Influence of Degree of Grafting and Grafting Temperature on the Permeabilities of Grafted Polypropylene Membranes

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ABSTRACT: Polypropylene dialysis membranes were prepared using cobalt-60 gamma radiation to directly graft 2-hydroxyethyl methacrylate (HEMA) onto polypropylene (PP) membranes. The surface structures of both the grafted membranes and the PP membrane were observed by using FTIR–PAS and ESCA methods. The X-ray diffraction diagrams of the PP and PP-*g*-HEMA membranes indicated a transformation process of the β-form toward the α-form crystallinity with increasing degree of grafting. The SEM data of the membrane grafted under a low grafting temperature showed many spheres of PHEMA embedded in the PP matrix, whose size was well distributed and increased with the degree of grafting. The influences of the degree of grafting and grafting temperature on the permeabilities of PP-*g*-HEMA membranes toward urea and creatinine were studied in a dialyzer. In all cases, the PP-*g*-HEMA membrane obtained under higher grafting temperature showed higher permeability toward those solutes. The permeation coefficients of urea and creatinine through the PP-*g*-HEMA membrane obtained at 59°C were about 10.4 and 28.8 times that through the PP membrane, respectively. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 83–89, 1998

Key words: radiation induced; degree of grafting; pp membrane; permeation coefficient

INTRODUCTION

Radiation-induced graft copolymerization is a well-known important method for altering the surface or bulk characteristics of a polymer substrate. In recent years, the scale of effort on application of this method for medical purposes to increase the biocompatibility of various polymeric materials has increased significantly because of its merits in simplifying the whole treating process, minimizing the processing time, and leaving no detrimental residue. Extensive investigations have been performed on the modification of PE, PTFE, silastics, and polyurethanes by radiation-induced graft polymerization of different monomers: 2-hydroxyethyl methacrylate (HEMA), *N*-vinylpyrrolidone, methacrylic acid, and acrylimide and its derivatives.[1–6] The graft of acrylamide, HEMA, 2,3-epoxypropyl methacrylate, and 2,3-dihydroxypropyl methacrylate onto polyurethane films was studied by Jansen et al.[7,8] The distribution of the grafted layer along the film thickness was examined using IR spectroscopy. Ohtsuka et al.[9] reported hemodialysis membranes prepared from latexes of acrylonitrile–methyl acrylate–acrylamide graft copolymerization onto poly(vinyl alcohol). The radiation-induced graft copolymerization of acrylamide onto the PE prosthesis was carried out by Pekala et al.[10,11] The hydrophilicity of the prosthesis was increased.

In this article, we report on polypropylene (PP) dialysis membranes prepared from the direct radiation grafting of HEMA onto PP membranes and dialysis experiments with these membranes toward urea and creatinine. The influence of grafting temperature and degree of grafting on

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the permeability and morphology of grafted membranes was investigated in detail. The surface morphology and structure of the membranes were determined using scanning electron microscopy, IR spectroscopy, and ESCA methods.

EXPERIMENTAL

Materials

The PP membranes were supplied by the Shanghai Institute of Plastic Research, containing no additives. Their melt index (MI) was 8.8 (g 10 min), and their density was 0.905. The specimens of 30 μm thickness were prepared by biaxially stretching at 190°C and were rapidly quenched at low temperature. HEMA, manufactured in Germany, was used as purchased, without further purification.

Grafting Procedure

The PP membranes were made into samples of 50 $\times$ 50 mm, washed with soap and ethanol, and dried at 60°C under a vacuum (10 mmHg) for 7 h. The initial weight W_0 was measured. The samples were immersed in the grafting solution (mixture of ethanol and monomer) in grafting vessels, while bubbling with N_2 gas for 20 min to remove the oxygen, and then irradiated in a 60,000 Ci cobalt-60 source under different grafting conditions.

