Characterization of Acrylic Acid-Grafted PP Membranes Prepared by Plasma-Induced Graft Polymerization

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ABSTRACT: Acrylic acid (AA)-*g*-polypropylene (PP) membranes were prepared by grafting AA on to a microporous PP membrane via plasma-induced graft polymerization. The grafting of AA to the PP membrane was investigated using Fourier transform infrared spectroscopy (FTIR). Pore-filling of the membranes was confirmed by field emission-scanning electron microscopy (FESEM) and energy dispersing X-ray (EDX). Ion exchange capacity (IEC), membrane electric resistance, transport number and water content were measured and analyzed as a function of grafting reaction time. The prepared AA-*g*-PP membranes showed moderate electrochemical properties as a cation-exchange membrane. In particular, membranes with a degree of grafting of 155% showed good electrical properties, with an IEC of 2.77 mmol/g dry membrane, an electric resistance of 0.4 Ω cm^2 and a transport number of 0.96. Chronopotentiometric measurements indicated that AA-*g*-PP membranes, with a high IEC had a sufficient conducting region in the membrane. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 2314–2320, 2007

Key words: membrane; ion-exchange membrane; plasma-induced graft polymerization; polypropylene; acrylic acid

INTRODUCTION

A demand for ion exchange membranes has been increasing for applications in batteries, fuel cell, sensors, and electrically driven processes.[1] The requirements for an ion exchange membrane with appropriate properties for a specific application has encouraged the development of new, advanced methods for ion exchange membranes including latex,[2] polymer blending,[3] paste methods[4] bulk polymerization[5] and graft polymerization.[6] In particular, the difficulty in preparing new monomers with ion exchange groups has led to extensive investigations into the modification of existing polymers which involve graft polymerization by means of electron-beam, γ-ray, and ultraviolet light irradiation or by a plasma.[6]

Plasma treatment is a very useful and effective method for modifying a surface of the polymer by introducing a functional group onto the surface of the polymer.[7] However, in spite of the widespread use of plasma treatment, the preparation of ion exchange membranes by this method has not been extensively studied. Several investigators attempted to prepare ion exchange membranes by modifying commercial porous membranes via a plasma polymerization coating.[8–12] Monomers containing —SO^{3-}, COO$^-$, and PO$_3^{2-}$ moieties are generally used. Among such monomers, acrylic acid (AA) containing a COO$^-$ moiety has received great attention due to its high polarity, high charge density and low price. However, a full investigation of the electrochemical properties of AA plasma polymer coated membranes has not been reported. In our previous study,[13] we reported on the preparation and characterization of an ion exchange membrane obtained by modifying microporous polypropylene (PP) membranes by a plasma polymerization coating of AA. However, in spite of the optimized experimental conditions for the membrane preparation, the electrochemical properties of the membranes were not satisfactory because the AA coating, produced by plasma polymerization showed only a limited ion exchange capacity (IEC) and the membranes also had a high ohmic resistance. Plasma-induced graft polymerization can be an alternative to plasma polymerization and, in some cases, improves the electrochemical properties of the membrane because a sufficient amount of monomers can be polymerized when the reaction is conducted using a liquid monomer solution. Plasma-induced graft polymerization consists of two steps: the first step is a plasma treatment to generate polymer radicals on the substrate membrane; the second is the grafting and polymerization of the monomer with the radicals.

TABLE I
Technical Data for the Celgard® 2500
Microporous Membrane

Properties	Unit	Typical value
Porosity	%	55
Pore size	μm × μm	0.209 × 0.054
Thickness	μm	20 (Measured value)

When a porous membrane is utilized as a substrate, plasma-induced graft polymerization occurs on both the outer surface of the membrane and on the surfaces of internal pores in the membrane.[14,15]

In this study, an attempt was made to prepare a cation exchange membrane by grafting AA on to a commercial microporous PP membrane via plasma-induced graft polymerization. The prepared AA-g-PP membranes were systemically characterized in terms of chemical and physical structure, IEC, membrane electrical resistance, water content, transport number and chronopotentiometric response.

