Nylon 4/HEMA Chemical Homografted Membrane

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SYNOPSIS

To enhance the degree of grafting, homografting copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto nylon 4 using a chemical initiator has been attempted. The factors that affect the grafting copolymerization are the concentration of reactants, reaction time, and temperature. The dialysis permeabilities of solutes, water content, surface energy, mechanical properties, and blood compatibility of the membrane were investigated. Under the same reaction conditions, the degree of grafting by the homografting method is remarkably higher than that of the heterografting method for the nylon 4–HEMA grafting system. The dialysis permeabilities of NaCl, vitamin B_{12}, and ovalbumin of the homografted membrane with a 14.8% degree of grafting are 2.760, 0.392, and 0.073×10^{-5} cm^2/min, respectively. These permeabilities are higher than the corresponding ones of ungrafted nylon 4 membrane. The mol ratios of adsorbed fibrinogen/albumin (F/A) of the heterografted membranes were found to decrease from 0.53 to 0.33, and the surface energy, to increase from 40.6 to 46.4 dyn/cm with the degree of grafting in the range of 12.5–29.9%, and their relationship is not remarkable for the homografted membranes for which the mol ratios of F/A are about 0.22–0.32 with the degree of grafting in the range of 14.8–103.8%. Observed from scanning electron micrographs of the membrane surface, denseness was found to be important to improve blood compatibility. Based on the dialysis permeabilities of solutes and the blood compatibility observed in this study, the homografted nylon 4/HEMA membrane can be considered as a hemodialysis material.

INTRODUCTION

Grafting copolymerization using the heterografting method has been reported by many authors.[1-7] Grafting is considered to occur only in the amorphous regions of the polymer when using this method.[8] However, if grafting is carried out using the homografting method where polymer dissolves in a solvent completely, the above-mentioned problem might be improved. Investigations of homografting copolymerization are still meager, probably due to the lack of relevant polymer–solvent systems.[8-14]

Nylon 4 (polypyrrolidone) has been regarded as a promising membrane material for separation purposes because of its excellent mechanical strength and inherent affinity to water. Previous investiga-

tions on nylon 4 membranes have been carried out by Lonsdale et al. and by Orofino (cited by Huang et al.[15,16]), who found that nylon 4 membranes behaved erratically in terms of their transport fluxes. Using the improved polypyrrolidone synthesis and membrane preparation method, significantly better performance of nylon 4 membranes was reported by Huang et al.[15,16]

To further improve the performance of nylon 4 membranes, Lai et al.[17] induced hydrophilic vinyl monomers to be heterografted onto nylon 4 membranes using Co^{60} irradiation for reverse osmosis desalination purposes. Jong et al.[18] used a chemical initiation method to heterograft different hydrophilic monomers onto nylon 4 membranes for reverse osmosis, ultrafiltration, and electrodialysis.

The purpose of this study was to utilize chemical initiation to homograft HEMA monomer onto nylon 4. The membranes so obtained are better than those prepared by the chemical heterografting method in terms of the degree of grafting. The factors that affect the grafting copolymerization, such as concen-

tration of reactants, reaction time, and temperature, will be considered. The dialysis permeabilities of solutes, water content, surface energy, mechanical properties, and blood compatibility of the membrane using homografting and heterografting methods are also investigated and compared.

EXPERIMENTAL

Materials

Nylon 4 was synthesized by CO_2-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as a catalyst.[17] The molecular weights of the samples, measured by a Cannon–Fenske viscometer with m-cresol as the solvent at 25°C, were about 25,000. Formic acid and normal propanol supplied by Nihon Shiyaku Industries Co. were used as a medium solvent and the casting solvent 2-hydroxyethyl methacrylate (HEMA) supplied by Merck Co., Germany, was purified by vacuum distillation. The distilled monomer was placed in a brown glass bottle and stored in a refrigerator at 4°C until use. Distilled water and methanol were used as a solvent for precipitation and extraction. Azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), or potassium peroxydisulfate (KPS) was used as initiator. All the above chemicals were reagent grade.

Homografting Copolymerization

Nylon 4 was added into a 250 mL flask containing the medium solvent and initiator. After nylon 4 and the initiator were completely dissolved under vigorous stirring, HEMA was added into the flask to the final total amount 40 mL. After vigorously stirring the solution in the flask for 10 min, the solution was degassed by putting the purified nitrogen through a freezer under a vacuum to remove oxygen, and the flask was sealed. The grafting copolymerization mixture was poured into excess distilled water to precipitate out the polymers. The polymers, which consisted of graft copolymer and unbound homopolymer, were filtered and dried.

