

UV-Induced Graft Polymerization of Polypropylene-g-glycidyl methacrylate Membrane in the Vapor Phase

Taek-Sung Hwang* and Jin-Won Park

Department of Chemical Engineering, Chungnam National University, Gung Dong, Yuseong, Daejeon 305-764, Korea

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Abstract: UV-induced graft polymerization of glycidyl methacrylate (GMA) to a polypropylene (PP) membrane was carried out in the vapor phase with benzophenone (BP) as a photoinitiator. Attenuated total reflection Fourier transform infrared spectroscopy, atomic force microscopy (AFM), and scanning electron microscopy (SEM) were utilized to characterize the copolymer. The degree of grafting increased with increasing reaction time, increased UV irradiation source intensity, and increased immersion concentration of the BP solution. The optimum synthetic condition for the PP-g-GMA membrane was obtained with a reaction time of 2 hrs, a UV irradiation source intensity of 450 W, and an immersion concentration of the BP solution of 0.5 mol/L. The pure water flux decreased upon increasing the degree of grafting and increasing the amount of diethylamino functional group introduced. The analysis of AFM and SEM images shows that the graft chains and diethylamino groups of PP-g-GMA grew on the PP membrane surface, resulting in a change in surface morphology.

Keywords: UV-induced graft polymerization, vapor phase, polypropylene, ion exchanger.

Introduction

Graft polymerization can be initiated by various methods, such as the use of high energy (γ -ray, e-beam), plasma, UV, excimer or Ar⁺ laser, chemical initiators and polymer oxidation.¹⁻⁷ Among these different techniques, radiation-induced graft polymerization is a well-known method of modifying the physicochemical properties of polymeric materials, and is of particular interest for achieving specifically desired properties, as well as excellent mechanical properties.^{8,9} It is one of the most convenient and most effective techniques for industrial use, because of the facility with which active sites can be created on many kinds of polymers, the effective penetration onto the polymer which can be achieved and the moderated reaction conditions. Radiation-induced graft polymerization can be classified based on three factors, (a) irradiation source, (b) irradiation opportunity, such as mutual, pre-irradiation,¹⁰⁻¹² and (c) monomer phase, such as vapor or liquid phase.¹³⁻¹⁵

Studies on separation using membranes have attracted a lot of interest. Membranes have been used conventionally for size based separations. The advantage of the ion exchange membrane is the possibility of controlling the pores size and obtaining long diffusive path lengths. Membranes containing

ion exchange groups are used more extensively in the separation or purification of proteins than in the medical industry.^{16,17}

Recently, Yamaguchi *et al.* introduced a "Pore control membrane" which allows plasma graft polymerization to be performed in the vapor phase.¹⁸ With graft polymerization in the vapor phase, it is possible to control of the pore size and the graft chain through the introduction of an ion exchange group, in the interior of the pores.¹⁹

In this study, to obtain the optimum synthetic conditions for aminated GMA grafted PP (PP-g-GMA) membranes, which adsorb protein such as γ -globulins, graft copolymerization of GMA to the PP membrane, using a UV irradiation source in a vacuum, was carried out in the vapor phase with BP as the photo initiator, and this was followed by subsequent functionalization with diethylamine. ATR-FTIR, AFM and SEM were utilized to characterize the membranes. We also confirmed that there was a variation in surface morphology and pure water flux according to the degree of grafting and functionalization, and examined the optimum synthetic conditions.

Experimental

Materials. PP membranes used as trunk polymers, with a mean pore size of 0.45 μ m and a diameter of 47 mm, were purchased from Whatman Co. UK. GMA was purchased from Junsei Chemical Co., Japan and was used after adding

*e-mail: tshwang@cuvic.cnu.ac.kr

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100 ppm of hydroquinone for the inhibition of the homopolymer. Benzophenone (99.5%), purchased from Aldrich Chemicals Co., USA, was used as a photoinitiator without any further purification. Diethylamine, which was used as the functionalization reagent, was obtained from Aldrich Chemical Co., USA. Other solvents were used after being obtained from Duksan Chemical Co., Korea. All reagents and chemicals used in these studies were of analytical grade.

