of final grafted polyethylene. The grafted polyethylene was immersed into 2N NaOH solution to convert Cl-form of VBTAC into OH-form, and then washed with distilled water. The quantity of NaOH liberated by immersing the grafted polyethylene film with OH-form in 5% NaCl aqueous solution was calculated by titration with 1/50 N HCl. The content of HEMA grafted onto the polyethylene substrates was determined by subtracting VBTAC content in the copolymer from the total degree of grafting.

X-ray Microanalysis. Graft distribution in the polymer substrate was observed X-ray microanalyzer (JEOL JXA-superprobe 773) after the VBTAC/HEMA-grafted polyethylene film was dried under reduced pressure. The grafted film was cut perpendicularly to its surface at liquid nitrogen temperature and its cross section was observed. X-ray microanalyzer was operated at accelerating voltage of 25 KV and current of 2.5×10^{-8} A.

RESULTS AND DISCUSSION

VBTAC [$\text{CH}_2=\text{CH}(\text{C}_6\text{H}_4)\text{CH}_2\text{N}(\text{CH}_3)_3^+\text{Cl}^-$] cannot be directly grafted to polyethylene because it is assumed that VBTAC monomer with highly ionized $\text{N}(\text{CH}_3)_3^+$ group is hardly compatible with hydrophobic polyethylene. In this study, the grafting of the binary mixture of VBTAC and HEMA in various solvents was carried out to introduce quaternary ammonium salt onto the polyethylene film effectively.

Fig. 1 shows the effect of solvents on the degree of VBTAC/HEMA grafting at the reaction temperature of 50°C. Solvents used for the grafting reactions were THF/MeOH (4/1, volume ratio), DMSO/MeOH (4/1, volume ratio), MeOH and water (Table 1). The degree of grafting was greatly influenced by the nature of solvents. It was found that the degree of grafting of VBTAC/HEMA in THF/MeOH solvent was higher than those in other solvents. The degree of grafting in the graf-

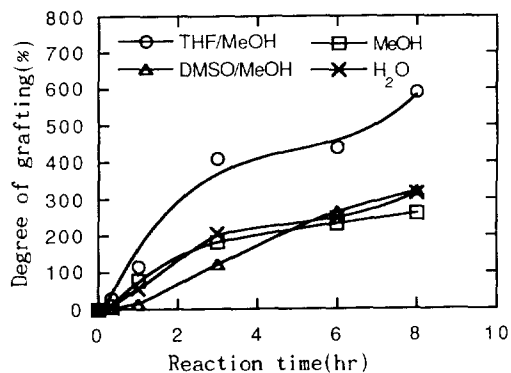


Fig. 1. Effect of solvent on the degree of grafting. Monomer concentration: VBTAC/HEMA (1/1 wt. ratio) 30 wt. %/L; irradiation dose: 200kGy; reaction temp.: 50°C.

Table 1. Abbreviation and Solubility Parameter of Solvents

	Abbr.	$\delta(\text{cal}/\text{cm}^3)^{1/2}$
Tetrahydrofuran	THF	9.1
Dimethylsulfoxide	DMSO	12
Methanol	MeOH	14.5
Water	H ₂ O	23.4
Tetrahydrofuran/ Methanol(4/1, vol. ratio) ^a	THF/MeOH	10.4
Dimethylsulfoxide/ Methanol(4/1, vol. ratio) ^a	DMSO/MeOH	12.5

^a The solubility parameter of solvent mixture was calculated by $\delta_m = (\phi_1 \delta_1^2 + \phi_2 \delta_2^2)^{1/2}$. δ_m , δ_1 and δ_2 are the solubility parameter of mixture and each solvent (ϕ_1 , ϕ_2), ϕ_1 and ϕ_2 are volume fraction of each solvent (ϕ_1 , ϕ_2).

ting system having water was lower than that in MeOH at the initial reaction time, reversed after the reaction time of 3 hour. Fig. 2 shows the degree of grafting-reaction time curves in various solvents at the reaction temperature of 30°C. The initial ratio of grafting at 30°C was low comparing to that at 50°C, but the degree of grafting continued to increase until 20 hour because the amount of the trapped radicals decreases slowly with increasing reaction time at low temperature. The effect of solvent on the degree of grafting had the similar trend regardless of reaction temperature.