Using the Soxhelt extraction method, PHEMA homopolymer was extracted from the prepared polymers in methanol for more than 48 h. The residue was dried in a vacuum oven at 50°C until constant weight was reached. The calculation of the degree of grafting, conversion, and grafting efficiency were the same as reported in the paper of Nishioka and Kosai.[8]

Heterografting Copolymerization

Dried pure nylon 4 membrane under vacuum was weighed and placed in a glass bottle. The required amounts of HEMA monomer, ethanol solvent, and AIBN initiator were added into the bottle and the membrane was soaked completely. Then, the solution was purged with nitrogen to remove oxygen. Grafting copolymerization was carried out under various monomer concentrations at 80°C for 1 h in a shaker bath. The grafted membrane was immersed in methanol for 4 h and then washed with methanol and distilled water several times to remove all the homopolymers. It was dried in a vacuum at 50°C until it reached constant weight. The degree of grafting was calculated as the percentage increase in weight over the original weight of the membrane.

Membrane Preparation

Membrane was prepared from a casting solution of grafted copolymer in formic acid/n-propanol solvent. The detailed procedure for the membrane preparation was reported in our previous paper.[19]

Surface Energy, Dialysis Permeability, and Water Content

The surface energy was estimated by the Kaelble and Moacanin method.[20] The dialysis permeability and water content of the membrane were measured by the methods reported in our previous paper.[19]

Instrumental Measurements

The microstructure of membranes was observed using a scanning electron microscope (SEM). The membranes were tested by the ASTM D-638 test method for their tensile strength and elongation at break with the Instron Universal Testing Machine Model 4302.

RESULTS AND DISCUSSION

Effect of Grafting Conditions on Grafting Copolymerization

Effect of Polymer Concentration

The degree of grafting decreases with an increase in polymer concentration within the range 1.25–7.5 g polymer per 100 mL solution, as shown in Figure 1. An increase in polymer concentration will increase the viscosity of the reaction solution. The move-
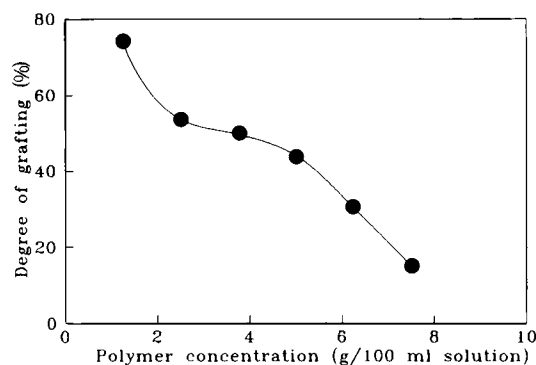
Figure 1 Effect of polymer concentration on degree of grafting of nylon 4-homo-*g*-PHEMA: initiator concn 0.375 g KPS/100 mL solution; HEMA concn 10 vol %; reaction condition: 80°C, 1 h.

ments of the monomer and the active site of the nylon 4 main chain are both restricted due to the increase of viscosity causing a decrease in degree of grafting. Similar observations were also reported by Lai and Shieh[21] and Misra et al.[22]

Poor membrane formation was observed when the casting solution with lower polymer concentration was used. Thus, the concentration of 5 g polymer per 100 mL solution was chosen for the latter investigation due to its suitable degree of grafting and good membrane formation.

Effect of Initiator Concentration

Several runs of grafting copolymerization were carried out under various initiator concentrations and the results are shown in Figure 2. The degree of grafting increases with an increase in initiator (KPS) concentration up to 0.375 g per 100 mL so-
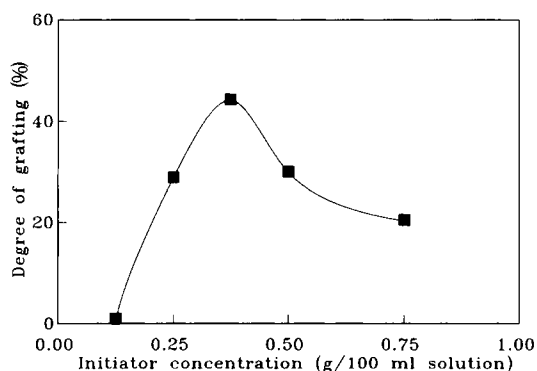

Figure 2 Effect of initiator (KPS) concentration on degree of grafting of nylon 4-homo-*g*-PHEMA: polymer concn 5 g/100 mL solution; HEMA concn 10 vol %; reaction condition: 80°C, 1 h.

lution and then decreases with a further increase in initiator concentration. The reason for this trend may be because an increase in initiator concentration increases the probability of the free radical to form polymer macroradicals on the polymer main chain and, consequently, the chances of creating grafted polymer chains with monomer are increased, leading to an increase in the degree of grafting. The decrease in degree of grafting in the higher initiator concentration might be due to the higher termination rate among primary radicals, polymer macroradicals, and growing grafted polymer chains.

