Preparation and Study of Cellulose Acetate Membranes Modified with Linear Polymers Covalently Bonded to Starburst Polyamidoamine Dendrimers

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ABSTRACT: Novel ion-selective membranes were prepared by means of the noncovalent modification of a cellulose acetate (CA) polymer with either poly(ethylene-*alt*-maleic anhydride) or poly(allylamine hydrochloride) chains covalently linked to Starburst amine-terminated polyamidoamine (PAMAM) dendrimers generations 4 and 3.5, respectively. Linear polymer incorporation within the porous CA membrane was performed with mechanical forces, which resulted in modified substrates susceptible to covalent adsorption of the relevant dendritic materials via the formation of amide bonds with a carbodiimide activation agent. The membranes thus prepared were characterized by chemical, physical, and spectroscopic measurements, and the results indicate that the dendrimer peripheral functional groups were the species that participated in the ion-exchange events. The prepared materials were also evaluated for their ion-exchange permeability with sampled current voltammetry experiments involving cationic and anionic species {$[Ru(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, respectively} as redox probe molecules under different pH conditions. As expected, although permeability was favored by opposite charges between the dendrimer and the electroactive probe, a clear blocking effect took place when the charge in the dendritic polymer and the electroactive complex was the same. Electrochemical impedance spectroscopy measurements, on the other hand, showed that the PAMAM-modified membranes were characterized by good selectivity and low resistance values for multivalent ions compared to a couple of commercial ion-exchange membranes. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2898–2906, 2008

Key words: dendrimers; membranes; modification; ion exchangers

INTRODUCTION

The development of new polymeric materials oriented to the design and construction of membranes represents one of the most important and active research areas in the world. Size exclusion and noncovalent interactions of species in solution and specifically positioned functional groups within a membrane structure have been successfully used to prepare materials that offer the possibility of the efficient separation of compounds in a given mixture; this has resulted in a wide variety of economically and technically feasible technologies that are currently being used in various industrial processes.[1,2]

Among the many reports directed toward the development of novel membrane materials, Sata and coworkers[3–6] have reported extensive and interesting work on the preparation and modification of ion-exchange membranes. They have, for instance, successfully used chloromethylstyrene and divinylbenzene copolymers to synthesize phosphonic acid and sulfonic acid cation-exchange membranes,[3] and they have modified commercial ion-exchange membranes with polyaniline in the presence of ammonium peroxodisulfate[4] and cyclodextrins[5] to improve membrane permeability properties. In a complementary fashion, other groups have also studied the transport properties of diverse membrane-type materials, including thin films of Prussian blue[7–9] or thiolated compounds chemically adsorbed on gold nanotubules,[10,11] which, as it was shown, could be electronically manipulated to allow or exclude the passage of either anions or cations.

On the other hand and since their appearance approximately 20 years ago, dendrimers have attracted the attention of the scientific community because of their fascinating structure and unique properties.[12–14] Dendritic molecules are monodisperse species characterized by a highly branched structure that expands radially from a single core, a feature that results in a globular molecule that is characterized by internal void regions and a chemical environment that can be significantly different from that of the surface groups.[15,16] Because of the unique chemical and structural properties of
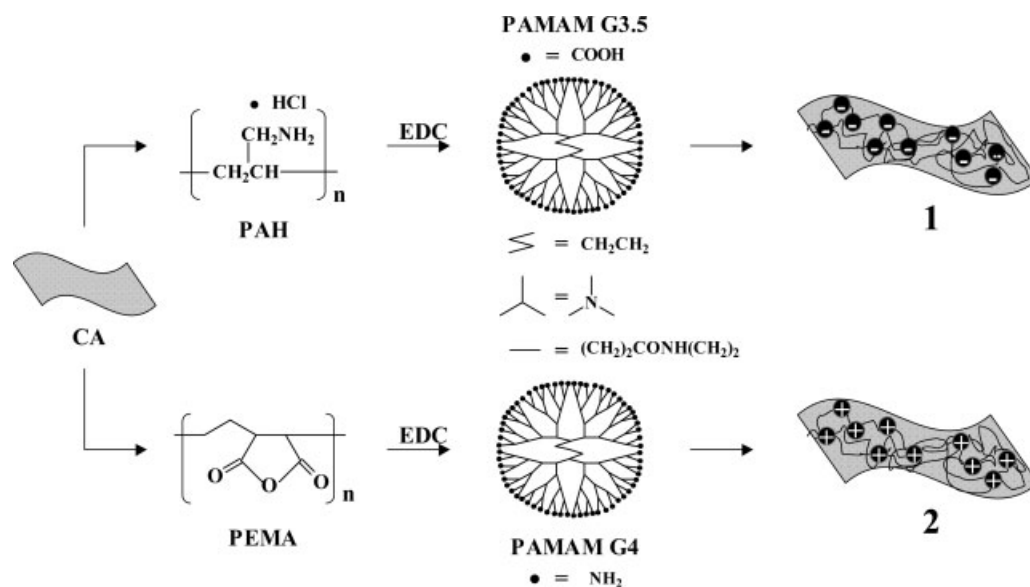
Scheme 1 Schematic representation of the CA modification protocol: the (1) the cation-exchange membrane and (2) the anion-exchange membrane.