Instruments. The amount of diethylamino groups introduced was determined by elemental analysis (EA 1110, CE Instruments, Milan, Italy) over the region $4000\text{--}400\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} to confirm the structure of the membrane, which was synthesized through a grafting reaction and subsequent functionalization. The ATR-FTIR spectra were obtained with an ATR-FTIR spectrometer (AIM-8800,

Shimadzu, Kyoto Co., Japan). The morphology change of the membrane was analyzed as a function of the degree of grafting and functionalization using AFM (SPM-9500J2, Shimadzu Co., Kyoto Co., Japan) and SEM (JSM-840A JEOL Co., Massachusetts, USA).

Grafting Copolymerization of GMA. UV induced graft polymerization was carried out in the vapor phase by means of the reaction apparatus depicted in Figure 1. The reaction apparatus was equipped with a medium pressure mercury lamp (7825, Ace glass Co., USA), a double walled quartz immersion well (7854-25, Ace glass Co., USA) and a cylindrical stainless steel cage (250 mesh). The main reactor body was made of stainless steel and Pyrex glass, with an inner diameter of 10 cm and a length of 18 cm.

Figure 2 shows the preparation procedure for PP-g-GMA

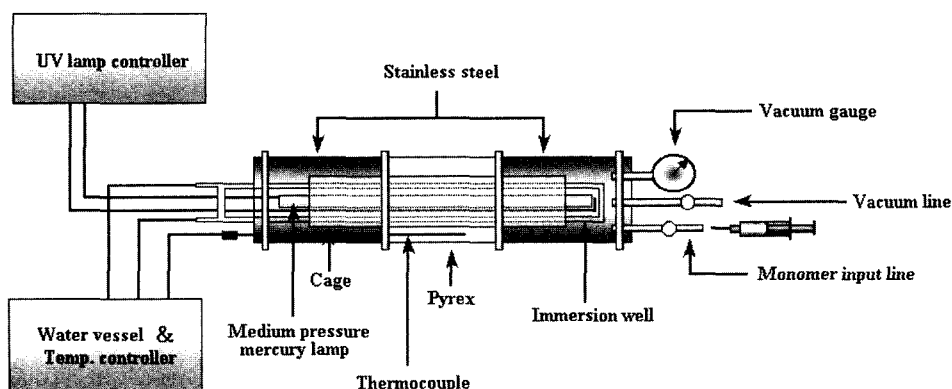


Figure 1. Schematic diagram for the UV induced graft polymerization process in the vapor phase.

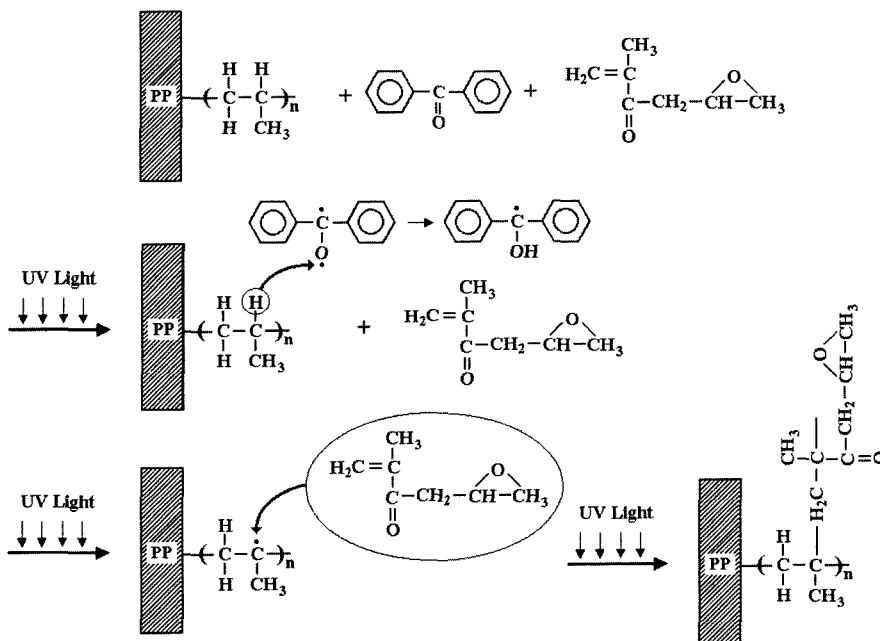


Figure 2. Preparation procedure for PP-g-GMA membrane by UV induced graft polymerization.