EXPERIMENTAL

Materials

A microporous PP membrane (Celgard® 2500, Hoechst Celanese, Germany) was used as a substrate. The technical values of the substrate membrane are listed Table I. AA (ACROS) was used as a grafting monomer to introduce an anion-fixed moiety onto the substrate membrane. To eliminate the presence of inhibitors in the AA, it was passed through an inhibitor removal column (Aldrich). A 3 wt % solution (80 mL for each reaction) was then prepared by dissolving the purified AA in water.

Membrane preparation

A square film (3 cm × 7 cm) of the substrate membrane was placed in a glass ampoule. Radicals were generated on the substrate membrane by a 30 s plasma treatment under a 10 Pa argon atmosphere in a radio-frequency plasma generator (model YSE-03F, Youngsin-RF, Korea). The plasma generator was operated at 13.65 MHz and delivered 10 W. After the plasma treatment, the substrate membrane was immediately immersed in the AA solution to initiate the graft polymerization. The reaction proceeded without being in contact with air at 50°C for a predetermined time. A low pressure in the glass ampoule was maintained by closing and sealing it completely. The grafted films were rinsed for 24 h with a water and methanol mixture to remove unreacted monomers. The prepared AA-g-PP membranes were dried in a vacuum oven at 50°C. The thicknesses of the dried membranes were measured by means of a micrometer (Mitutoyo, Japan). The scheme for the preparation of the AA-g-PP membranes is illustrated in Figure 1.

Chemical verification and morphological evaluation

The chemical structure of the prepared membranes was confirmed by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, 460 Plus, Jasco, Japan). Pore structures of the membranes before and after grafting were observed using a field emission scanning electron microscope (FESEM, S-4700, Hitachi, Japan). The graft distribution over a cross section of the membrane was analyzed by an energy dispersing X-ray (EDX, Hitachi, Japan).

Electrochemical characterization

The electrochemical properties of the prepared membranes were determined using a procedure described in a previous report.[16] The water content of the membrane was determined by measuring the weight of the wet and dry membrane. The transport number of counter ions through the membranes was measured by the emf method using a two-compartment diffusion cell and a pair of Ag/AgCl reference electrodes. Electrical resistance was measured using a clip cell and LCZ meter (2321, NF Electronic Instruments, Japan) at 100 kHz with membranes conditioned in $0.5M$ NaCl solution for 24 h. Chronopotentiometric curves were obtained using a conventional two-compartment cell (each volume of 150 cm^3) using a 0.025 mol dm^{-3} NaCl as the electrolyte. The IEC was determined by measuring the number of ion-exchange groups in the membrane by a back titration method. The membranes, in the COOH, form were immersed in a $0.1N$ NaOH solution at room temperature for 24 h. They were then washed with distilled water to remove the excess NaOH. The NaOH remaining in the solution was titrated with $0.01N$ HCl solution.
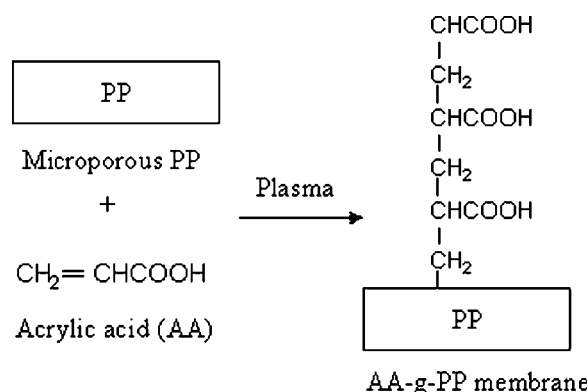