The swelling behavior of the polyethylene film in solvents such as THF/MeOH, DMSO/MeOH,

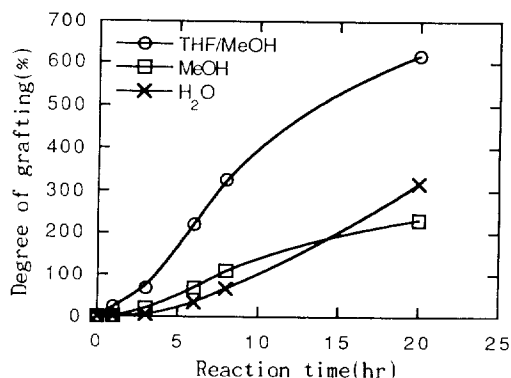


Fig. 2. Effect of solvent on the degree of grafting. Monomer concentration : VBTAC/HEMA(1/1 wt. ratio) 30 wt. %/L ; irradiation dose : 200kGy ; reaction temp. : 30°C.

MeOH and water was examined to find out the effect of solvent on the degree of grafting(Fig. 3). Percent swelling was high when THF/MeOH mixture was used as a solvent.

The solubility of polymer in a solvent is governed by the free energy of mixing.

$$\Delta G_m = \Delta H_m - T\Delta S_m$$

where ΔG_m , ΔH_m and ΔS_m , are Gibbs free energy change, enthalpy change and entropy change, respectively. Solubility of two substances will be observed if ΔG_m on mixing is negative. Since ΔS_m is always positive for dissolution of polymer by solvent, ΔG_m is determined by the enthalpy term ΔH_m .

Hildebrand et al.¹¹ proposed the following formula.

$$\frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \phi_1 \phi_2$$

where V =volume of the mixture, δ =solubility parameter, and ϕ =volume fraction in the mixture. $(\delta_1 - \delta_2)^2$ must be small for the components to be miscible, since ΔH_m is proportional to $(\delta_1 - \delta_2)^2$. The solubility parameter of THF/MeOH mixture was found to be $10.4(\text{cal}/\text{cm}^3)^{1/2}$ which is approximately close to the solubility parameter of polyethylene¹¹ which is $8(\text{cal}/\text{cm}^3)^{1/2}$ (Table 1). Thus,

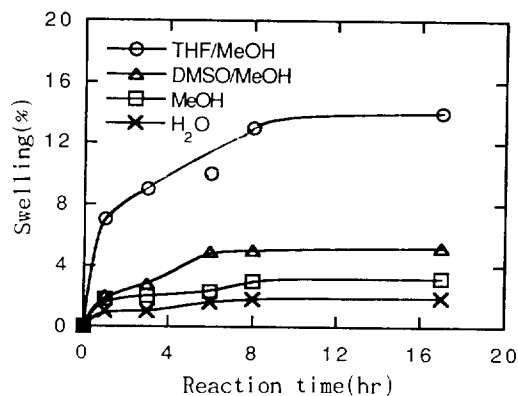


Fig. 3. Effect of time on the percent swelling of the polyethylene film in various solvents. Monomer concentration : VBTAC/HEMA(1/1 wt. ratio) 30 wt./L ; swelling temp. : room temp..

THF/MeOH in the grafting system may be capable of bringing the monomer as near as possible to polyethylene radicals because THF/MeOH is more miscible with polyethylene than other solvents. A better swelling of the polyethylene film in THF/MeOH may be one of the reasons that the high degree of grafting can be obtained.

