

pH-Switchable, Ultrathin Permselective Membranes Prepared from Multilayer Polymer Composites

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In this report, we describe novel polymeric composite films formed from multilayers of amine-terminated dendrimers and poly(maleic anhydride)-*c*-(methyl vinyl ether) (Gantrez) grafted onto Au-coated Si wafers. These composite membranes exhibit fully reversible, pH-switchable permselectivity for both cationic and anionic redox-active probe molecules. The pH-dependent change in charge of the dendrimer amine groups and the carboxylic groups derived from the random coil polyanhydride chains serve as independent ion gates. These gates pass cations only at high pH, anions only at low pH, and both cations and anions at intermediate pH (Figure 1). Polymeric materials demonstrating this switchable permselective function have not previously been reported. Dispersions of cationic and anionic polyelectrolytes usually result in spontaneous flocculation and precipitation due to strong electrostatic interactions,¹ but the layer-by-layer synthetic approach used here avoids this problem.

Responsive or "smart" membrane systems have been studied previously. Such materials have applications in controlled release, selective filtration, electronic devices, and chemical sensors and biosensors.^{2–9} Anionic or cationic polymeric membranes that have permselectivity toward electroactive counterions due to the membrane charge have also been studied.^{10–12} For example, Anson *et al.* have studied membrane systems derived from polyelectrolytes such as the polysulfonated fluoropolymer Nafion, poly(acrylic acid), and poly(4-vinylpyridine) that show electrostatic binding of electroactive counterions.¹⁰ These materials are related to those described here, but they are not pH switchable between cationic and anionic forms. Moreover, previous work has typically involved much thicker cast films. Recently, Martin and co-workers developed an electronically switchable, ion-exchange membrane system consisting of cylindrical nanoscopic metal tubules whose surface

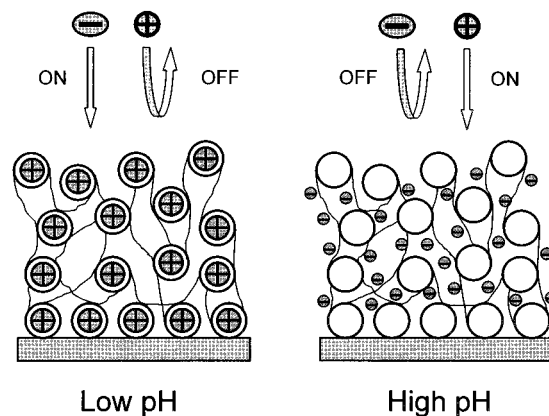


Figure 1. Schematic illustration of the pH-switchable "On/Off" function of the composite film. The polyamine dendrimer units are covalently attached to the Gantrez polymer network. At high pH the film has a net negative charge that excludes anions but passes cations; at low pH it is positively charged and excludes cations but passes anions; and at intermediate pH, it passes both cations and anions.

potential can be electronically manipulated to either pass or exclude anions and cations.¹³ Our new work uses a nanocomposite polymeric ultrathin film that relies on homogeneously dispersed pH-responsive amine and carboxyl groups to induce fully reversible permselectivity into an electrode-supported membrane.

The highly functionalized composite thin films were synthesized in a covalent, layer-by-layer fashion by using a general method recently developed in our laboratories.¹⁴ First, a self-assembled monolayer (SAM) of dendrimers on a Au-coated Si wafer was prepared by immersion of the substrate in a methanol solution containing a fourth generation, amine-terminated Starburst (PAMAM) dendrimer.¹⁵ The resulting dendrimer SAM, denoted as layer D0, was then allowed to react with Gantrez, to afford a first layer of Gantrez (Gz1) covalently linked to D0 *via* amic acid bonds. Repetitive sequential deposition leads to additional covalently linked layers of the G4 PAMAM dendrimer and Gantrez: D1, Gz2, D2, and so on. Although the topmost layer is chemically distinct from those underlying it, we believe that the film interior is more or less homogeneous, as shown in Figure 1. These composite films consist of dendritic units having amphoteric internal and peripheral amine groups mixed with the Gantrez network containing amphoteric carboxyls. This structure constitutes the basis for the permselective, pH-responsive supramolecular gate.

The extent of ionic permeability of the D2 films was investigated under different pH conditions by using anionic $\text{Fe}(\text{CN})_6^{3-}$ and cationic $\text{Ru}(\text{NH}_3)_6^{3+}$ as redox probe molecules. Figure 2 shows cyclic voltammograms of electrodes modified with the D2 films in an aqueous solution containing 5 mM of either $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Ru}(\text{NH}_3)_6^{3+}$ buffered at pH 3.0, 7.0, and 11.0. The shape and magnitude of these voltammograms are significantly affected by pH. For example, the peak current density resulting from $\text{Fe}(\text{CN})_6^{3-}$ reduction is about $750 \mu\text{A}/\text{cm}^2$ at pH 3.0 while there is essentially no reduction current at pH 11.0. The voltammetric results clearly indicate that the D2 films are open ("On") to the negatively charged probe, $\text{Fe}(\text{CN})_6^{3-}$, at pH 3.0, but impermeable ("Off") to the probe at pH 11.0. This responsive behavior is fully reversible to repetitive switching of the pH for up to at least 10 cycles.