Table I. Reaction and Operation Conditions of UV Induced Graft Polymerization in Vapor Phase

Reaction Time (hrs)	0.5, 1.0, 1.5, 2.0, 2.5, 3.0
Immersion Conc. of BP Solution (mol/L)	0.05, 0.1, 0.5, 1.0
Intensity of UV Irradiation Source (Watt)	200, 300, 450, 500

membrane by UV induced graft polymerization.

To synthesize the PP-g-GMA membranes, PP membrane was first washed with acetone and distilled water and then dried in a dry oven at 60°C. A weighed sample of PP membranes (1.0 g on average) was immersed in a BP solution (0.05~1.00 mol/L) in methanol for 24 hrs at 30 cm.²⁰ Methanol was then evaporated from the membranes at room temperature. Thereafter, the membranes were stored in a desiccator over BP and reacted within 24 hrs of the termination of the BP immersion step. The membrane, immersed in BP solution, was put in the cage. To remove the air, nitrogen was purged through the reactor for 30 min and then the reactor was degassed at 10⁻² torr using a vacuum pump. The GMA monomer (100 mL) was inserted into the reactor by means of a syringe. UV induced graft polymerization in the vapor phase was initiated at a reaction temperature of 60°C. Table I shows the reaction and operation conditions for each trial.

After the grafting reaction, and until the homopolymer and unreacted monomer were removed by benzene, which resulted in no subsequent weight decrease, the copolymers were vacuum dried at 60°C lower, and then the degree of grafting was calculated using Eq. 1.

$$\text{Degree of grafting}(\%) = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_g is the weight of PP-g-GMA membrane, and W_o is the weight of original PP membrane used.

Functionalization Reaction. To introduce the anion exchange functional group, the PP-g-GMA membrane was immersed in the diethylamine-water (50:50, v/v) solution in a reactor and then functionalized at 50°C for 24 hrs.²¹ Following the functionalization reaction, the membrane was washed with acetone and distilled water, and dried in a dry oven at 60°C. The amount of diethylamino groups introduced was determined by elemental analysis.

Pure Water Flux of Membrane. The pure water flux experiments were carried out in a stirred test cell (XFUF 047, millipore, Massachusetts, USA) at room temperature. The membranes were precompactd for 30 min at 0.1 MPa.²¹ The pressure was then dropped to 0.1 MPa and the pure water flux was measured volumetrically at room temperature. The permeation flux of the liquid was calculated by dividing the permeation rate by the inside surface area. Then, the pure water flux was obtained from the following Eq. (2).

$$\text{Pure water flux} = \frac{(\text{Amount of permeation water})}{(\text{Surface area})(\text{permeation time})} \quad (2)$$

Results and Discussion

Figure 3 shows the ATR-FTIR spectra of the copolymers which were synthesized by means of the grafting reaction and functionalization. As shown in Figure 3(b), the ATR-FTIR spectrum included characteristic peaks of GMA which were attributed to the carbonyl (>C=O) and epoxy (-COC-) stretching vibration band between 1720 and 910 cm⁻¹. The spectra shown in Figure 3(c) is the ATR-FTIR spectra which provides confirmation of amination. The characteristic peak intensities of the carbonyl and epoxy stretching vibration bands at 1720 and 910 cm⁻¹ decreased remarkably and new broad absorption peaks at 3400 cm⁻¹ due to hydroxyl (-OH) and secondary amine (-NH) appeared in Figure 3(c).

Figure 4 shows the degree of grafting, for the PP membrane which was immersed in 0.5 mol/L BP solution, as a function of the reaction time and the intensity of UV irradiation.