The grafted membranes were extracted in ethanol for 8 h. The extracted membranes were then washed with distilled water and dried at 60°C under vacuum (10 mmHg) for 7 h. The dried membrane weight (W_g) was determined. The degree of grafting [$G(\%)$] was calculated using the following equation:

$$G(\%) = (W_g - W_0)/W_0 \times 100$$

Characterization of Membranes

The structures of membranes were studied by a Nicolet 170 SX Fourier transform infrared photoacoustic spectroscopy (FTIR–PAS) and an Escalab MK-II electron spectroscope by a chemical analysis (ESCA) technique. Their surface morphologies were observed by a Hitachi x-650 scanning electron microscope (SEM). A Rigaku D/Max-rA wide-angle X-ray diffraction instrument was used to investigate the crystallinity of these membranes. The element components of the PP and PP-*g*-HEMA membranes were determined in a PE240-C Element Analyzer.

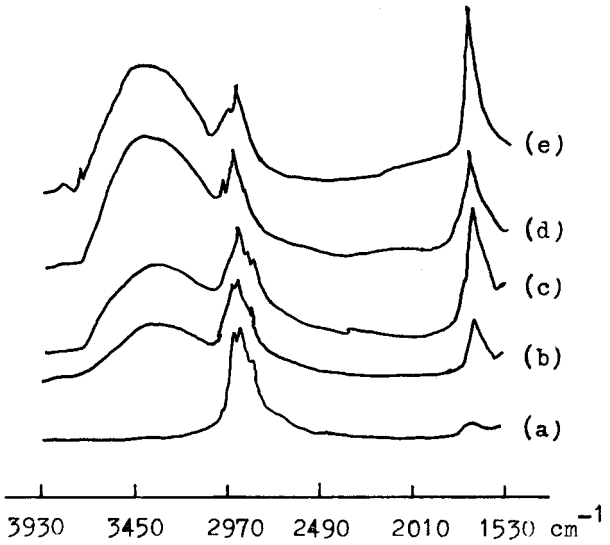

Figure 1 FTIR–PAS spectra of the PP and PP-*g*-HEMA membranes with different degrees of grafting (%): (a) 0; (b) 30; (c) 60; (d) 100; (e) 160.

Dialysis Experiment

The PP-*g*-HEMA membrane (or PP membrane) was fixed in a quartz dialysis cell as a partition membrane. An aqueous solution with the appropriate concentration of solute was poured into the left compartment of the cell and an equal volume of distilled water was put into the right. The cell was immersed in a constant temperature bath set at 37 $\pm$ 0.5°C. The dialysis procedure was carried out with continuous stirring.

The concentration of the solute in both left and right cells was determined by UV spectroscopy. The permeation coefficients were calculated by an equation found in the literature.[12]

RESULTS AND DISCUSSION

Surface Structure

For a medical polymer, it is very important that the material has not only a certain strength and stability but also good biocompatibility. The surface structure and morphology of the materials have a great influence on anticoagulation. The main purpose of radiation-induced grafting of HEMA onto a PP membrane is the improvement of blood compatibility and the prevention of coagulation.

The structures of PP and PP-*g*-HEMA membranes were measured using FTIR–PAS and ESCA methods, as shown in Figures 1 and 2.

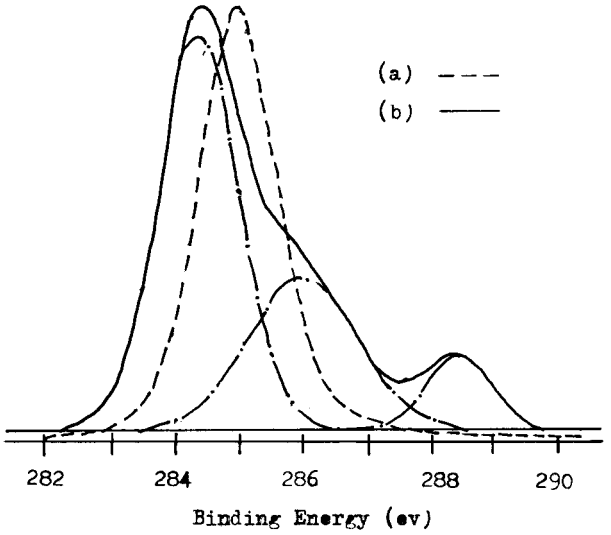

Figure 2 ESCA spectra of C_{1s} for the PP and PP-*g*-HEMA membranes: (a) PP; (b) PP-*g*-HEMA 84% graft.