Effect of Monomer Concentration

The effect of monomer concentration on grafting is shown in Figure 3. As the monomer concentration increases, the monomer conversion increases and the grafting efficiency decreases. However, the degree of grafting increases and reaches a maximum at 20 vol % and then decreases with further increasing of the monomer concentration, being due to that an increase in monomer concentration increases the possibilities to form homopolymer and grafting polymer and leads to the increase in conversion and degree of grafting.

Homopolymerization and grafting copolymerization occurred simultaneously and competed against each other during the polymerization process. At higher monomer concentration, homopolymerization increases much faster than does grafting copolymerization. On the other hand, the grafting PHEMA chains are formed rapidly on nylon 4. Monomer diffusion into the polymer backbone
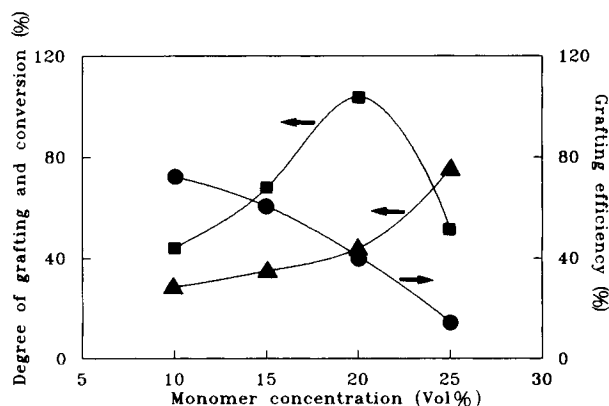

Figure 3 Effect of monomer concentration on degree of grafting of nylon 4-homo-*g*-PHEMA using KPS as a initiator: polymer concn 5 g/100 mL solution; initiator concn 0.375 g/100 mL solution; reaction condition: 80°C, 1 h; (■) degree of grafting; (▲) conversion; (●) grafting efficiency.

would be restricted and would lead to a decrease in degree of grafting and grafting efficiency.

Effect of Reaction Temperature and Time

Rising polymerization temperature tends to accelerate the rate of grafting and leads to an increase in degree of grafting, as shown in Figure 4. This could be due to rapid decomposition of the initiator and an increase of the rate of monomer diffusion and dissolution.

The effect of reaction temperature on the degree of grafting within the range 50–80°C is also indicated in Figure 4. The degree of grafting at 50°C is remarkably lower than that within 60–80°C, which could be due to that the decomposition of KPS initiator is less complete at 50°C and an increase in the reaction temperature favors the decomposition of initiator within the range 60–80°C.

Increase in reaction time prolongs the time of grafting copolymerization and this leads obviously to an increase of degree of grafting.

Effect of Different Initiators

AIBN or BPO is also used as the initiator for the grafted HEMA onto nylon 4, and the results are shown in Figure 5. At 10 vol % monomer concentration, the degree of grafting of the grafting copolymerization using AIBN, BPO, and KPS as initiators are 183.4, 134.7, and 44.1%, respectively. It is remarkable that the initiating abilities of AIBN and BPO are more active than that of KPS in the homografting system. This phenomenon could be explained by the fact that the solubility of hydrophobic initiator, AIBN or BPO, is better than that of the
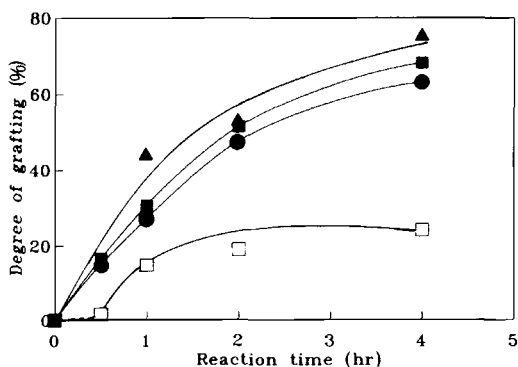

Figure 5   Effect of monomer concentration on degree of grafting of nylon 4–homo-g-PHEMA using KPS, AIBN, or BPO as an initiator: initiator concn 0.375 g/100 mL solution; reaction condition: 80°C, 1 h; initiator: (■) KPS; (●) BPO; (▲) AIBN.

hydrophilic initiator, KPS, in the formic acid/n-propanol solution system.