An accelerating effect on the degree of grafting of VBTAC/HEMA was observed when MeOH was mostly replaced by THF, even though THF is hardly miscible with VBTAC, PVBTCAC and PHEMA. The behavior may be explained by the polymer chain entanglement as well as swelling property of solvent. When MeOH is replaced mostly with THF, the chain entanglement of PVBTCAC and PHEMA may increase. Therefore, termination rate is greatly reduced while propagation rate is hardly affected, so rising to a large increase in the degree of grafting. Burchill et al.¹² reported an accelerating effect of MeOH in the graft polymerization of methyl methacrylate onto the polypropylene film in benzene which is both a swelling agent of polypropylene and a good solvent for polymethyl methacrylate. The authors attributed this behavior to the swelling of the film and polymer chain entanglement.

The degree of grafting of only HEMA was also

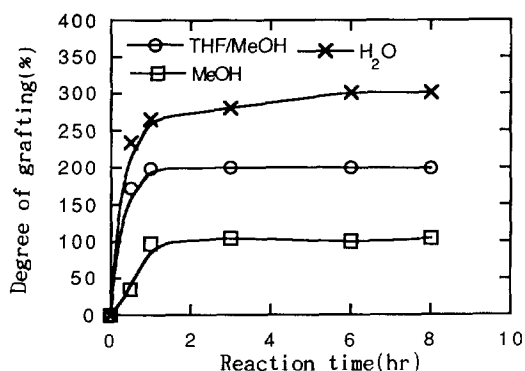


Fig. 4. Effect of solvent on the degree of grafting of HEMA. HEMA concentration : 30 wt %/L ; irradiation dose : 200kGy ; reaction temp. : 50°C.

shown to be sensitive to the type of solvent as shown in Fig. 4. The degree of grafting of HEMA in THF/MeOH was higher than that with MeOH. The dilution of HEMA with THF/MeOH leads to the enhanced access of monomers to the grafting sites in polyethylene. However, among the solvents, water was the most effective in the grafting of HEMA. This tendency may be ascribed to the fact that the organic solvents such as MeOH and THF can accelerate the chain transfer reaction which leads to the lower reactivity in the grafting of HEMA. Water has practically zero chain transfer constant. Therefore, side reaction induced by chain transfer is small in the grafting system having water. Water does not have swelling function for polyethylene as shown in Table 1. Accordingly, the effect of water cannot be considered to relate directly to the swelling of the polymer substrate. This effect has been understood as a gel effect.¹³⁻¹⁴ The presence of water may produce the increase in viscosity of grafted polyethylene media, which causes the increase in the rates of propagation and chain initiation. In the other hand, the termination rate is small because the viscosity of the reaction medium is high and the mobility of the polymer radical is very small.

The effect of the composition of THF and MeOH on both the total degree of VBTAC/HEMA grafting, and the composition of VBTAC/HEMA in the

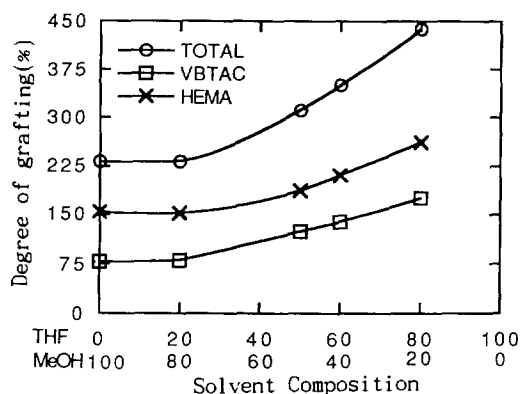


Fig. 5. Effect of solvent composition on the degree of grafting. Reaction time : 6 hour. Other grafting conditions are the same as in Fig. 1.