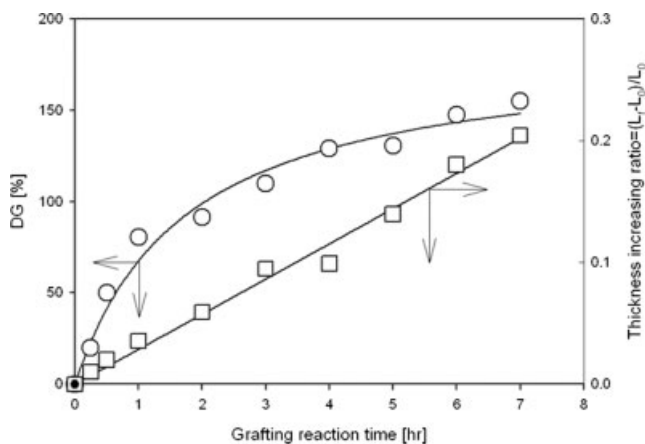**Figure 1** Scheme for the preparation of AA-g-PP membrane.

Figure 2 DG and thickness increasing ratio with grafting reaction time.

RESULTS AND DISCUSSION

Behavior of grafting as a function of reaction time

Figure 2 depicts the change in the degree of grafting (DG) and thickness increasing ratio of the membrane with grafting reaction time. The DG and thickness increasing ratio are defined as follows:

$$\text{Degree of grafting (DG)} = \frac{W_f - W_0}{W_0} \times 100 \quad (1)$$

$$\text{Thickness increasing ratio} = \frac{L_f - L_0}{L_0} \quad (2)$$

where W and L are the weight and thickness of the membrane and the subscripts 0 and f refer to the situation before and after grafting.

The DG abruptly increased at the initial stage of the grafting reaction and then increased more slowly, while the thickness increasing ratio increased linearly with grafting reaction time. The pattern of the increase in membrane thickness reflects the graft distribution over the cross section of the membrane during the grafting reaction. The linear increase in membrane thickness indicates that AA sufficiently diffused into the internal pores of the PP substrate membrane because of the relatively low reaction rate of AA and the grafting reaction occurred uniformly over the cross section of the membrane.[17,18]

Figure 3 shows FESEM images of the surfaces of the AA-g-PP membranes as a function of DG. The pores of substrate membrane were progressively filled with the grafted monomers with grafting reaction time. Most of the pores at the surface were filled when the DG approached 155% as indicated in Figure 3(c). Figure 4 shows cross sections of the same membranes that are shown in Figure 3. As the grafting reaction proceeded, more internal pores of PP membranes were filled with more grafted monomers. Most