As shown in Figure 4, the degree of grafting increased with increasing reaction time and increasing UV irradiation source intensity. The degree of grafting of the PP-g-GMA membrane, when analyzed according to the reaction time, at first increased rapidly and then tailed off after 2 hrs of reaction time. The degree of grafting showed a maximum with a UV irradiation source intensity of 500 W. The explanation for this behavior is that the initiator activation was increased by increasing the intensity of the UV irradiation source.

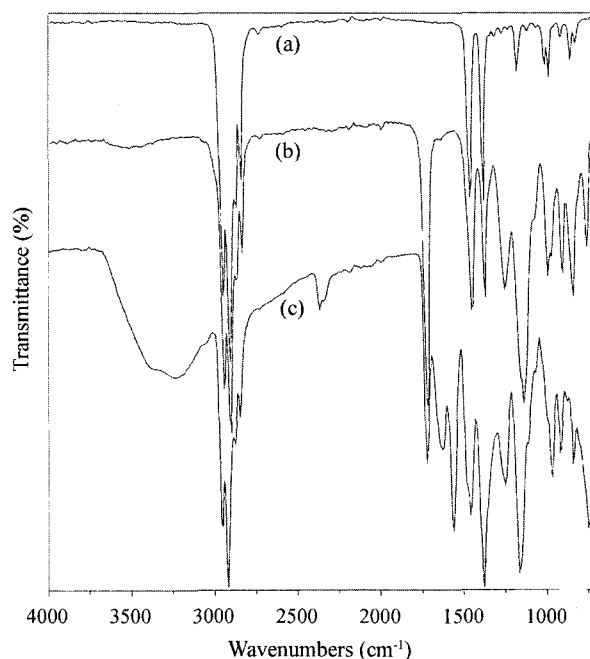


Figure 3. FT-IR spectra of (a) PP membrane, (b) PP-g-GMA membrane, and (c) aminated PP-g-GMA membrane.

However, using a UV irradiation source intensity of 500 W, was inappropriate for the preparation of the PP-g-GMA membrane, because the mechanical properties of the membrane were decreased in this case.

Figure 5 shows the degree of grafting for the PP membrane prepared using a UV irradiation source intensity of 450 W as function of the reaction time and immersion concentration of the BP solution.

As shown in Figure 5, the degree of grafting increased with increasing immersion concentration of BP solution. BP acting as a photoinitiator via immersion promoted the grafting reaction onto the PP membrane. This result fitted well with the results of Ulbricht *et al.*²³

However, the degree of grafting of the PP membrane, which was immersed in 0.5 mol/L BP solution, was higher

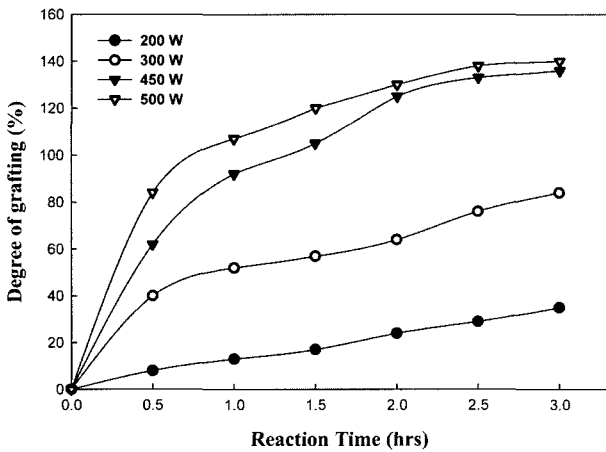


Figure 4. Effect of intensity of UV irradiation source on the degree of grafting for the PP membrane (Immersion conc. of BP solution 0.5 mol/L).