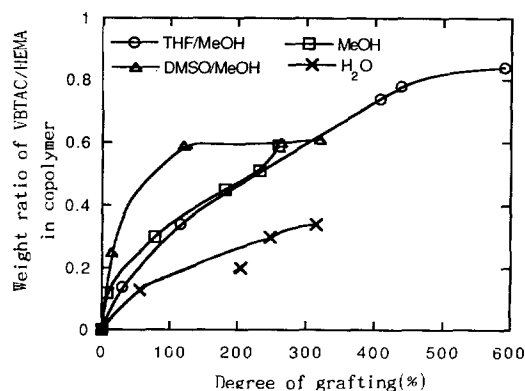


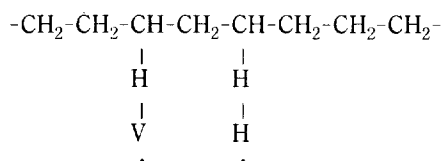
Fig. 6. Weight ratios of VBTAC/HEMA in the copolymer vs. the total degree of VBTAC/HEMA grafting. Grafting conditions are the same as in Fig. 1.

grafted polymer was shown in Fig. 5.

An accelerating effect on the degree of VBTAC/HEMA was observed when MeOH was mostly replaced by THF. It was found that VBTAC and HEMA in the copolymer was not affected by the composition of THF/MeOH.

Fig. 6 shows weight ratios of VBTAC/HEMA in the copolymer vs. the total degree of VBTAC/HEMA grafting when VBTAC/HEMA were grafted onto the polyethylene film as shown in Fig. 1. In case of the low degree of grafting, the weight ratio of VBTAC/HEMA was extremely low. However, weight ratios of VBTAC/HEMA in the copolymer

increased with increasing the total degree of VBTAC/HEMA grafting. This indicates that VBTAC in the beginning of grafting reaction can be hardly grafted onto the polyethylene film owing to the extremely low accessibility of hydrophilic VBTAC onto hydrophobic polyethylene film, but can be only grafted to the growing radicals of HEMA which was already grafted to polyethylene. Thus, HEMA is mostly grafted to polyethylene in the beginning of grafting reaction, and then VBTAC starts grafting reaction. The grafting reaction of VBTAC/HEMA comonomer onto the pre-irradiated polyethylene film can be shown as follows :



where H and V denote HEMA[CH₂=C(CH₃)COOCH₂CH₂OH] and VBTAC[CH₂=CH(C₆H₄)CH₂N(CH₃)₃⁺Cl⁻] monomers, respectively.

It is generally believed that the reactivity in copolymerization was unaffected by the reaction medium, except in the case of acidic or basic water-soluble monomers in aqueous solutions of different pH or in the case of heterogeneous copolymerization.

It was shown that in the free radical grafting of VBTAC/HEMA comonomer, their reactivities were strongly influenced by the solvent used in the reaction. The copolymers obtained in water are always much lower on VBTAC than the copolymers obtained in THF/MeOH, DMSO/MeOH, MeOH as shown in Fig. 6. The concentration of VBTAC in the copolymer against the mole percent of VBTAC in the monomer feed was plotted in Fig. 7. There can be seen large differences between reactivities in each solvent. The reactivities of VBTAC and HEMA during grafting in organic solvent were greatly different from the cases in aqueous grafting media. The composition of VBTAC in the copolymer increased with increasing VBTAC in feed up to 70 mole % when THF/MeOH was used as

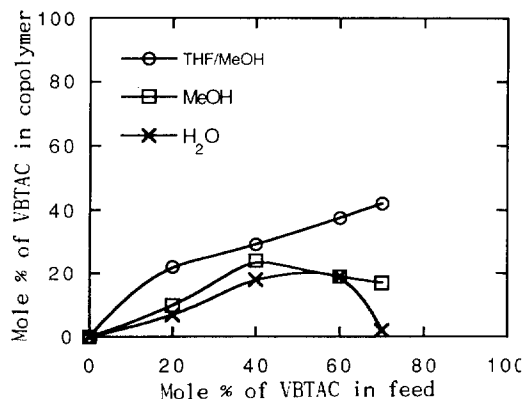
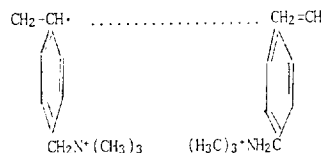