of the internal pores were filled when the DG approached 155%. The cross section of the membrane with 155% of the DG as shown in Figure 4(c) was also analyzed by EDX. In Figure 5, the transverse distribution of carbon and oxygen of the membrane are presented with FESEM images. The transverse distributions of carbon and oxygen were uniform, which were caused by uniformly filled pores over the cross section of the membrane. The FESEM and EDX results shown in Figures 4 and 5 were in reasonable agreement with the results for the membrane thick-
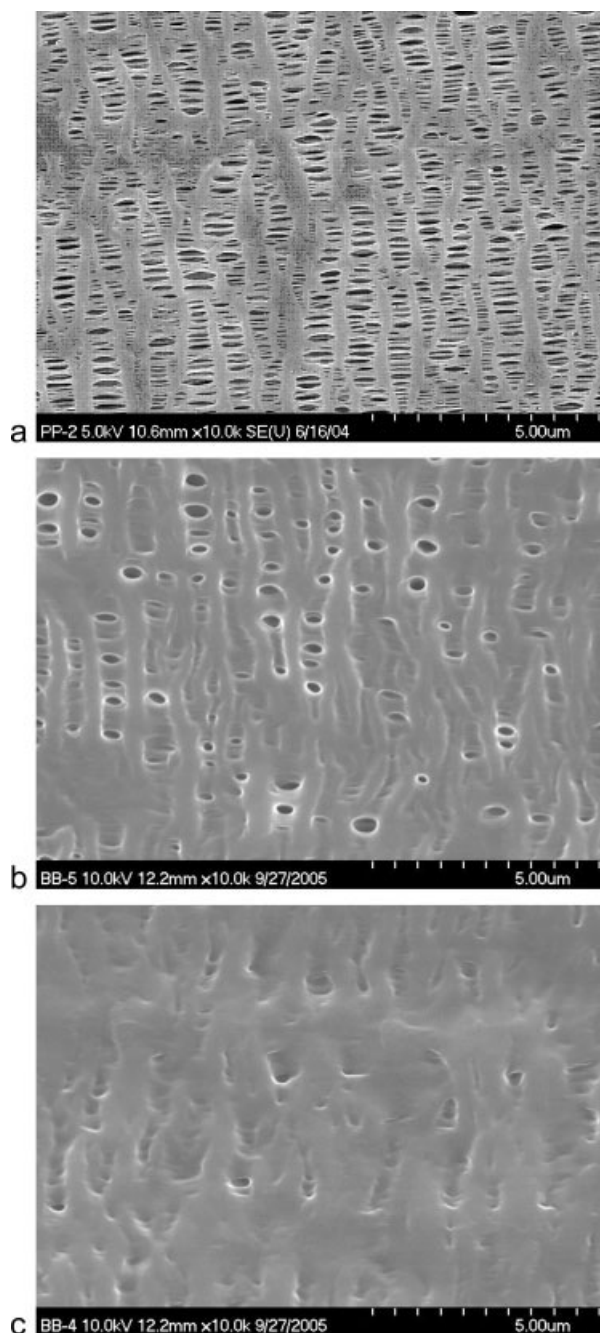

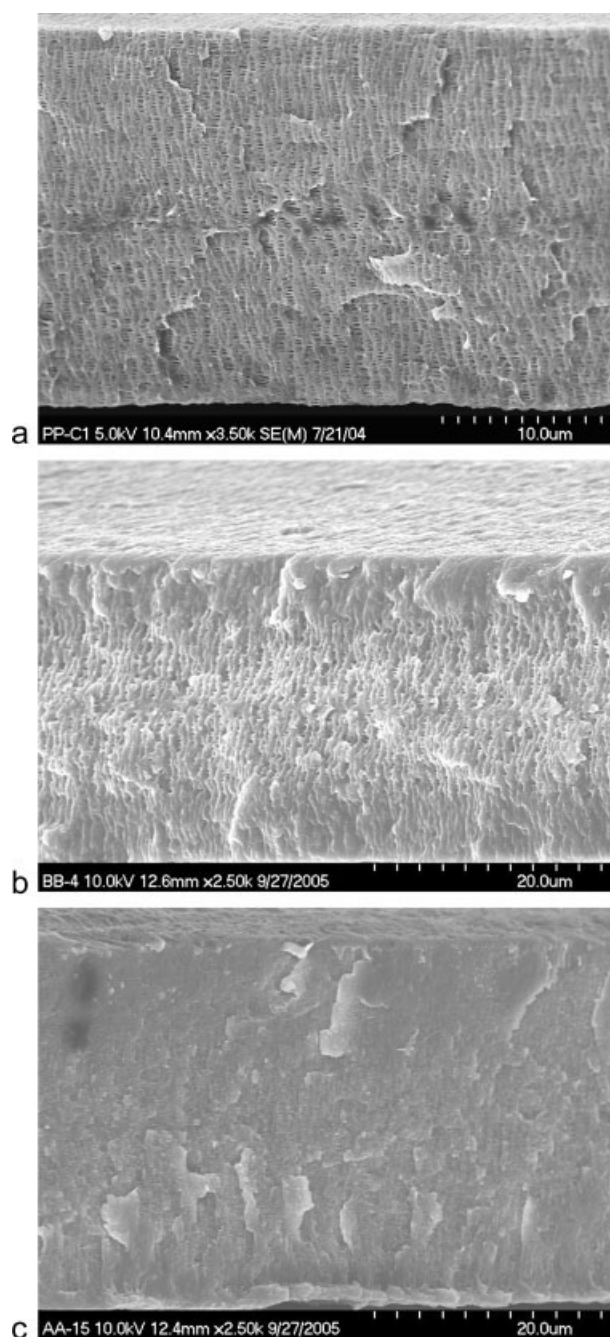**Figure 3** FESEM micrographs of the surface of (a) original PP, (b) 110% and (c) 155% (×10,000).