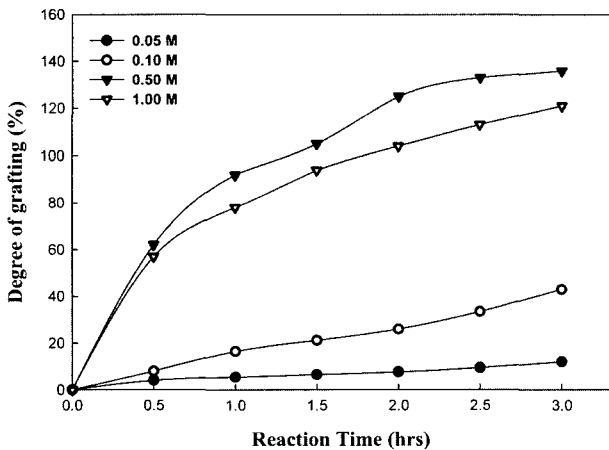


Figure 5. Effect of immersion conc. of BP solution on the degree of grafting for the PP membrane (Intensity of UV irradiation source 450 W).

than that in 1.0 mol/L BP solution. This was because the amount of radicals produced on the surface of the PP membrane as a result of the UV irradiation was increased, which caused the reaction to terminate easily. This result is in accordance with that reported by Wendal *et al.* for a graft filling membrane prepared by the photo-induced graft polymerization of methyl acrylate onto PAN based membranes.²⁰

Figure 6 shows the variation in the amination conversion and ion exchange capacity of the aminated PP-g-GMA membrane at 12 hrs of reaction time and a reaction temperature of 50 °C. The amination conversion was decreased with increasing degree of grafting. The amination conversion decreased because diethylamine did not permeate into the membrane as the degree of grafting increased. It showed that the highest ion exchange capacity obtained was 1.68

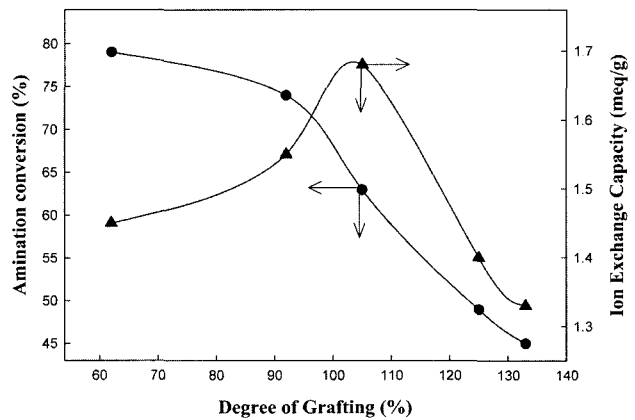


Figure 6. Conversion and anion exchange capacity of the aminated PP-g-GMA membrane depending on the degree of grafting (Reaction time : 15 hrs, and reaction temp. : 50 °C).

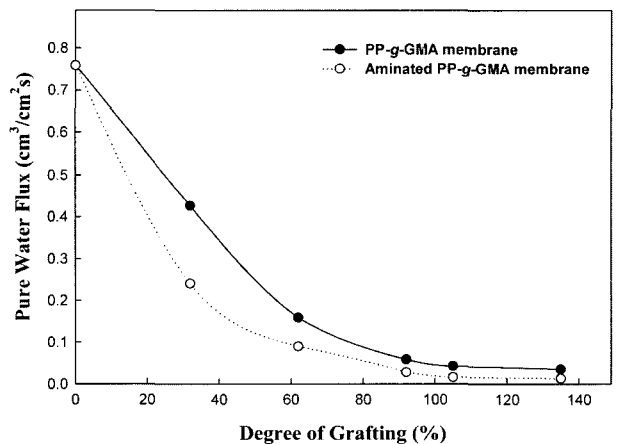


Figure 7. Pure water fluxes of the PP-g-GMA membrane and aminated PP-g-GMA membrane according to the degree of grafting.

meq/g at a degree of grafting of 105%. The amination conversion of the aminated PP-g-GMA membrane ranged from 45 to 80%.

Figure 7 shows the pure water flux of the PP membrane, the PP-g-GMA membrane and the aminated PP-g-GMA membrane as function of the degree of grafting.