Effect of Heterografting Method

The degree of grafting increases with increasing monomer concentration, as shown in Figure 6. Under the same reaction conditions, the degree of grafting of heterografting and homografting HEMA onto nylon 4 are 12.5 and 183.4%, respectively, when 10 vol % monomer concentration is used. In the heterografting system, grafting occurs only in amorphous regions. However, in the homografting system, all the nylon 4 chains can be exposed to participate in the grafting reaction, leading to a higher degree of grafting. Similar observations were also reported by Nishioka et al.[8-10] and Tsuzuki et al.[11]

Figure 4   Effect of reaction time and temperature on degree of grafting of nylon 4–homo-g-PHEMA: polymer concn 5 g/100 mL solution; initiator concn 0.375 g KPS/100 mL solution; reaction temperature: (□) 50°C; (●) 60°C; (■) 70°C; (▲) 80°C.
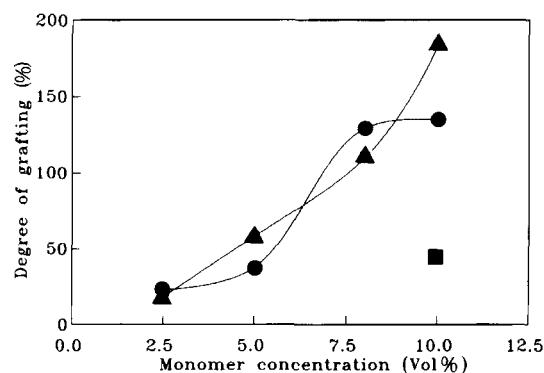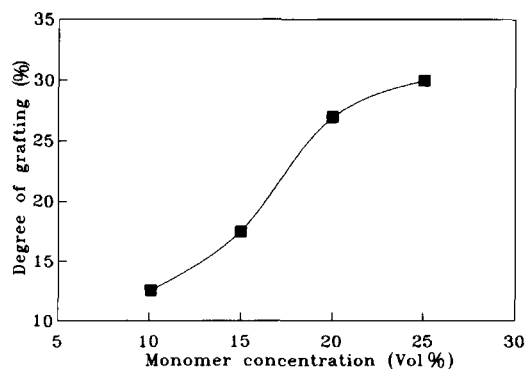

Figure 6   Effect of monomer concentration on degree of grafting of nylon 4–hetero-g-PHEMA membrane: initiator concn 0.375 g AIBN/100 mL solution; reaction condition: 80°C, 1 h.

Effect of Degree of Grafting on Membrane Performances

Morphology of the Membrane

Figure 7 shows the SEM of the nylon 4–homo-*g*-PHEMA and nylon 4–hetero-*g*-PHEMA membrane surface structure. The grafted PHEMA chains increase the denseness of the membrane surface with increasing degree of grafting from 12.5 to 29.9% for heterografted membranes. Homografted membranes within the range of 14.8–103.8% degree of grafting are denser than those of heterografted membranes. It is understood that increasing the amount of grafted PHEMA will cause an increase in denseness of the membrane. This structure will affect the dialysis permeabilities of solutes, water content, surface energy, mechanical properties, and blood compatibility of the membrane.

Water Content of the Membrane

The water content of the membrane is affected by the hydrophilicity and morphology of the membrane. Generally, higher hydrophilicity of the membrane and a larger amount of free volume in the membrane lead to its higher water content. The percent of water content of ungrafted nylon 4 membrane and the nylon 4-homo-*g*-PHEMA membrane with a 14.8% degree of grafting are 46.9 and 48.0, respectively, as shown in Figure 8. As the degree of grafting increases up to 103.8%, the percent of water content drops to 30.3. This is due to the water content of the nylon 4-homo-*g*-PHEMA membrane with a 14.8% degree of grafting being higher than that of ungrafted nylon 4 membrane because of the incorporated hydrophilic grafted PHEMA chains. The increase of the amount of grafted PHEMA probably forms cross-linking between the PHEMA chains; this will decrease hydrophilicity of the O — H groups of the PHEMA chains and lead to a decrease in the hydrophilicity of the membrane.

The water content of the nylon 4-hetero-*g*-PHEMA membrane decreases as the amount of grafted PHEMA increases, because the higher amount of grafted PHEMA will reduce the free volume in the membrane.

Surface Hydrophilicity of the Membrane

The surface hydrophilicity of the membrane can be measured in terms of the data of the water-contact angle and surface energy. The smaller the water-contact angle and the higher the surface energy, the better the surface hydrophilicity.

From Table I, the water-contact angle is 71° and

the surface energy is 41.8 dyn/cm for the nylon 4-homo-*g*-PHEMA membrane with a 14.8% degree of grafting. These values are better than that of ungrafted nylon 4 membrane, which has a water-contact angle of 78° and a surface energy of 41.0 dyn/cm. The poor surface hydrophilicities of the membranes will result when the degree of grafting is higher than 14.8%.

The water-contact angle decreases from 67 to 58° and the surface energy increases from 40.6 to 46.4 dyn/cm with an increase in the degree of grafting from 12.5 to 29.9%. These can be attributed to the grafting PHEMA chains formed on the surface of the nylon 4 membrane, which improve the surface hydrophilicity of the nylon 4-hetero-*g*-PHEMA membrane.