Figure 4 FESEM micrographs of the cross sections of (a) Original PP (×3500); (b) 110% (×2500); and (c) 155% (×2500), respectively.

ness depicted in Figure 2, indicating a the uniform graft distribution.

Figure 6 shows the FTIR spectra of the base PP membrane, the AA-*g*-PP membrane measured in the attenuated total reflection (ATR) mode. In the AA-*g*-PP membrane, IR peaks corresponding to C=O stretching from the AA moiety were observed at 1721 cm^{-1}. These peaks, however, were not observed in the base PP membrane, indicating that AA was successfully grafted to the base membrane.

Electrochemical properties of AA-*g*-PP membrane

Since the electrical resistance of an ion exchange membrane is a primary determinant of the energy requirement for an electrically driven process, a low electric resistance is necessary.[1] The electrical resistance of the prepared AA-*g*-PP membranes was measured. Figure 7 shows the relationship between IEC and electrical resistance as a function of the DG of membranes. The IEC increased and the electrical resistance decreased with increasing DG because of the introduction of AA onto the base membrane. These results are consistent with the general relationship between IEC and electrical resistance.[19] In Table II, the electrical resistance of the membrane with 130% DG was compared with that of a commercial cation exchange membrane CM-1, which has the same IEC as that of the prepared membrane. The specifications of CM-1 can be found elsewhere.[20] Even though the acid group (COO^{-}) of the AA-*g*-PP membrane is weaker than the (SO$_3^{-}$) of CM-1, the electrical resistance of the prepared membrane was much lower than that of CM-1 due to the use of a substrate membrane with a low thickness. This indicates that the prepared membranes are economically attractive due to the low power consumption as the result of the low resistance of the membrane.

Figure 8 represents the relationship between IEC and water content as a function of the DG of the AA-*g*-PP membranes. Generally, the water content of an ion exchange membrane significantly depends on IEC and increases with increasing IEC because of the induction of hydration.[19] The water content of the prepared AA-*g*-PP membrane increased slightly with increasing IEC. Moreover, as listed Table II, the water content of the prepared membrane was much higher than that of CM-1. The low sensitivity with IEC and the high water content may be due to the noncrosslinked structure of the grafted AA by the plasma-induced graft polymerization without the use of a crosslinker.

Figure 9 shows the relationship between IEC and transport number as a function of the DG of AA-*g*-PP membranes. The transport number increases with increasing DG because more ion exchangeable groups excluded more coions. As listed Table II, the transport number of the prepared membrane was lower than that of CM-1. There are two reasons for the low transport number of the membrane. One is the weak acidity of COO^{-} with the AA-*g*-PP membrane. The other is the high water content as shown in Figure 8 and Table II.