When the FTIR–PAS spectra of Figure 1(a) with 1(b–e) are compared, it is seen that in the spectra of the PP-*g*-HEMA membranes two new absorption peaks appear, one at about 3400 cm^{-1} (hydroxyl group) and the other at 1720 cm^{-1} (ester carboxyl group). The two new peaks of PP-*g*-HEMA membranes all increase with the degree of grafting. The results prove that HEMA was grafted onto the PP membrane.

The ESCA spectrum of the PP membrane [Fig. 2(a)] shows only one 285.0 eV C_{1s} peak of carbon atoms connecting hydrogen or other carbon atoms. As compared with Figure 2(a), in the ESCA spectrum of 2(b), there appears two new C_{1s} peaks of 286 and 288.5 eV, ascribed to the C—O and O—C=O bonds, respectively. The O_{1s}/C_{1s} values of the PP-*g*-HEMA membranes increase with the degree of grafting, as shown in Table I.

In Figure 3, the WAXD patterns of the PP and its grafted membranes are shown. The diffraction diagram of the PP membrane shows a β-form crystallinity, with two peaks appearing at around $2\theta = 14°$ and 21°. But from the diffraction diagrams of the PP-*g*-HEMA membranes, four peaks

Table I O_{1s}/C_{1s} Values of PP and PP-*g*-HEMA Membrane Surfaces

Sample No.	Degree of Grafting (%)	O_{1s}/C_{1s}
1	0	0.026
2	30	0.383
3	84	0.605

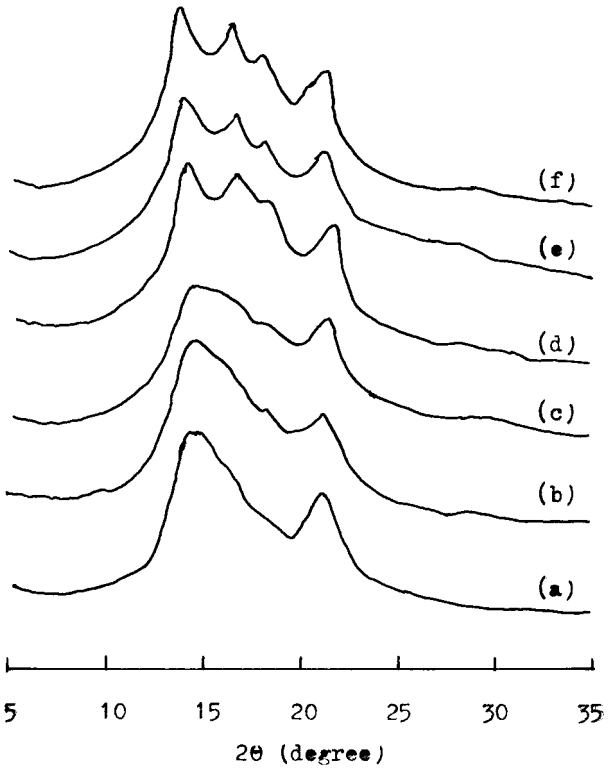

Figure 3 The X-ray diffraction diagrams of PP and its grafted membranes with various degrees of grafting (%): (a) 0; (b) 30; (c) 60; (d) 84; (e) 100; (f) 160.

can be identified in the α-form crystalline structure of PP, which corresponds to the reflections of (110), (040), (130), and (041). This diagram shows the presence of three phases: the monoclinic crystalline phase, the "smectic" phase, and the amorphous noncrystallizable phase.[13] When the spectra of Figure 3(a–e) are compared with each other, we find a transformation process of the β-form toward the α-form crystallinity with an increasing degree of grafting.