### Dialysis Permeabilities of the Solutes of the Membrane

The solute permeabilities of the nylon 4–homo-*g*-PHEMA membrane were measured by the dialysis equipment as shown in Figure 9. The permeabilities of NaCl, vitamin B_{12}, and ovalbumin of the ungrafted nylon 4 membrane were found to be 1.633, 0.071, and 0.030 × 10^{-5} cm^2/min, respectively. At a degree of grafting lower than 14.8%, the permeabilities of the NaCl, vitamin B_{12}, and ovalbumin were reduced to 2.760, 0.392, and 0.073 × 10^{-5} cm^2/min, respectively. When the degree of grafting is higher than 14.8%, the solute permeabilities decrease with increasing degree of grafting. Vitamin B_{12} and ovalbumin cannot permeate through the membranes when the degree of grafting is higher than 51.4%. These phenomena are probably due to that a large number of grafted PHEMA chains form cross-linking, which decrease the hydrophilicity of the O — H groups of the PHEMA chains.

The effect of the degree of grafting on the dialysis permeabilities of the solutes for heterografted HEMA onto nylon 4 membranes is shown in Figure 10. The permeability of NaCl decreases remarkably to 0.424 × 10^{-5} cm^2/min for a 29.9% degree of grafting, and vitamin B_{12} and ovalbumin cannot permeate through any of the grafted membranes at any degree of grafting. This is because the grafted PHEMA chains form on the nylon 4 membrane, masking the pores of the membrane, which is called the mask effect. Thus, the solute permeabilities decrease with increasing degree of grafting.
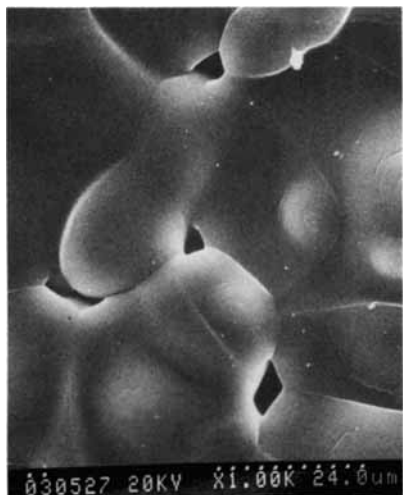
The permeabilities of NaCl, vitamin B_{12}, and ovalbumin of the homografted membrane with a water content under 30.3% are 0.0178, 0, and 0 × 10^5 cm^2/min, respectively, and those for the membrane
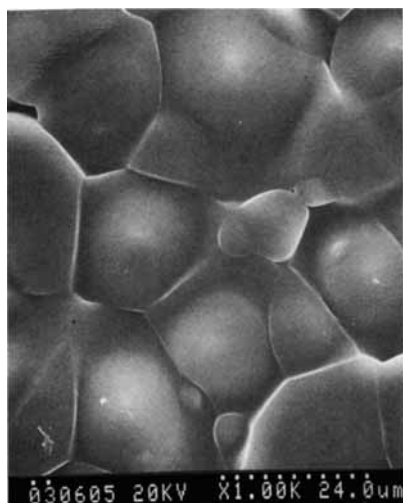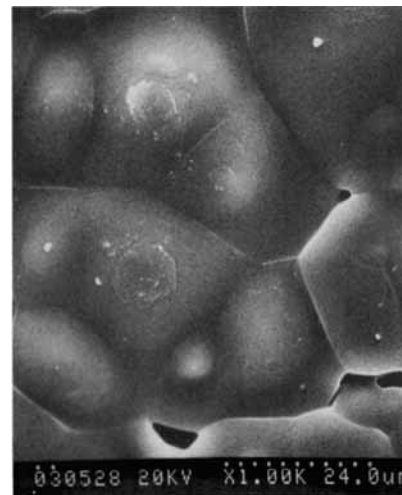
(A)
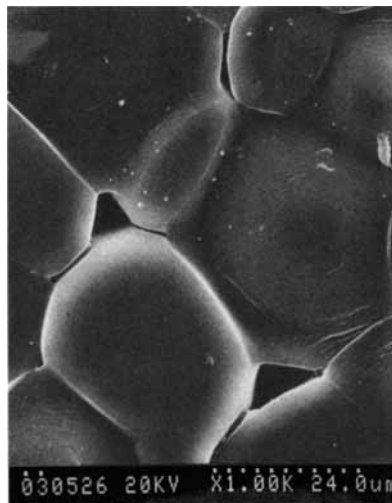
(B)

(C)

(D)

Figure 7   Scanning electron micrographs of membrane surface: degree of grafting: (A) ungrafted nylon 4; (B) 12.5%, (C) 26.9%, (D) 29.9% of heterografting method; (E) 14.8%, (F) 27.2%, (G) 51.4%, (H) 103.8% of homografting method.

with a water content under 48.0% are 2.760, 0.392, and 0.073×10^5 cm^2/min, respectively. From the data, the relationship between water content and solute permeability can be obtained: that increasing the water content in the membrane will help the solutes permeating through the membrane, resulting in an increase in solute permeability. This phenomenon is also observed for heterografted membranes.