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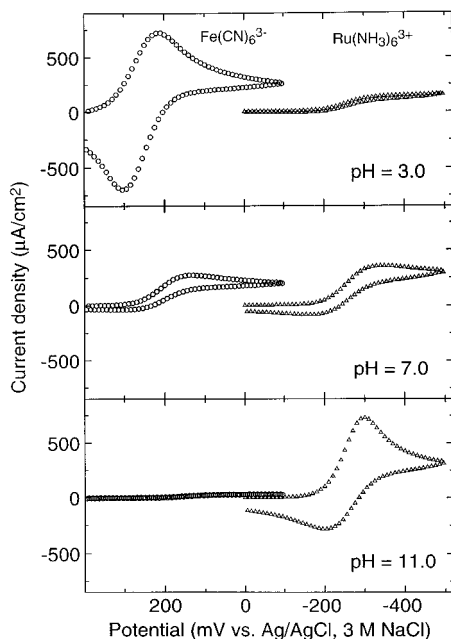


Figure 2. Cyclic voltammograms of the electrode modified with D2 films in aqueous 0.5 M Na₂SO₄ electrolyte solutions containing 5 mM of Fe(CN)₆³⁻ or Ru(NH₃)₆³⁺ buffered at pH 3.0, 7.0, and 11.0. The scan rate was 50 mV/s and the electrode area was 0.09 cm².

Importantly, the “On/Off” behavior of the D2 films/membranes is reversed when cationic species such as Ru(NH₃)₆³⁺ are used as a probe. In this case, the composite films are turned “On” at high pH (11.0) and are “Off” at low pH (3.0). This process is also fully reversible, but note that the “Off” function for Ru(NH₃)₆³⁺ is not as efficient as it is for Fe(CN)₆³⁻, which is due to differences in the mass transfer rates of the two different redox probes in the film.¹⁶

We attribute the switching behavior of these multilayer composite films to the presence of the ionizable amine and carboxylic groups in the membrane. To support this contention, we measured the IR spectrum of a D2 film after treatment with strong acid and base solutions containing 0.01 M SO₄²⁻. Upon treatment with 0.01 M H₂SO₄, the film attains a net positive charge as evidenced by the incorporated SO₄²⁻ counterions. These SO₄²⁻ IR markers are apparent in Figure 3A in the range of 1070 to 1260 cm⁻¹. The other major peaks in the spectrum are the amide I and II bands associated with the dendrimers and dendrimer/Gantrez covalent linkages at 1671 and 1561 cm⁻¹, respectively, and the acid carbonyl band derived from Gantrez at 1724 cm⁻¹. When the same film is treated with a pH 12 NaOH solution containing 0.01 M Na₂SO₄, it becomes negatively charged as a result of deprotonation of the carboxyl groups derived from the Gantrez network. This change is evident in the IR spectrum from the loss of the acid carbonyl band originally present at 1724 cm⁻¹ and the SO₄²⁻-related bands at low energy (Figure 3B).¹⁷ Additionally, carboxylate bands appear at 1587 (convoluted with the amide II band) and 1403 cm⁻¹.

We measured the ellipsometric thickness of the D2 films in their dry and solvent-swollen states to determine if there are gross physical changes in the composite film as a function of

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(17) Methanol was employed as a solvent in preparation of the PAMAM dendrimer solution used for the film preparation. The residual shoulder peak at 1716 cm⁻¹ stems from methyl esters that were generated from reaction of the grafted Gantrez with the methanol solution of the PAMAM dendrimer in the film synthesis.

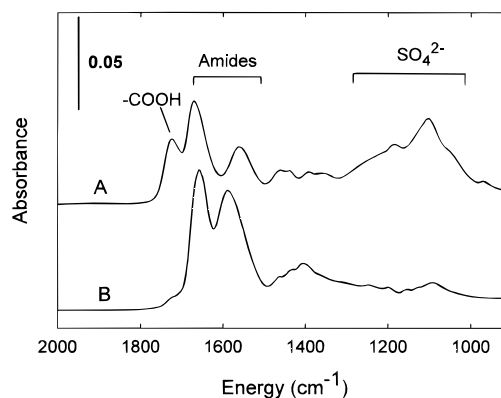


Figure 3. FTIR-external reflectance spectra of a D2 film grafted on a Au-coated Si wafer: (A) after the film was treated with an aqueous 0.01 M H₂SO₄ solution; (B) after the film was treated with an aqueous NaOH solution at pH 12. The basic solution contained 0.01 M Na₂SO₄.

pH. The D2 films are 24 ± 1 nm thick when dry in either the protonated or deprotonated state. They swell in aqueous solutions as evidenced by an increase of film thickness to 46 ± 2 nm, but the thickness change is pH independent. Taken together, the IR and ellipsometry results suggest that the switchable nature of these membranes is dominated by electrostatic interactions between the film and the redox-probe ions rather than a pH-dependent change in film structure.

We also examined thinner (14 nm, dry) D1 films to determine the extent of their pH-dependent “On/Off” behavior. In accordance with the D2-film results, the D1 films are open to Fe(CN)₆³⁻ at pH 3.0 and Ru(NH₃)₆³⁺ at pH 11.0. However, the “Off” state of the D1 films leaks to a much greater extent than the D2 films, because they are thinner and have a lower total internal charge.

In summary, we have designed and synthesized a new type of pH-responsive ultrathin composite film that contains amphoteric polyamine dendrimer units attached to an amphoteric random coil polymer (Gantrez) *via* covalent bonds. These materials function as supramolecular gates as a function of pH: at low pH cations are excluded from the film, but anions easily penetrate, while at high pH the opposite behavior obtains. Additionally, the “On/Off” responsiveness of the composite films is stable and reversible, and the gating function of these films is remarkably efficient given their nanoscopic thickness. Further study of such films as ion-selective and controlled release membranes is currently underway.

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Supporting Information Available: FTIR-external reflectance spectra of the multilayer composite films at different grafting stages, complex impedance plots for electrodes modified with D2 films, and cyclic voltammograms of Fe(CN)₆³⁻ and Ru(NH₃)₆³⁺ at naked Au electrodes and at electrodes modified with D1 films (4 pages). See any current masthead page for ordering and Internet access instructions.