Morphology

With various grafting temperatures, the transparency of samples is different. Their properties and scaning electron micrographs are shown in Table II and Figure 4, respectively. There are distinct spheres of PHEMA embedded in the matrix of the membrane at the low grafting temperature, whose size is rather well distributed and increases with the degree of grafting. The PP-*g*-HEMA membranes are opaque. With increasing grafting temperature, the surface of PP-*g*-HEMA membranes appears to be a regular gathering structure similar to a "large intestines" type, as shown in Figure 4(d). The grafted membrane is

Table II Properties of PP and PP-*g*-HEMA Membranes Obtained at Various Grafting Temperatures

Sample No.	Degree of Grafting (%)	Grafting Temperature (°C)	Elemental Analysis (C%)	Elemental Analysis (H%)	Thickness (μm)	Transparency
1	0		85.59	14.24	30	Transparent
2	100	30	69.37	10.76	50	Nontransparent
3	114	40	67.91	10.53	55	Translucent
4	113	50	69.56	10.61	52	Transparent
5	107	60	69.79	11.19	50	Transparent
6-PHEMA			53.97	7.71		Transparent

translucent when the grafting temperature is about 40°C, while over 40°C, the PP-*g*-HEMA membranes are transparent and their surfaces are smooth. Microphase-separated copolymers may appear clear if the dispersed phase is smaller than the wavelength of visible light or if the grafted copolymers have equal or nearly equal indices of refraction. The transparency of samples