dendrimers, a number of potential applications have been proposed, some of which include the design and preparation of chemical sensors,[17–19] the dendritic encapsulation of transition-metal ions,[20–23] the controlled release of small compounds,[24] and their use in membrane chemistry,[25,26] among many others.[27,28]

In the area of membrane construction with dendrimers, Crooks and coworkers[29–31] have developed novel polymeric composite films formed from multilayers of amine-terminated polyamidoamine (PAMAM) dendrimers and poly(maleic anhydride)-c-(methyl vinyl ether) (Gantrez) grafted onto Au-coated Si wafers. Because of the protonation properties of the amine surface groups of the surface anchored PAMAM dendrimers, these composite materials exhibited pH-switchable permeation selectivity for anionic and cationic redox-active probe molecules. The membranes reported by Crooks and coworkers, however, were prepared as ion-exchange thin films on top of a solid electrode, and following their ideas, we became interested in the preparation of similar PAMAM-dendrimer-based coatings that could be directly constructed within the structure of a porous membrane material. Considering that PAMAM dendrimer molecules can also be obtained with —COOH terminal groups, we also wanted to extend the idea of Crooks and coworkers to a pH-tunable cation-exchange membrane.

In this article, we report our results on the covalent attachment (via carbodiimide coupling[32–34]) of PAMAM generation 3.5 (G3.5) and generation 4 (G4) dendrimers[35,36] (bearing 64 carboxylic acid or amine terminal groups, respectively) to linear polymers characterized by complementary carboxylic or amine side groups [poly(allylamine hydrochloride) (PAH) and poly(ethylene-alt-maleic anhydride) (PEMA), respectively], which were previously incorporated into the structure of commercial cellulose acetate (CA) membranes, as shown in Scheme 1. The modified materials thus prepared showed that, as expected, the permeability of electroactive probe molecules was pH dependent and that the ion-exchange capacity (mmol/g) values, as measured with the Fisher and Kunin method,[37–39] fell within the range that characterizes commercial ion-exchange membranes.

EXPERIMENTAL

Materials

PEMA (molecular weight = 100,000–500,000), poly (allylamine) hydrochloride (molecular weight = 15,000), $FeCl_2 \cdot 4H_2O$, (1-[3-dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC), HOC (COOH)(CH₂COOH)₂, and G3.5 and G4 Starburst PAMAM dendrimers were obtained from Aldrich with the highest available purity and were used without further purification. Analytical-grade $Ru(NH_3)_6Cl_3$ and $K_3Fe(CN)_6$ were obtained from Strem Chemicals and Merck, respectively. KCl, KI, KBr, NaCl, $CaCO_3$, Na_2SO_4, $Na_2S_2O_3 \cdot 5H_2O$, $FeCl_3$, and Na_2CO_3 were purchased from J. T. Baker, and LiCl was purchased from Fluka Chimie. Whereas the supporting electrolyte solutions for electrochemical experiments consisted of phosphate buffer solutions (pH 12, 7, and 2; ionic strength = 0.1) made with KH_2PO_4, Na_2HPO_4, and H_3PO_4 (all obtained from J. T. Baker), the solutions used for ion-
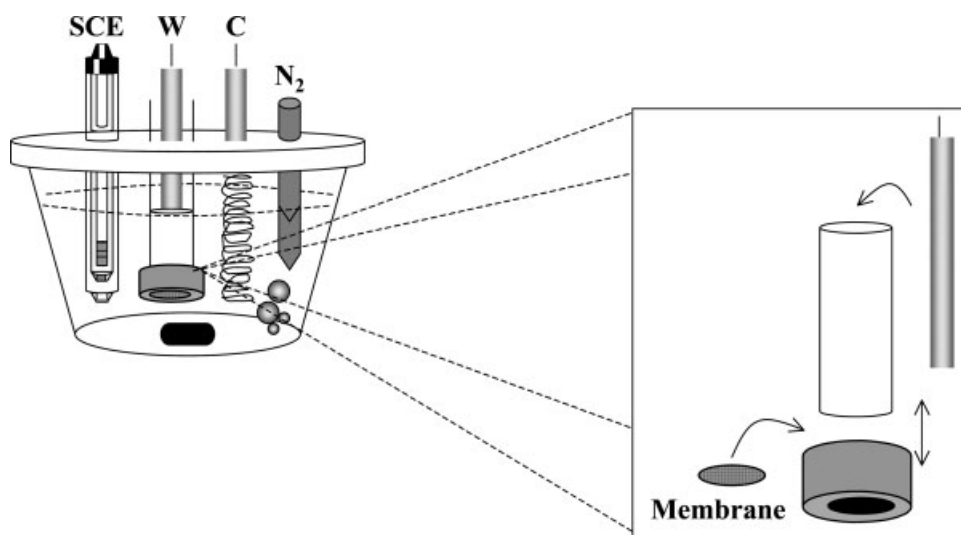
Figure 1 Schematic representation of the electrochemical cell used for the SCV and EIS experiments, where W is the working electrode, C is the counter electrode, and SCE is the reference electrode.