Fig. 7. Monomer-copolymer composition curves for co-grafting of VBTAC and HEMA. Grafting conditions are the same as in Fig. 5.

a solvent. On the other hand, when water was used in the grafting system, the composition of VBTAC in the copolymer not only was low, but decreased drastically along with the decrease in graft yield at 70 mole % of VBTAC in feed. This grafting behavior may be explained as following. The ionization power of organic solvents against VBTAC may be weak comparing to water. Thus, organic solvents may not have sufficient ionization power to free the ions from each other. As a result, VBTAC may exist in the form of an ion pair of CH₂=CH(C₆H₄)CH₂N⁺(CH₃)₃Cl⁻. In the grafting media using water, the power of attraction between N⁺(CH₃)₃ and Cl⁻ may be weak or a part of VBTAC may be exist as cation of CH₂=CH(C₆H₄)CH₂N⁺(CH₃)₃. Therefore, the low degree of VBTAC in the copolymer obtained in water can be attributable to the decrease in reactivity by electrostatic repulsion between cationic vinyl benzyl trimethyl ammonium ions as followings.



Water was most effective solvent in the grafting of only HEMA, but poor solvent in the grafting of the binary mixture of VBTAC/HEMA. It is assu-

med that this behavior may be caused by the decrease in reactivity of VBTAC in water media.

The effect of film thickness on the degree of VBTAC/HEMA grafting was examined when various solvents were used in the grafting system (Fig. 8, 9 and 10). It appeared from the results that the degree of grafting was much dependent on the nature of solvent and the reaction time. The degree of grafting of thick film was low in the initial reaction time, and increased continuously up to the grafting level of thin film when THF/MeOH or MeOH was used as a solvent. However, when water as a solvent was used for grafting media, thick film of 75 μm had lower degree of grafting

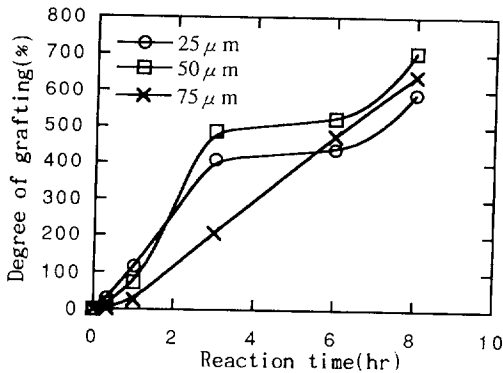


Fig. 8. Effect of film thickness and solvent on the degree of grafting. Solvent : THF/MeOH(4/1 vol. ratio). Other grafting conditions are the same as in Fig. 1.

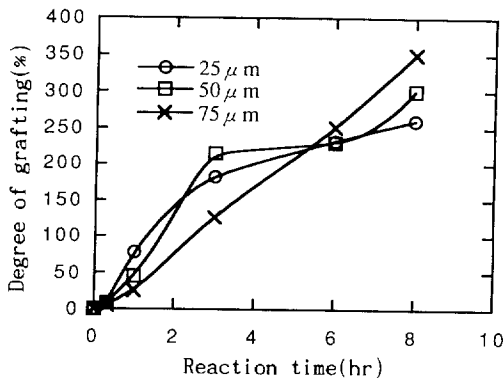


Fig. 9. Effect of film thickness and solvent on the degree of grafting. Solvent : MeOH. Other grafting conditions are the same as in Fig. 8.

than that of thin film until the grafting reaction of 8 hour. The phenomena may be attributable to the low diffusion of monomers into the polyethylene film owing to non-swelling of water to polyethy-