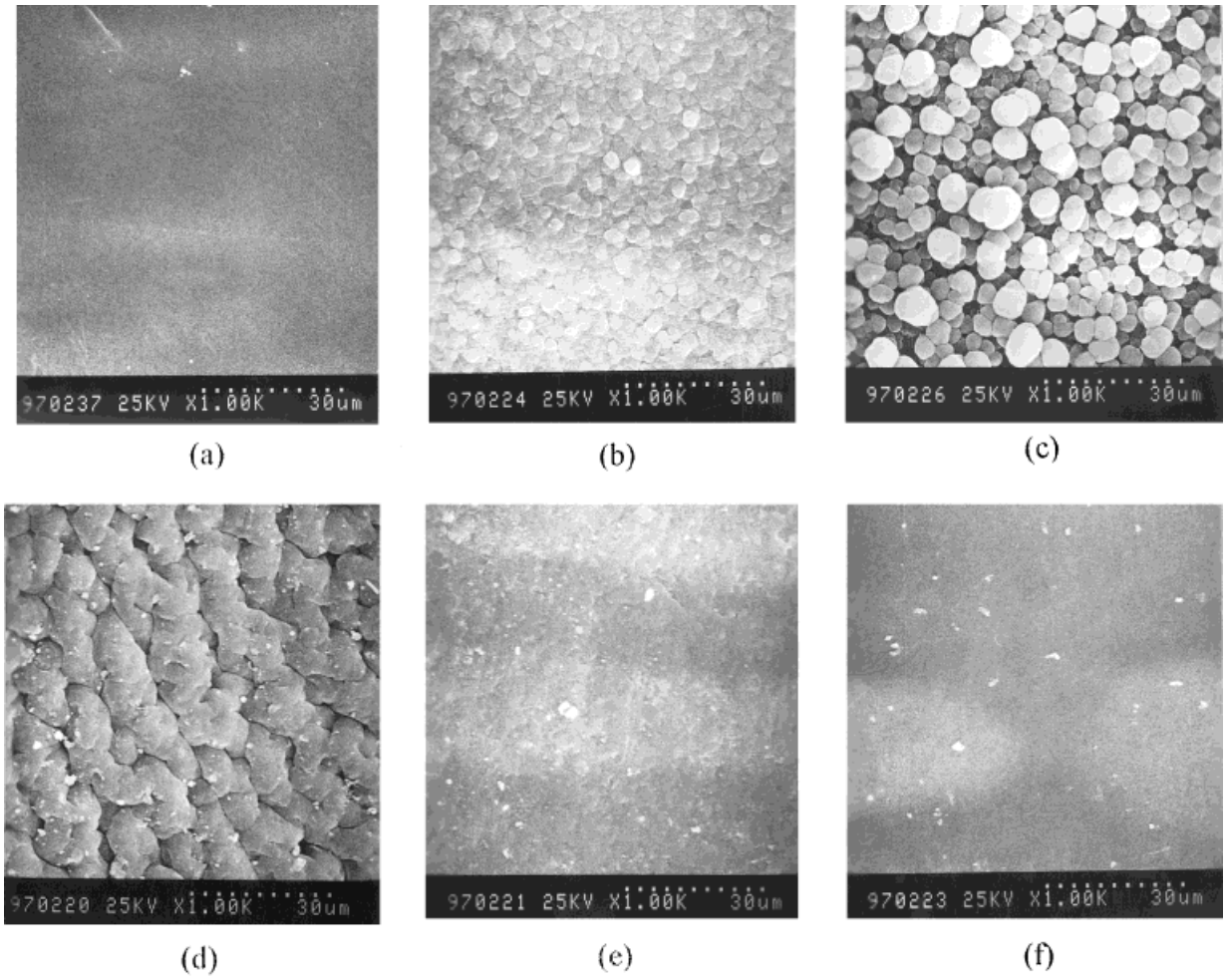

Figure 4 The scanning electron micrographs of membranes: (a) 0% graft; (b) 27% graft; (c) 64% graft. Their grafting temperatures are all 13°C. (d) 114% graft, (e) 134.5% graft, and (f) 134% graft are for membranes with grafting temperatures of 40, 51, and 59°C, respectively.

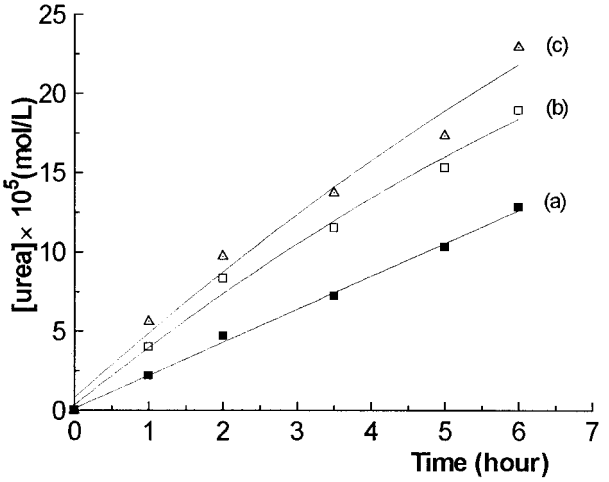

Figure 5 Change in the concentration of urea through PP and PP-*g*-HEMA membranes in a dialysis cell at 37°C: (a) 0% graft; (b) 47% graft; (c) 101% graft. Their thickness is 26, 30, and 40 μm, respectively.

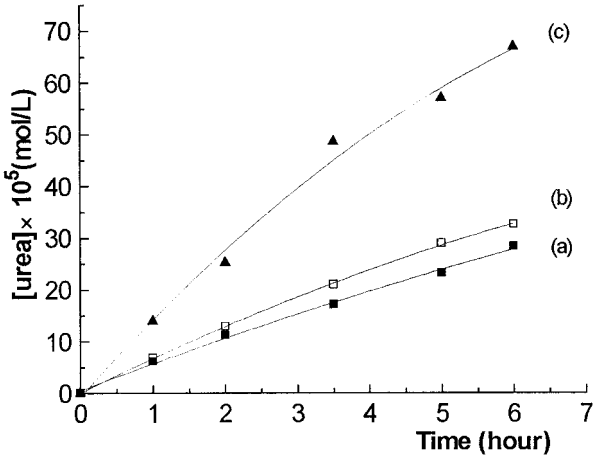

Figure 7 Change in the concentration of urea through PP-*g*-HEMA membranes obtained at different grafting temperatures: (a) 13°C, 140% graft; (b) 41°C, 135% graft; (c) 59°C, 134% graft. Their thickness is 46, 43, and 45 μm, respectively.

4 and 5 in Table II may be explained as that, under a higher grafting temperature, HEMA monomer diffuses into the PP membrane to graft-copolymerize; therefore, the formed dispersion is smaller than the wavelength of visible light.