exchange capacity determinations were prepared from NaOH and HCl solutions. For all of the electrochemical experiments, we removed oxygen by bubbling the electrolytic solution with 99.99% purity nitrogen gas (Praxair) for at least 30 min. All of the aqueous solutions were prepared with deionized (DI) water (resistivity (ρ) $\geq$ 18 MΩ cm).

Substrate preparation

Commercially available CA filters (Osmonics, average pore diameter = 0.22 μm) were used as the templates to prepare the dendrimer-modified materials. In the first step, the linear polymer (either PEMA or PAH) was incorporated into the membrane structure by placement of the unmodified membrane in a syringe filled with a 0.1 mM solution of the linear polymer and forcing of the liquid to pass through the membrane. This operation was repeated three times with a fresh solution each time and a change in the side of the membrane so that noncovalent incorporation of the polymer could take place within the polymeric structure of the membrane. After careful rinsing with DI water, the noncovalently modified PAH-membrane modified material, was exposed for 12 h to a G3.5 PAMAM dendrimer/EDC (5.5 mM and 0.5M, respectively) aqueous solution characterized by dendrimer-activated carboxylic acid functional groups. In a symmetrical fashion, the PEMA-membrane material was first exposed to a 0.1M EDC aqueous solution to activate the polymer side-chain carboxylic acid functional groups and then immersed in a 6 mM aqueous solution of G4 amine-terminated PAMAM dendrimer for 12 h to promote the covalent attachment of a fraction of the amine surface groups of the dendrimer molecules to the activated side groups of the linear polymer (see Scheme 1). Membranes 1 and 2 were then rinsed with plenty of DI water to remove remaining reagents and byproducts and prepared for characterization studies, as described in the following sections.

Characterization, equipment, and methods

The determination of ion-exchange capacity for the dendrimer-modified membranes and the identification of ion-exchange groups by means of corresponding pK_a determination were carried out with the method reported by Fisher and Kunin.[37–39] In this way, a known weight of the prepared cationic or anionic membranes were immersed in 0.1M solutions of either HCl or NaOH, respectively, for 20 min. After careful rinsing with plenty of DI water to remove the remaining acid or base, the cationic or anionic membranes were introduced into a 10-mL flask containing DI water and titrated with 0.1 mM solutions of either NaOH or HCl. The ion-exchange capacity was determined from the amount of NaOH or HCl consumed at the end point, and the pK_a values were computed with the first and second derivative method.[40,41]