To obtain data on the quantitative fraction of the conducting region of the prepared AA-*g*-PP membranes, chronopotentiometric curves were obtained. Chronopotentiometry is a powerful electrochemical method, which is used to monitor changes in elec-
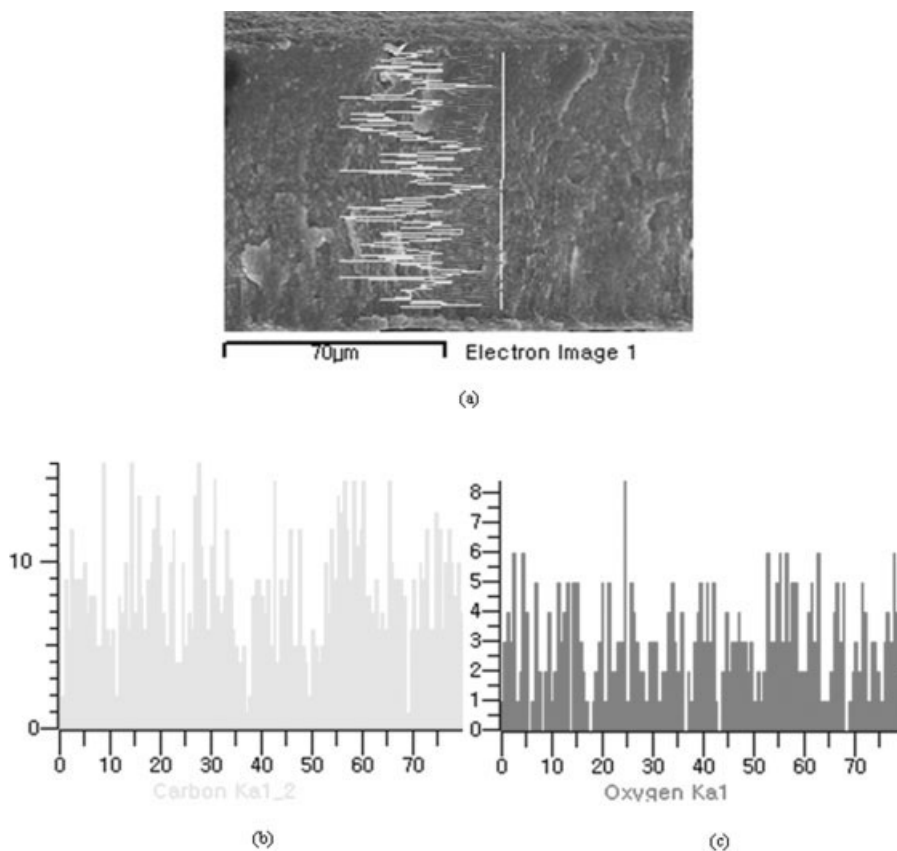
Figure 5 (a) FESEM-EDX images of the AA-*g*-PP membrane with 155% DG; (b) transverse distribution of carbon; (c) transverse distribution of oxygen.

trode potential produced by a controlled current as a function of time and has been used to study kinetic effects, such as adsorption and transport phenomena, near an electrode surface. It has also been used to study transport processes near and through ion exchange membranes.[21–27] The total potential drop

measured is composed of the overvoltage of the membrane potential and the ohmic potential drop which is caused by concentration polarization in the ion exchange membrane. The resulting changes in potential give essential information regarding polarization phenomena, electrical conductivity, heterogeneity, and the values for permselectivity and transport number of the ion exchange membrane. Choi
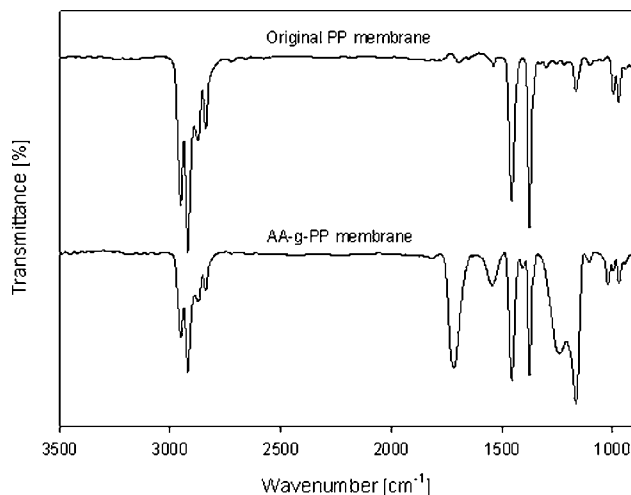