As shown in Figure 7, the pure water flux of the PP-g-GMA membrane decreased from 0.759 to 0.035 $\text{cm}^3/\text{cm}^2 \cdot \text{s}$ as the degree of grafting increased. This reduction occurred because the interior pore of the flat-disc PP membrane was filled with graft chains as the degree of grafting increased. On the other hand, after amination, the pure water flux of the aminated PP-g-GMA membranes was remarkably reduced. This proves that the pores of the PP-g-GMA membranes became sufficiently filled as the amount of diethylamino group introduced increased, since it is well-known, that the diethylamino group has a very high hydrophobicity.

Figure 8 shows the three-dimensional AFM images of the original PP membrane, the PP-g-GMA membrane and the aminated PP-g-GMA membrane.

As shown in Figure 8, the original PP membrane (Figure 8(a)) had a lot of pores with such shapes as the rib-cage shape and showed a nodular morphology.²⁴ The PP-g-GMA membranes (Figure 8(b)) exhibited considerable growth of graft chains compared to the original PP membranes. The surfaces of the original PP membranes (Figure 8(a)) and PP-g-GMA membranes (Figure 8(b)) had a relatively rougher topography, while that of the aminated PP-g-GMA membrane (Figure 8(c)) was much smoother, because of the pores being filled following the introduction of the diethylamino group. Therefore, the average roughness of the aminated PP-g-GMA membrane (Figure 8(c)) was decreased as a function of the amount of diethylamino group introduced.

Figure 9 shows the surface morphology of the original PP membrane, the PP-g-GMA membrane and the aminated PP-g-GMA membrane.

The samples were placed onto a bronze stud, and sputter coated with gold before observation. The original PP membrane (Figure 9(a)) has many homogeneous pores, while the PP-g-GMA membrane (Figure 9(b)) has heterogeneous pores due to the growth of the graft chains. However, the appearance of the pores on the PP-g-GMA membrane was retained after the grafting reaction. When functionalized with the diethylamino group, the surface of the PP membranes (Figure 9(c)) was covered with a small amount of the functional group, somewhat reducing the surface porosity.

Conclusions

The PP-g-GMA membrane was synthesized by UV induced graft copolymerization with GMA onto a PP membrane, followed by subsequent functionalization with diethylamine. The degree of grafting increased with increasing reaction time, increasing UV irradiation source intensity and increas-