Cyclic voltammetry (CV), sampled current voltammetry (SCV),[42–44] and electrochemical impedance spectroscopy (EIS) experiments were carried out in a 30-mL, two-compartment glass cell in which a saturated calomel electrode (SCE), a platinum wire, and a gold minielectrode (Cypress Systems, Inc.) were properly fitted as the reference, counter, and working electrodes. As shown in Figure 1, although the two compartments were separated by the membrane under study, the Au working electrode was positioned in the small compartment on one side of the membrane, and the other two electrodes were located in the second compartment. CV and SCV
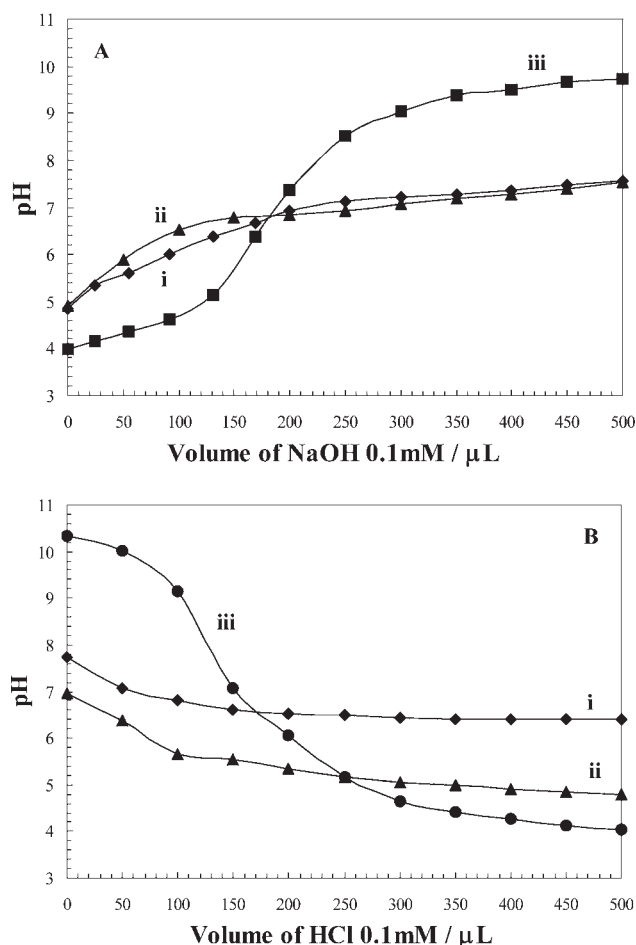
Figure 2 Titration curves of the (A-i,B-i) unmodified CA membranes and PAMAM-dendrimer-modified CA membranes prepared in the (A-ii,B-ii) absence and (A-iii,B-iii) presence of the coupling agent EDC. A is the cation-exchange membrane and B the anion-exchange membrane.

experiments were performed with an EG&G Princeton Applied Research model 263 A instrument coupled to EG&G Princeton Applied Research Research Electrochemistry 4.40 data-acquisition software loaded onto a Pentium-based PC. In the case of the EIS measurements, a VoltaLab radiometer potentiostat/galvanostat coupled to a PGZ 301 interface loaded with Volta Master 4.0 version 1.2 controlling and data-acquisition software was used. In these experiments, a potential amplitude of 10 mV around the open-circuit potential was used, and 10 points per decade in the 100 kHz–100 Hz frequency range were registered. Membrane resistance was computed with this technique from the difference in the resistance values between the working and counter electrodes in experimental setups fitted with and without the relevant membrane.[45–47]

Micro-Raman spectroscopy measurements of the modified membranes were carried out with a Renishaw spectrophotometer (λ = 785 nm) coupled to an Olympus microscope with a 50× objective

lens. The samples were measured at least four randomly selected points of the substrate's surface to ensure the homogeneity of the measured spectrum. The samples were kept in a desiccator for 24 h before the characterization experiments.

Scanning electron microscopy (SEM) experiments were carried out with a Jeol scanning electron microscope (model JSM-5400LV). In a previous preparation step, the membranes were covered with a thin film of conducting colloidal graphite.

RESULTS AND DISCUSSION

Commercial CA membranes were modified with either PAH or PEMA linear polymers, as described in the Experimental section. As shown in Scheme 1, these experimental protocols were expected to give rise to a couple of dendrimer-modified membranes, membranes 1 and 2, bearing a relatively large number of either carboxylic acid or amine functional groups positioned on the surface of the covalently attached dendrimer molecules.

The preliminary characterization of membranes 1 and 2 was carried out with the method reported by Fisher and Kunin,[37–39] as described in the Experimental section. The titration curves resulting from these experiments are shown in Figure 2, and interestingly, in both cases, the presence of acidic or basic functional groups in the dendrimer-containing materials could easily be detected by simple comparison with the curves associated with the unmodified CA membrane. The computation of the number of acid or base functional groups per gram of membrane material resulted in the information presented in the second column of Table I, in which it is clearly shown that the ion-exchange capacity of the two modified membranes corresponded to values that fell within the limits reported for commercial materials (0.5–2.5 mmol/g).[38,48]

The evaluation of the first and second derivatives of the curves presented in Figure 2, on the other hand, also allowed the calculation of the pK_a value of the ion-exchange groups in the two membranes under study. The obtained results clearly suggest that the functional groups detected in the titration

TABLE I
Ion-Exchange Capacity and pK_a Values of PAMAM-Dendrimer-Modified Membranes 1 and 2 and the pK_a Values of the Surface Groups of the Related PAMAM G3.5 and G4.0 Dendrimers in Aqueous Solution

Membrane	Ion-exchange capacity (mmol/g)	Experimental pK_a	PAMAM pK_a
1	0.71 ± 0.01	3.72 ± 0.04	3.79
2	0.66 ± 0.01	9.84 ± 0.07	9.52

experiment corresponded to the terminal moieties of the PAMAM dendrimers covalently incorporated within the polymeric structure because the experimentally obtained values were very close to those reported in the literature for PAMAM hyperbranched polymers[49–51] (cf. the third and fourth columns of Table I).