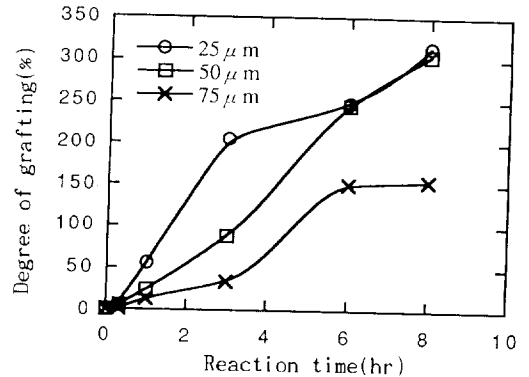


Fig. 10. Effect of film thickness and solvent on the degree of grafting. Solvent : Water. Other grafting conditions are the same in Fig. 8.

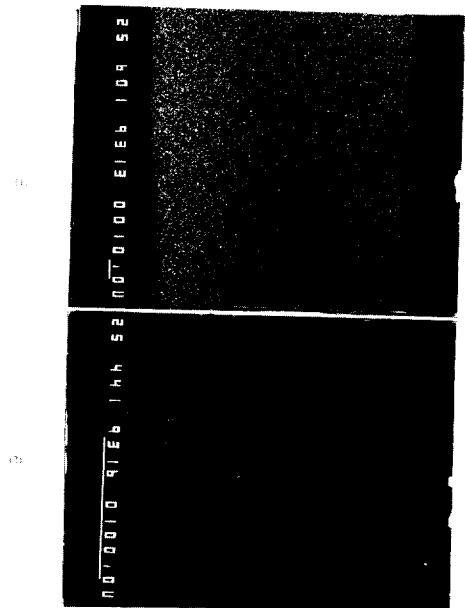


Fig. 11. XMA photographs of the polyethylene film grafted with VBTAC/HEMA in THF/MeOH and H_2O . Reaction time : 8hr. Film thickness : 75 μm . Other grafting conditions are the same as in Fig. 1. (1) solvent : THF/MeOH, degree of grafting : 639%, (2) solvent : water, degree of grafting : 154%.

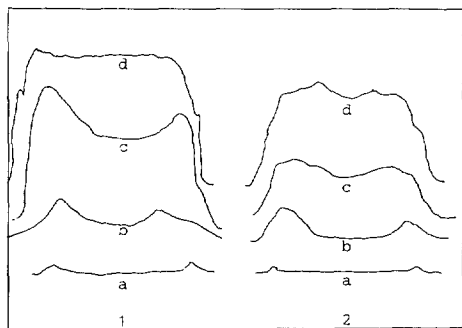


Fig. 12. XMA profiles of the polyethylene film grafted with VBTAC/HEMA in (1) THF/MeOH and (2) H₂O. Grafting conditions are the same as in Fig. 1. (1) : a) Degree of grafting(D. G) : 30%, reaction time(R. T) : 20 min., b) D. G : 116%, R. T : 1hr., c) D. G : 408%, R. T : 3hr., d) D. G : 590%, R. T : 8hr. (2) : a) D. G : 5%, R. T : 20min., b) D. G : 56%, R. T : 1hr., c) D. G : 205%, R. T : 3hr., c) D. G : 315%, R. T : 8 hr.

lene. To examine the distribution of this grafted layer, the cross section of the grafted film was observed using X-ray microanalyser. As shown in Fig. 11, the chloride spots were not observed in the middle of film of 75 μ m when water was used for the grafting system.

Fig. 12 shows the XMA photographs of the grafted film with various degree of grafting in the presence of THF/MeOH and water. The non-grafted layer was observed in the middle of the film at low degree of grafting. However, as the degree of grafting increased, the non-grafted layer disappeared. Thus, grafting begins at the surface and then continue to proceed to the inside of the polymer substrate as a result of stepwise diffusion of HEMA and VBTAC. The distribution of grafted layer has the similar trend regardless of the type of solvent

when thin film of 25 μ m was used for grafting, except the low grafted layer in water media generally.

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