Permeability

It is seen in Figures 5 and 6 that the permeation rate of urea and creatinine to the grafted membranes increases with the degree of grafting. The average permeation rates of urea and creatinine

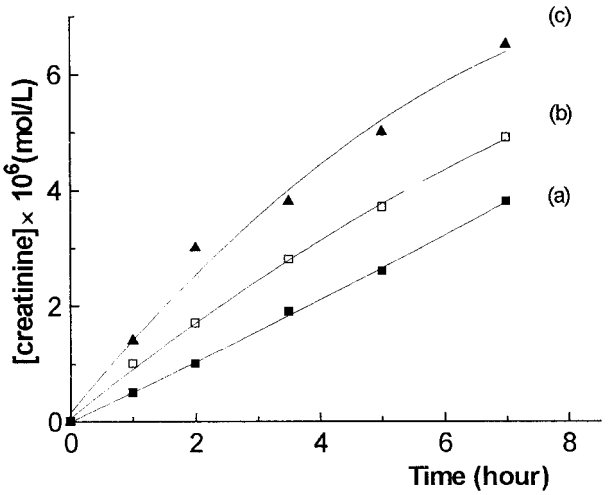

Figure 6 Change in the concentration of creatinine through PP and PP-*g*-HEMA membranes in a dialysis cell at 37°C: (a) 0% graft; (b) 47% graft; (c) 101% graft. Their thickness is 26, 30, and 40 μm, respectively.

through the PP-*g*-HEMA membrane of 101% graft are about 3.6 and 4.4 times that through the PP membrane, respectively. The permeation process is a function of the diffusion and solubility of the permeated solute in the membrane. Thus, the enhanced permeability which the PP-*g*-HEMA membranes exhibit in this study must be interpreted on the basis of solubility and diffusion effects. To permeate hydrous solutes, the hydrophilicity and crystallity of the membrane are important factors controlling the permeation rate. It is obvious that with a higher degree of grafting hydrophilicity and amorphous regions of the membrane increase, thus benefiting the mobility of the macromolecule chain segments and improving the diffusion of the permeated solute in the membrane. Compared with the PP-*g*-HEMA membrane, the permeation rate of urea or creatinine through the PP membrane is very low, due to its hydrophobic macromolecular chain retarding the diffusion of these hydrous solutes.

With PP-*g*-HEMA membranes having the same degree of grafting, their permeation properties are different if the temperature of the grafting reaction is varied. The results are shown in Figures 7 and 8. The ratios of the average permeation rate of urea and creatinine through the PP-*g*-HEMA membrane obtained at 59 to 13°C are 2.3 and 5.8, respectively, the reason being that the increase in grafting temperature improves the monomer diffusibility as well as the mobility of the polymeric chain segments. So, the grafting reaction occurs at not only the surface, but also inside the PP membrane. The graft of HEMA onto

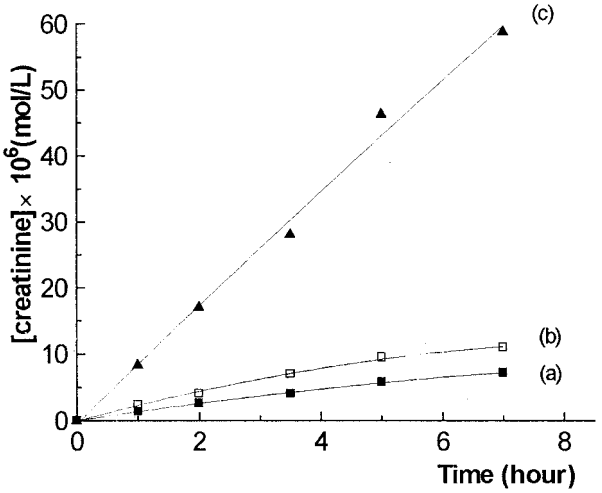

Figure 8 Change in the concentration of creatinine through PP-*g*-HEMA membranes obtained at different grafting temperatures: (a) 13°C, 140% graft; (b) 41°C, 135% graft; (c) 59°C, 134% graft. Their thickness is 46, 43, and 45 μm, respectively.