The presence of PAMAM dendrimer molecules within the membrane polymeric structures of membranes 1 and 2 was further supported by control experiments in which the Fisher and Kunin method[37–39] was carried out with membranes prepared as previously described but without the addition of the coupling agent EDC. Under these preparation conditions, dendrimer covalent incorporation within the polymeric structure of the membrane was not expected because peptide bonds could not be formed, and the PAMAM dendrimer molecules were expected to be washed away during the rinsing stages of the experimental protocol. Consistent with this idea, a set of titration curves similar to those obtained for the clean unmodified CA membrane were obtained [see Fig. 2(A-ii,B-ii)].

The covalent bonding between the hyperbranched PAMAM dendrimers and their corresponding linear polymers in modified membranes 1 and 2 was also studied with micro-Raman spectroscopy experiments. Figure 3(A-i,B-i) shows the spectrum of an unmodified CA membrane, which was characterized by one signal at 1725 cm^{-1}, which corresponded to the vibration of the carboxylic unit of the acetate ester group of the polymeric substrate (v, C=O).[52,53] Treatment of this material with the corresponding linear polymer plus the PAMAM dendrimer in the absence and presence of the coupling agent EDC resulted in two sets of membranes characterized by an additional peak at 1615 cm^{-1}, which corresponded to the vibration stretching signal of the C=O bond of an amide group[54] [see Fig. 3(A-ii,iii,B-ii,iii)]. Because this set of membranes was not rinsed with DI water after exposure of the linear-polymer-modified membrane to the hyperbranched polymer aqueous solution, the amide-related peak was expected in the four modified membranes because of the fact that both PAMAM dendrimer molecules contained multiple amide units within their chemical structure. Careful inspection of the spectra presented in Figure 3(A-ii,iii,B-ii,iii), however, reveals that the relative intensity of the amide-related peak in Figure 3(A-iii,B-iii) was about 8 ± 1.5% larger than that observed in Figure 3(A-ii,B-ii) when all of the peak intensities were normalized to the corresponding signal of the ester group. This peak intensity difference indicated that the relative amount of amide functional groups in the EDC-modified membranes was larger than that measured when the coupling agent was absent; this suggests that, under the for-
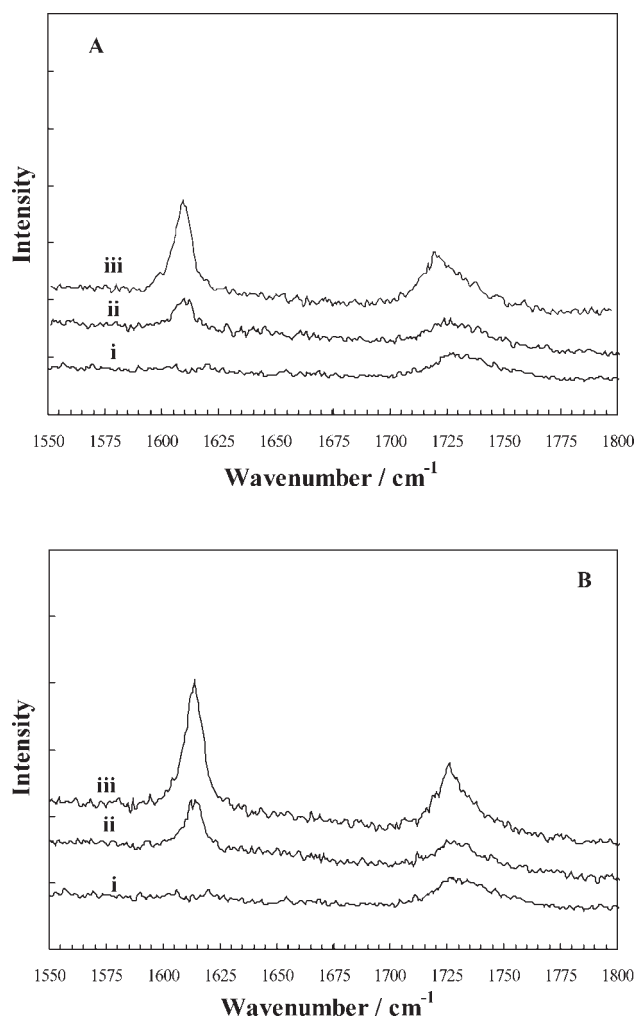