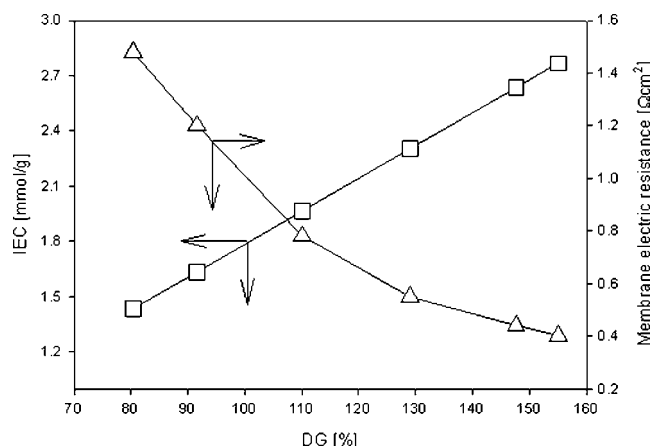**Figure 6** ATR-FTIR spectra of original PP and AA-*g*-PP membranes.

Figure 7 Behavior of IEC and electrical resistance of the membranes as a function of the DG.

TABLE II
Comparison of the General Properties of the Prepared Membranes With CM-1

Properties	AA-g-PP membrane (130 % DG)	CM-1
IEC (mmol/g)	2.3	2.3
Thickness (μm)	22	145
Membrane electric resistance (Ω cm²)	0.50	1.45
Transport number (emf)	0.91	0.98
Water content (%)	75	36

et al.[28] reported that a quantitative fraction of the conducting region of ion exchange membrane can be estimated using chronopotentiometric curve of ion exchange membrane and the following modified Sand equation.

$$\varepsilon = \frac{2i\tau^{1/2}(\bar{t}_k - t_k)}{C_0 z_k F(\pi D)^{1/2}} \quad (3)$$

where ε is the fraction of the conducting region of an ion exchange membrane, i is the current density, τ is the transition time determined by chronopotentiometric measurements, $\bar{t}_k$ and t_k are the transport numbers of the counterion k in the membrane and solution phase, respectively. D is the diffusion coefficient of the electrolyte in the solution, F, the Faraday constant, C_0, the concentration, and z, the charge number. The chronopotentiometric curves of the AA-g-PP membranes are represented in Figure 10. The potential drop across the membrane at a constant current density (25.0 A m^{-2}) is shown for the tested membranes as a function of time. Table III lists the results of the chronopotentiometry calculated using the modified Sand equation. The transition time (τ) was determined through the intersection of the tangents with
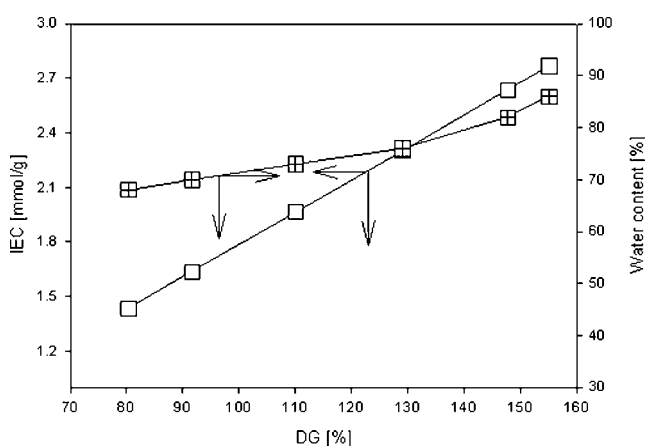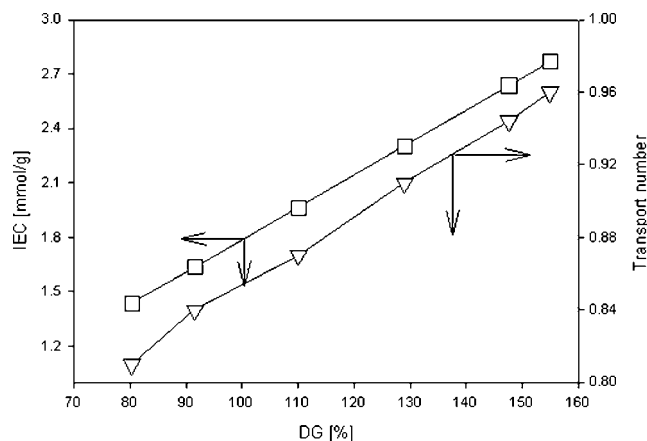
Figure 9 Behavior of IEC and transport number of the membranes as a function of the DG.