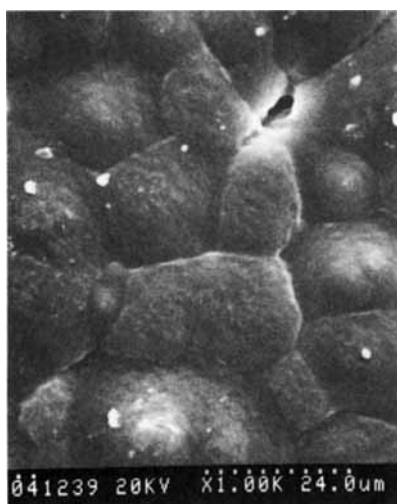High-surface energy (or surface hydrophilicity) reveals that the solute can easily permeate through

the membrane. An opposite trend is found in our experimental data for these heterografted membranes. This is because the grafted PHEMA masks the pores of membrane surface, which will predominate over the effect of surface hydrophilicity on solute permeability. The relationship between surface energy and solute permeability is not so obvious for the homografted membranes. This reveals that the solute permeability is determined by the hydrophilicity of the membrane and not by the surface
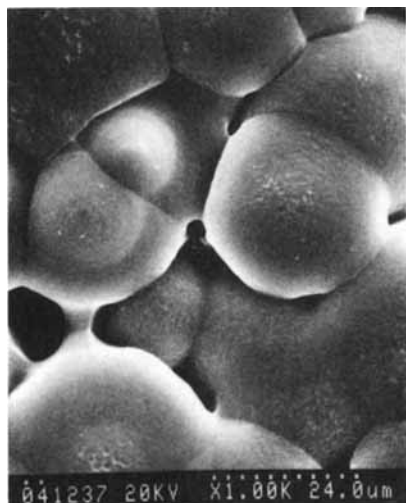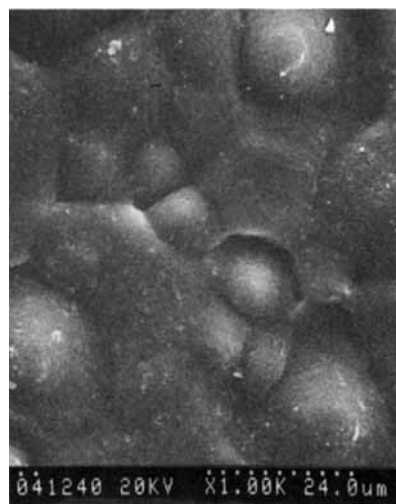
(E)
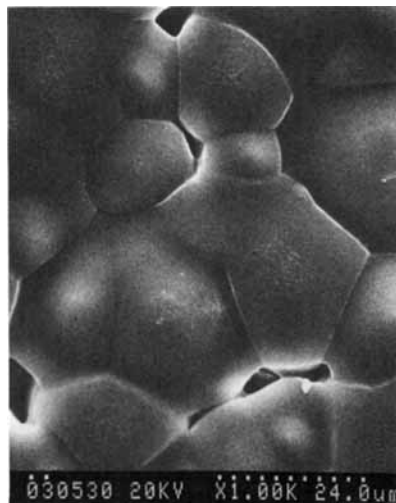
(F)

(G)

(H)

Figure 7   (continued from the previous page)

hydrophilicity. Thus, it is believed that there may not be a direct relationship between the surface energy and the solute permeability of the membrane in our study.

Blood Compatibility of the Membrane

Albumin has a thromboresistant ability, whereas fibrinogen promotes platelet adhesion onto the polymer surfaces. Therefore, the mol ratio of adsorbed fibrinogen to adsorbed albumin (F/A) was used to

evaluate the blood compatibility of the membranes in our research.

Figure 11 shows that the mol ratios of adsorbed F/A are about 0.22–0.32 with the degree of grafting ranging from 14.8 to 103.8% for the homografted membranes. F/A decreases from 0.53 to 0.33 for the heterografted membranes with increasing degree of grafting from 12.5 to 29.9%. This indicates that the grafted membranes improve the blood compatibility of the ungrafted nylon 4 membrane because the grafted PHEMA hydrogel is essentially a good material of blood compatibility.
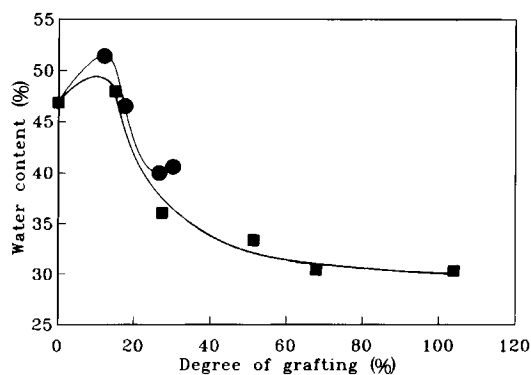
Figure 8 Effect of degree of grafting on water content of membrane; grafting methods: (■) homografting; (●) heterografting.