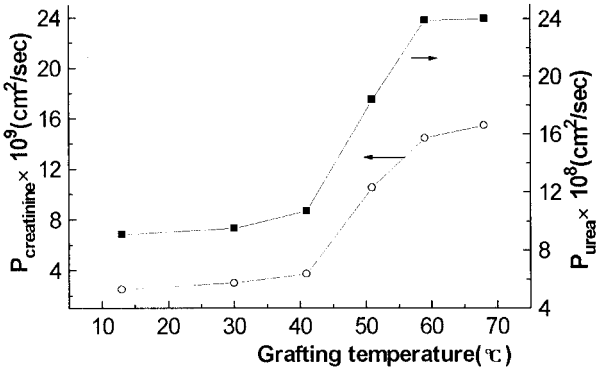

Figure 9 A relation of permeation coefficients of urea and creatinine through PP-*g*-HEMA membranes and the grafting temperature.

the whole PP membrane increases its amorphous content to yield a "looser" membrane similar to a "hole channel" mechanism which exhibits enhanced permeability toward various solutes. As compared with the surface graft, the whole graft not only changes the surface morphology, but also influences the inside regular integrity of the membrane, making a contribution to the permeability of water toward the inside of the membrane, which enhances the plasticization effect of the water on the membrane with a resulting increase in the permeation rate.

The permeation coefficients of PP and PP-*g*-HEMA membranes obtained at different degrees of grafting are listed in Table III. In this table, the ratios of the permeation coefficients of urea and creatinine, through a PP-*g*-HEMA membrane of 140% graft, to that through a PP membrane are 4.0 and 5.0, respectively. The grafting temperature has a great effect on the permeabilities of the PP-*g*-HEMA membrane. The plots of permeation coefficients of urea and creatinine through the PP-*g*-HEMA membranes versus grafting temperature are shown in Figure 9. The permeation coefficients increase rapidly with increasing grafting temperature in the range of 40–60°C. Beyond this range, the curves appear to level out. It can be deduced that the grafting reaction occurs only at the surface of the PP membrane under a low grafting temperature, while above 40°C, it trends to a whole graft.

CONCLUSIONS

1. The X-ray diffraction diagrams of the PP and its modified membranes indicate a transformation process of the β form toward the α-form crystallinity with an increasing degree of grafting.
2. The transparency of the PP-*g*-HEMA membranes increases with the grafting temperature. The transparency of the grafted membranes under a higher grafting temperature

Table III Permeability of the PP and PP-*g*-HEMA Membranes with Different Degrees of Grafting

Sample No.	Grafting Temperature (°C)	Degree of Grafting (%)	Thickness (μm)	Permeation Coefficient (cm^2/s)	
				Urea × 10^8	Creatinine × 10^9
1	13	0	26	2.3	0.5
2	13	47	30	4.7	1.1
3	13	101	40	8.3	2.2
4	13	140	46	9.1	2.5
5	41	135	43	10.7	3.7
6	59	134	45	23.9	14.4

may be deduced to be due to the monomer diffusing into the inside of the PP membrane to graft copolymerize, with the formed dispersion being smaller than the wavelength of visible light. The SEM data of the grafted membranes show clearly many spheres of PHEMA embedded in the PP matrix under a low grafting temperature. The size of these spheres is rather well distributed and increases with the degree of grafting.

3. The grafting temperature has a great effect on the permeability of the PP-*g*-HEMA membrane. The permeation coefficients of urea and creatinine through the PP-*g*-HEMA membrane obtained at 59°C were about 10.4 and 28.8 times that through the PP membrane, respectively. When the grafting reaction occurred at a higher temperature, the graft process tends to the "whole graft," thus increasing its amorphous content to yield a "looser" membrane which exhibits enhanced permeability toward various solutes.
4. The permeability of the PP membrane can be improved by using radiation-induced graft copolymerization of hydrophilic monomers, such as HEMA, onto a PP matrix and can also be controlled by changing grafting conditions, for example, grafting temperature.
5. These investigations of the permeabilities of PP-*g*-HEMA membranes prepared using the direct radiation method under different grafting conditions indicate the possibility of their practical use as dialysis membranes.

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