the first and second stages of the curve. The calculated transport number ($\bar{t}_k$) of the tested membrane was less than unity, indicating the presence of a nonconducting region existed in the membrane. The fraction of conducting region (ε) was calculated using the diffusion coefficient of NaCl, 1.61×10^{-5} cm²/s and the transport number for Na⁺ ion in the solution phase, 0.396, obtained from the literature.[29] The results show that the fractional conducting region of the membrane increases with increasing IEC, indicating that more charged groups are present on the membrane surface. The membrane with an IEC of 2.77 mmol/g had a high fractional conducting region of 0.930 comparable to that 0.922 of CM-1.[18]

CONCLUSIONS

AA-g-PP membranes, prepared by plasma-induced graft polymerization, were characterized. As the grafting reaction proceeded, the pores of the substrate
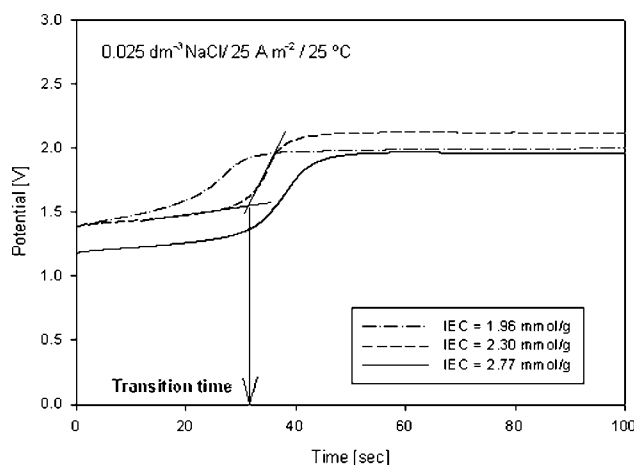
Figure 8 Behavior of IEC and water content of the membranes as a function of the DG.

Figure 10 Chronopotentiometric curves of the AA-g-PP membranes.

TABLE III
Electrical Properties Obtained From
Chronopotentiometric Curves of AA-*g*-PP Membranes

Characteristic values	IEC (mmol/g)		
	1.96	2.30	2.77
Transition time, τ (sec)	22.57	30.94	31.98
Transport number, $\bar{t}_k$	0.870	0.910	0.960
Fraction of conducting region, ε	0.657	0.834	0.930

membrane were progressively filled with grafted AA over the cross section of the membranes. Complete pore-filling was achieved when the DG approached 155%. The prepared AA-*g*-PP membrane showed moderate electrochemical properties as a cation-exchange membrane. In particular, the membranes with a DG of 155% showed good electrical properties such as an IEC of 2.77 mmol/g dry membrane, an electric resistance of 0.4 Ω cm^2. Even though the AA-*g*-PP membrane had a high water content (86%) caused by the noncrosslinked structure by plasma-induced graft polymerization without the use of a crosslinker, the transport number of the membrane with DG of 155% was 0.96, comparable to that of a commercial membrane, CM-1 with sulfonic acid groups because of the high conduction region in the membrane. Chronopotentiometric curves of the membranes revealed that the membrane had a high IEC and a satisfactory conducting region. The results of this study showed that plasma-induced graft polymerization represents a promising method for preparing carboxylic acid cation-exchange membranes with moderate electrical properties.

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