Figure 9 Effect of degree of grafting on solute permeability of nylon 4–homo-g-PHEMA membrane; solutes: (●) NaCl; (■) vitamin B_{12}; (▲) ovalbumin.

Within the wide range of the degree of grafting for homografted membranes, the mol ratios of adsorbed F/A are not different, which may be because the grafted PHEMA hydrogel is uniformly distributed on the nylon 4 backbone. Thus, the homografted membranes show similar behavior. The F/A value decreases to 0.33 for the heterografted membrane with a 29.9% degree of grafting, due to that the amount of PHEMA hydrogel deposited onto the nylon 4 membrane surface will be increased with increasing degree of grafting. The blood compatibilities of these membranes are better than that of ungrafted nylon 4 membrane.

From the data obtained, the mol ratios of ad-

sorbed F/A decrease with decreasing water content in heterografted membranes. However, the amount of the water content in the membrane does not affect the blood compatibilities of homografted membranes. This suggests that the blood compatibility has no relationship to the water content.

Figure 12 shows that the mol ratios of adsorbed F/A decrease with increasing surface energy of heterografted membranes. From the data in Table I and Figure 11, the relationship between the F/A value and the surface energy is not obvious for homografted membranes. The surface energy of homografted membranes is lower than that of heterografted membranes. From the above-mentioned phenomenon, we can deduce that increasing the surface energy can improve the blood compatibility; however, the denseness of the surface structure of the membrane should play a more important role in our study.

Compared to the mol ratios of adsorbed F/A between homografted and heterografted membranes,

Table I Effect of Degree of Grafting on Surface Hydrophilicity of the Membrane

Grafting Methods	Degree of Grafting (%)	Water-Contact Angle (deg)	Surface Energy (dyn/cm)
Ungrafted	0	78	41.0
Homografted[a]	14.8	71	41.8
	27.2	82	37.8
	51.4	80	39.2
	67.7	80	40.5
	103.8	80	38.7
Heterografted[b]	12.5	67	40.6
	17.5	67	40.6
	26.9	66	43.5
	29.9	58	46.4

[a] Polymer conc 5 g/100 mL solution; initiator conc 0.375 g KPS/100 mL solution.
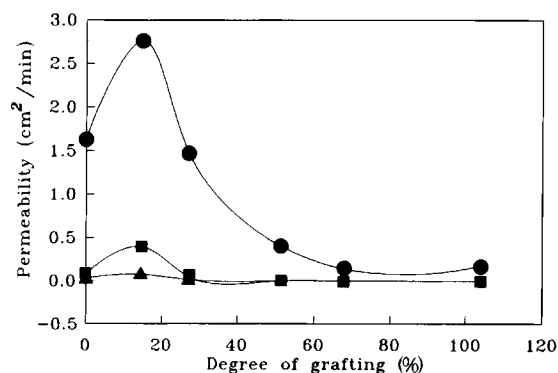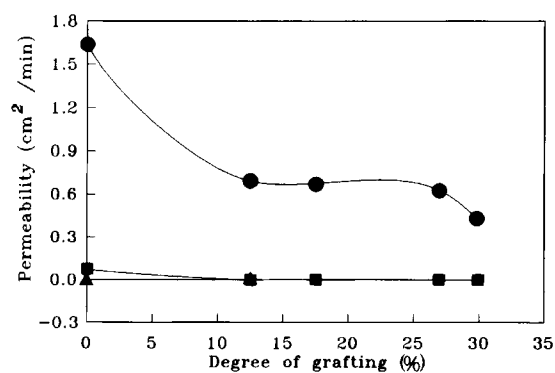[b] Initiator conc 0.375 g AIBN/100 mL solution.