Figure 3 Representative Raman spectra of the (A-i,B-i) unmodified CA membranes and PAMAM-dendrimer-modified CA membranes prepared in the (A-ii,B-ii) absence and (A-iii,B-iii) presence of the coupling agent EDC. A is the cation-exchange membrane and B is the anion-exchange membrane.

mer synthetic conditions, the PAMAM dendrimer–linear polymer peptide bond was actually formed in the modified membranes 1 and 2.

A complementary morphological study of the modified membranes was also performed with SEM experiments, as described in the Experimental section. As shown in Figure 4, membrane modification was clearly supported from the obtained results because there was a noticeable difference in the structure of the unmodified CA substrate compared to the images obtained for the modified membranes 1 and 2. In the later cases, a coating on top of the membrane surface, which presumably corresponded to the linear polymer–PAMAM dendrimer species, was easily distinguished.

The presence of PAMAM dendrimer molecules within the polymeric structure of the modified membranes 1 and 2 should have provided charge-
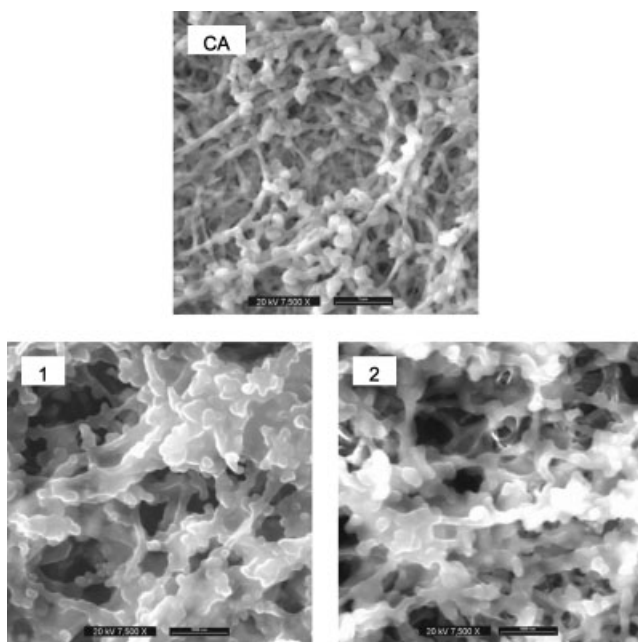
Figure 4 SEM images (7500×) of an unmodified CA membrane and the PAMAM-dendrimer-modified CA membranes 1 and 2.

selective permeability to these materials when the terminal groups of the dendrimer were ionized, and therefore, experiments aimed to test this property were carried out in the following stage of the study. As described in the Experimental section, membranes 1 and 2 were fit into an electrochemical cell containing a buffered phosphate electrolyte ($I = 0.1$) at pH values of 2, 7, and 12. The external solution (see Fig. 1) was then loaded with 0.1 mM of either $[Fe(CN)_6]^{3-}$ or $[Ru(NH_3)_6]^{3+}$, which are widely used electroactive probes characterized by electrochemical reversible behavior.[7,11,19] CV experiments with membranes 1 and 2 revealed that, as expected, the voltammetric response of the electroactive compounds increased with time as the densely charged ions permeated the membrane and reached equilibrium conditions after 3 min. Therefore, SCV experiments were carried out with each membrane with the electroactive cationic or anionic probe at every pH condition considered after a 5-min equilibration time. The results obtained for membranes 1 and 2 under neutral pH conditions are shown in Figure 5, and interestingly, whereas membrane 1 was relatively permeable to the $[Ru(NH_3)_6]^{3+}$ ion and blocked the permeation of the anionic redox molecule $[Fe(CN)_6]^{3-}$, membrane 2 reflected the opposite situation for the two electroactive probes considered. The ion-selective permeability of membranes 1 and 2 shown in Figure 5 was expected on the basis of the ionization state of the terminal groups of both the PAMAM dendrimer molecules, which, at pH 7,

were characterized by positive charges in the amino and negative charges in the carboxylic acid functional groups of the relevant dendrimers (see Table I).