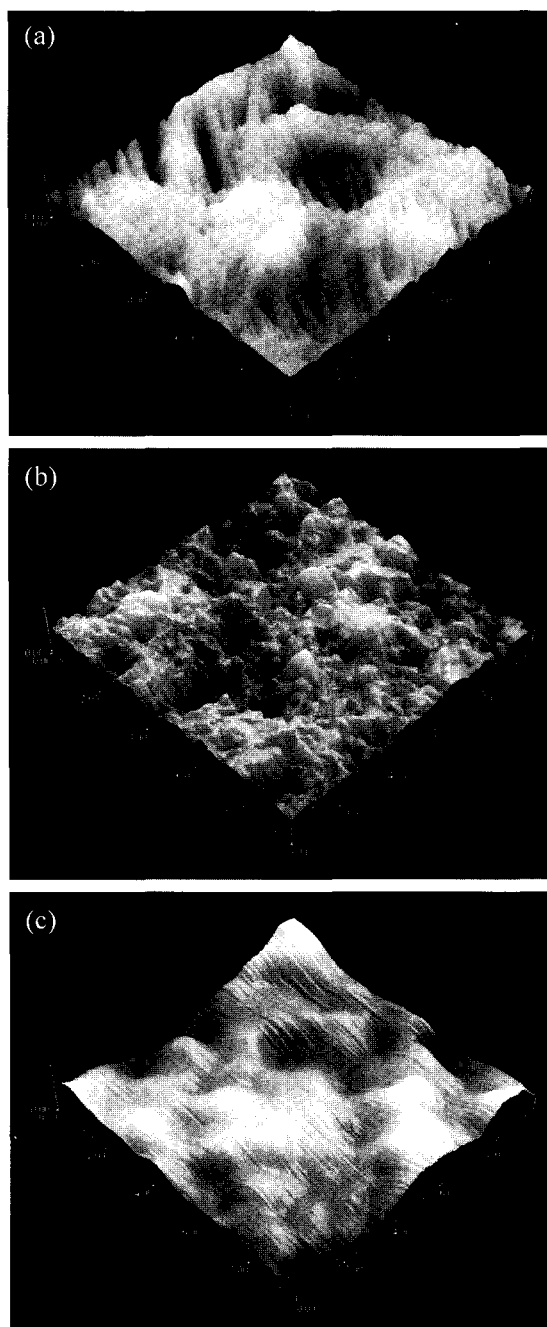


Figure 8. AFM image of PP membranes : (a) original, (b) PP-g-GMA membrane, and (c) aminated PP-g-GMA membrane (Reaction time 2 hrs and UV irradiation source 450 W). The average roughness (nm): (a) 190.8, (b) 232.0, and (c) 109.1.

ing BP concentration. It also increased rapidly at first before tailing off after 2 hrs of reaction time. The degree of grafting of the PP membrane immersed in 0.5 mol/L BP solution was higher than that of the PP membrane immersed in 1.0 mol/L BP solution. The pure water flux of the PP-g-GMA decreased from 0.759 to 0.035 $\text{cm}^3/\text{cm}^2 \cdot \text{s}$ as the degree of

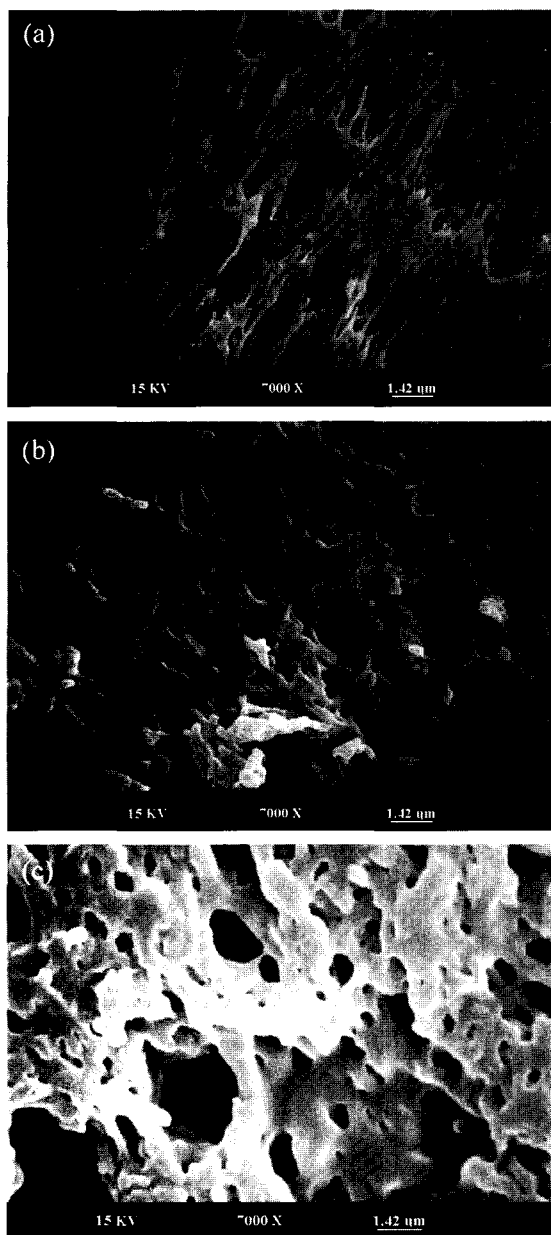


Figure 9. SEM image of PP membranes : (a) original, (b) PP-g-GMA membrane, and (c) aminated PP-g-GMA membrane (Reaction time 2 hrs and UV irradiation source 450 W).

grafting increased. After amination, the pure water flux was remarkably reduced. Based on the result of the AFM analysis, the surface of the original PP membrane had a somewhat rougher topography, while that of the PP-g-GMA membrane and that of the aminated PP-g-GMA membrane were much smoother. Based on the results of the SEM anal-

ysis, the PP-g-GMA membrane had heterogeneous pores due to the growth of the graft chains and in the case of the aminated PP-g-GMA membrane, the pores were found to be filled by the diethylamino group.

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