Figure 10 Effect of degree of grafting on solute permeability of nylon 4–hetero-g-PHEMA membrane; solutes: (●) NaCl; (■) vitamin B_{12}; (▲) ovalbumin.
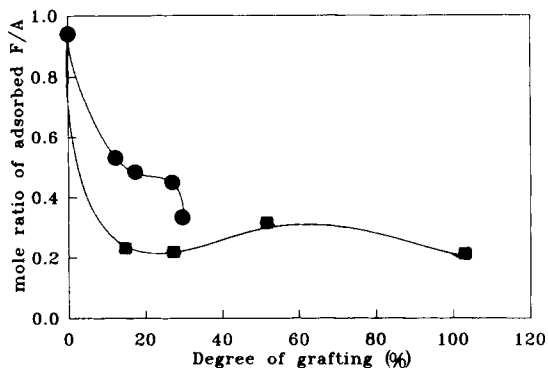
Figure 11 Effect of degree of grafting on mol ratio of adsorbed F/A of membrane; grafting methods: (■) homografting; (●) heterografting.
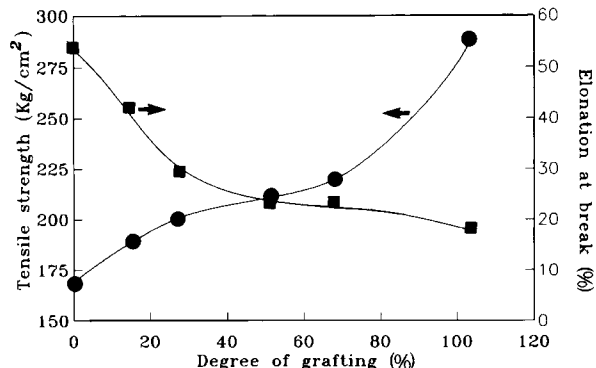
the blood compatibility of the former is better than that of the latter. This phenomenon is due to that the grafting distribution of homografted membranes is more homogeneous than that of heterografted membranes and that the surface structure of homografted membranes is denser than that of heterografted membranes from the observation of SEM.

Mechanical Properties of Membrane

Mechanical properties of membranes are shown in Figure 13. The tensile strength and elongation at break of ungrafted nylon 4 membrane are 169.2 kg/cm^2 and 53.2%, respectively. When the degree of grafting is increased to 103.8%, the tensile strength is also increased to 288.7 kg/cm^2 and elongation at break is decreased to 18.4%. These phenomena could be attributed to the forming of the inter- and intra-molecular cross-linking by carboxyl and hydroxyl groups of the grafted PHEMA chains of nylon 4–homo-g-PHEMA. In general, the tensile strength

Figure 12 Effect of surface energy on mol ratio of adsorbed F/A of nylon 4–hetero-g-PHEMA membrane.

Figure 13 Effect of degree of grafting on mechanical strength of nylon 4–homo-g-PHEMA membrane: (●) tensile strength; (■) elongation at break.

will increase and the percent of elongation at break will decrease with increasing degree of grafting.

CONCLUSIONS

Homografted HEMA onto nylon 4 by utilizing chemical initiation is first adopted to enhance the degree of grafting. Various reaction conditions will affect the grafting copolymerization. The reaction solution of the grafting copolymerization is a uniform phase for the homografting system, which is favorable to grafting. Also, the degree of grafting of the homografting method is remarkably higher than that of heterografting method at the same reaction conditions.

The dialysis permeabilities of NaCl, vitamin B_{12}, and ovalbumin of the homografted membrane with a 14.8% degree of grafting are 2.760, 0.392, and 0.073 $\times 10^{-5}$ cm^2/min, respectively. These permeabilities are higher than those of the ungrafted nylon 4 membrane. The mol ratios of adsorbed F/A of the homografted membranes are about 0.22–0.32 with the degree of grafting in the range of 14.8–103.8%. The F/A values of the heterografted membranes decrease from 0.53 to 0.33 with degree of grafting in the range of 12.5–29.9%. The blood compatibilities of both homografted and heterografted membranes are better than that of ungrafted nylon 4 (0.94).

Increasing the amount of the water content in the membrane will increase the solute permeabilities of homografted and heterografted membranes. By increasing the degree of grafting, the surface energy increases and the mol ratio of adsorbed F/A decreases for heterografted membranes. However, the relationship between them is not obvious for the
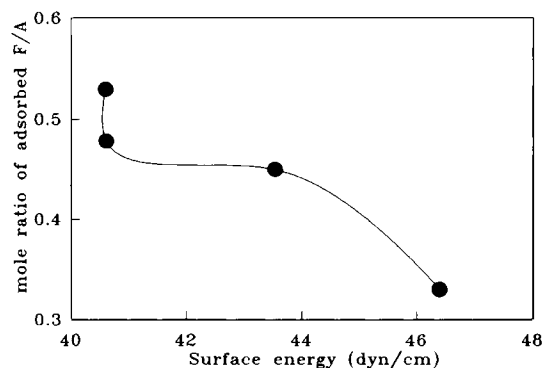
homografted membranes. To obtain better blood compatibility and the dense surface structure, the membrane is casted from a copolymer incorporated with hydrogel PHEMA. Based on the dialysis permeabilities of solutes and blood compatibilities, the homografted nylon 4/HEMA membrane prepared in this study can be considered as a hemodialysis material.

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