The extreme pH conditions of the electrolytic solution, on the other hand, were expected to result in the selective ionization of one of the PAMAM dendrimers incorporated in membranes 1 and 2, as can be inferred by the inspection of Table I. In this way, similar experiments as those previously discussed were carried out at pH 2 and 12, and the relevant results, obtained in terms of limiting current densities, are presented in Figure 6, along with those previously measured under neutral conditions. Inspection of the relevant data showed that the ion-permeation selectivity, as reflected by the current density difference between the two membrane-modified materials, held under these extreme pH conditions, but its magnitude was clearly smaller than that observed at neutral pH conditions. These observations can be explained the fact that, although
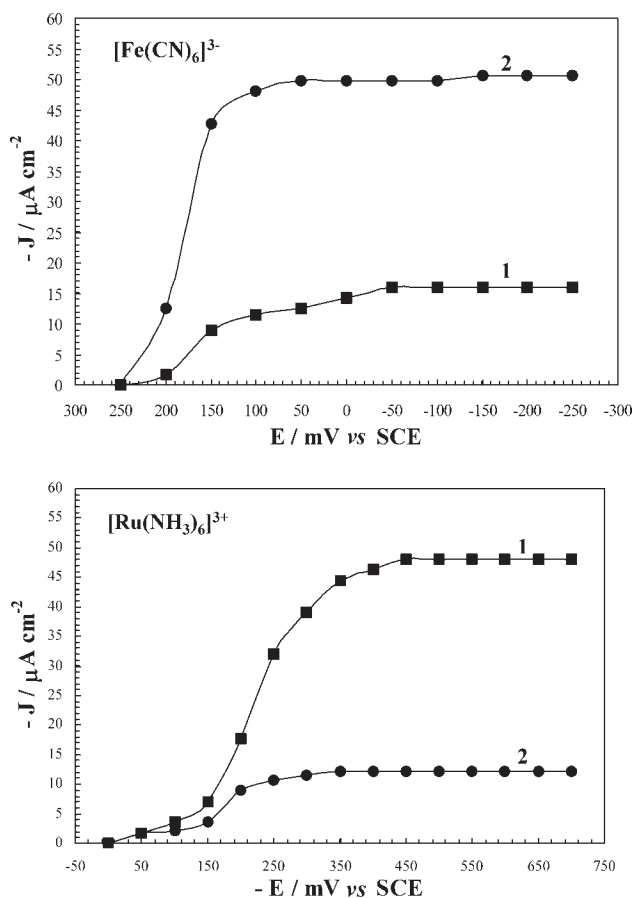

Figure 5 SCV responses obtained from 0.1 mM solutions of the cationic or anionic probe molecules dissolved in a phosphate-buffered (pH 7, $I = 0.1$) aqueous medium with the experimental setup presented in Figure 1 and modified membranes 1 and 2. E is potential and J is current density.
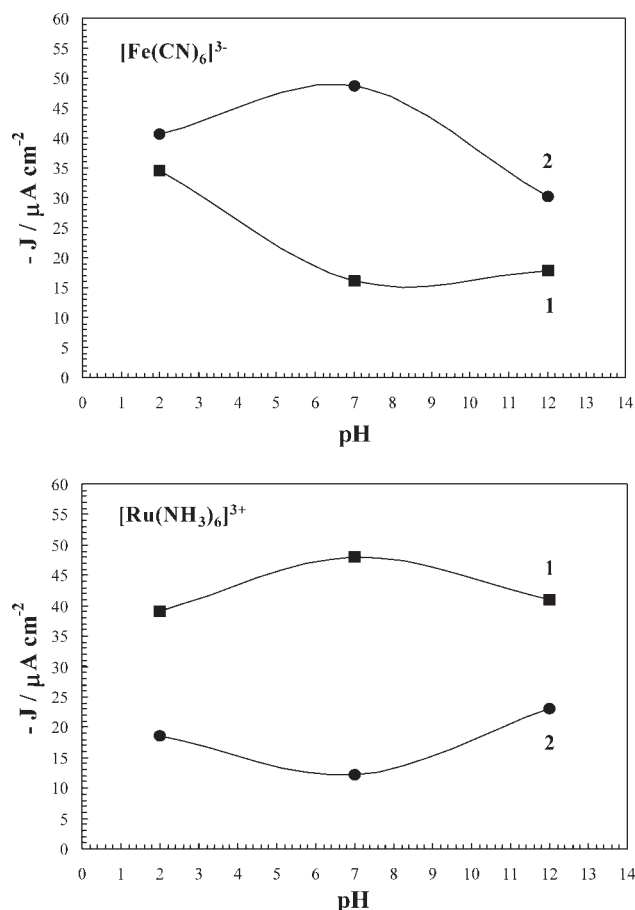
Figure 6 Plot of the limiting current density as a function of the phosphate-buffered pH ($I = 0.1$) obtained from the SCV experiments carried out with the electrochemical cell depicted in Figure 1 and with the two electroactive probes and modified membranes 1 and 2. J is current density.

brane 1 and neutral amino moieties were expected for membrane 2.

The ion-selective permeability presented in Figure 5 for the novel materials under study was also explored with SCV experiments with commercial Ionac ion-exchange membranes (anionic and cationic with ion-exchange capacities of 1.0 and 1.4 mmol/g, respectively) with similar thickness values (~ 0.018 mm, obtained from Sybron Chemicals, Inc.) to those that characterized membranes 1 and 2 (~ 0.016 mm), as computed from perfilometry measurements. Analysis of the corresponding SCV data revealed that no permeation took place for either the $[Ru(NH_3)_6]^{3+}$ or $[Fe(CN)_6]^{3-}$ electroactive species under the conditions considered (data not shown); this clearly suggests that the dendrimer-based modified membranes 1 and 2 constitute a promising type of ion-exchange membranes particularly suited for densely charged ions in aqueous media.

To understand the later observations and to explore the behavior of Ionac membranes and ion-exchange membranes 1 and 2 immersed in solutions of nonelectroactive electrolyte species, we focused our attention on the evaluation of membrane resistance to the permeation of ions characterized by different charge densities. EIS experiments were, therefore, carried out, as described in the Experimental section, in neutral aqueous solutions of the relevant ion ($0.1M$). The resistance to permeation of monovalent, divalent and trivalent ions across the membranes under study was measured. The results obtained from these experiments are presented in Table II, and interestingly, whereas the dendrimer modified membranes 1 and 2 showed similar resistance values for monovalent and divalent ions compared to those obtained with the commercial materials, there was a substantial difference between the novel and the commercial Ionac membrane substrates when trivalent ions were used. This

under pH 2 conditions neutral carboxylic acid functional groups characterized membrane 1 and protonated amino functionalities must have existed for membrane 2, a symmetrical situation held at pH 12, where ionized carboxylic groups prevailed for mem-

TABLE II
Resistance Values/10^{-3} Ω of the Unmodified CA, Commercial Ionac, and PAMAM-Modified Membranes 1 and 2 Obtained from the EIS Experiments

	Membrane				Membrane		
Ion	CA	1	Ionic cation exchange	Ion	CA	2	Ionic anion exchange
Li^+	0.127	0.141	0.173	Cl^-	0.081	0.090	0.138
Na^+	0.127	0.139	0.198	Br^-	0.074	0.099	0.137
K^+	0.102	0.147	0.217	I^-	0.040	0.128	0.243
Ca^{2+}	0.227	0.246	0.250	$(CO_3)^{2-}$	0.206	0.235	0.216
Cu^{2+}	0.238	0.288	0.340	$(SO_4)^{2-}$	0.174	0.265	0.257
Fe^{2+}	0.184	0.332	0.336	$(S_2O_3)^{2-}$	0.110	0.267	0.591
Fe^{3+}	0.291	0.528	1.658	$(C_6H_5O_7)^{3-}$	0.369	0.570	2.247
$[Ru(NH_3)_6]^{3+}$	0.375	0.705	2.741	$[Fe(CN)_6]^{3-}$	0.358	0.685	2.422

observation, which was consistent with the SCV experiments previously described, probably reflected the particular number and specific distribution of ion-exchange groups that characterized the dendrimer-modified membranes presented in this article.

Experiments aimed to study the effect of the ionized group distribution in these materials on the ion-exchange selectivity and the chemical and mechanical stability of these membranes under different operation conditions are currently being carried out in our laboratory.

CONCLUSIONS

In this study, we showed that CA membranes could be conveniently modified by the noncovalent incorporation of linear polymers, which could be further used as templates for the covalent incorporation of PAMAM dendrimer molecules. The resulting materials were shown to bear ion-exchange groups associated with the PAMAM dendrimer molecules, whose ionization state was pH dependent. As suggested by electrochemical experiments, the novel membranes reported in this article were also shown to have ion-selective permeability to densely charged ions, a property that was shown to be maximized at neutral pH values. When compared to a couple commercial ion-exchange membranes, the materials reported in this article were also found to be characterized by a significantly lower resistance to highly charged ions, a feature that makes them a promising material for the development of a new type of ion-exchange membranes.

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