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Electrosensitive Permeability of Membranes with Oriented Polyelectrolyte Nanodomains

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Polyelectrolyte hydrogels exhibit reversible contraction and expansion (actuation) in response to an “on−off” direct current electric field.[1−6] This electrosensitivity results from the migration of hydrated ions and water in the network to the electrode bearing a charge opposite in sign to that borne by the polymer network. Osada and co-workers[1,3−5] conducted several groundbreaking experiments on polyelectrolyte gels, such as poly(methacrylic acid) (PMAA) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS), revealing that when the electric field is applied isometrically (i.e., keeping the membrane’s macroscopic dimensions constant), the contractile stress in the membrane reversibly expands and contracts the gel network in response to the electric stimulus. They also demonstrated that the pore size of the gel network was proportional to the strength of the electric field applied. Using this electrokinetic phenomenon, a polyelectrolyte membrane can act as an electrically activated “chemical valve” or “permeability valve” regulating the transport of specific chemicals through the membrane. This concept was demonstrated by Weiss et al.[7] in their work on the size-specific permeability of fluorescent solutes of different molecular weights through PMAA in response to an electrical stimulus. However, the application of pure polyelectrolyte membranes to membrane-based separation processes is limited due to their weak mechanical integrity.

In this study, we report the electrosensitive permeability of a new class of polymer−polymer nanocomposite membrane with oriented polyelectrolyte nanodomains normal to the plane of the membrane. In this composite, a track-etched membrane with an oriented nanoporous structure was used as the matrix, which provides mechanical durability, while the polyelectrolyte gel fills the pores (covalently bound and cross-linked) and regulates transport properties in the desired direction. Membranes with this oriented nanostructure exhibit enhanced transport properties[8] and are of particular interest for a variety of applications, including chemical and biological defense.

The nanocomposite membranes were synthesized using an oxygen plasma-initiated surface graft polymerization technique as described previously.[8] Polyester track-etched (PETE) membranes (50 and 100 nm pore diameter, 12 μm thickness, Universite Catholoque de Louvain, prepared by bombarding the membrane with heavy metal ions followed by chemical etching to generate nanopores in the damaged tracks) were used as the matrix, while 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (99%) (Aldrich) and *N*,*N*′-methylenebis(acrylamide) (BisA) (≥98%) (Aldrich) were used as the monomer and cross-linker, respectively. Figure 1 shows the surface and cross-sectional morphology of the composite membrane in the dry state. Solid PAMPS gel rods fill the pores completely and are covalently bound to the pore walls (Figure 1b2). Meanwhile, the top/bottom surface of PETE matrix was covered with PAMPS gel layer (Figure 1b1).

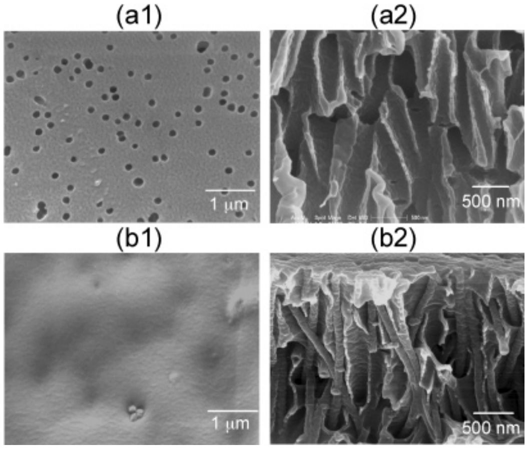

Figure 1. SEM images of (a) original PETE membrane (100 nm pore diameter), (b) PAMPS gel-*g*-PETE nanocomposite (grafting conditions: 20 wt % AMPS, 2 wt % (to monomer) BisA cross-linker, 50 °C, 4 h): 1, surface view; 2, cross-section view.

The transport properties of dimethyl methylphosphonate (DMMP) (99%, Aldrich), a simulant of the nerve agent Sarin, in the original PETE and nanocomposite membranes were measured using a side-by-side glass diffusion cell equipped with a thermal jacket.[9] Membranes were prehydrated in ultrapure deionized, reverse osmosis (RO) water (resistivity ∼ 16 MΩ cm) for at least 48 h. In a typical experiment, the donor compartment was charged with 10 vol % DMMP aqueous solution, while the receptor compartment was filled with water. The membrane, which was sandwiched by two pieces of porous carbon cloth (electrodes), was clamped between the two compartments. The electrodes were connected to a dc power supply using platinum wire. The concentration of DMMP that permeates through the membrane was measured continuously as a function of time on the receptor side with a real-time in-line Fourier transform infrared, attenuated total reflectance (FTIR-ATR) (Nicolet 6700 Series; Specac Inc.) spectrometer for detection. Infrared spectra were continuously recorded throughout each experiment at 12 s intervals using 32 scans and 4 cm^{-1} resolution for each collected spectrum. In all experiments, both the side-by-side diffusion cell and ATR cell were temperature controlled (35 °C) with the same circulating water bath (Neslab RTE10, Thermo Electron Co.).

Figure 2 shows the permeability of the nanocomposite membranes with and without electric actuation. When an electric field (10 V) was applied, the membrane was nearly impermeable, but permeable when the electric field was removed (Figure 2a). The electric field was applied again after ∼3 h, and the same electrosensitive barrier properties were observed (reversible process). Without applied voltage, the nanocomposite membrane exhibited a permeability of 2.84×10^{-8} cm^2/s (Figure 2b). This was similar to the permeability in the region where no voltage was applied in Figure 2a and was also an order of magnitude lower than that of the original (unfilled) PETE membrane (2.45×10^{-7} cm^2/s; Figure 2c).

The breakthrough time (∼13 min) after the applied voltage was removed in Figure 2a was similar to the breakthrough time in Figure 2b, where no voltage was applied. In comparison, no actuation behavior was observed with the original PETE

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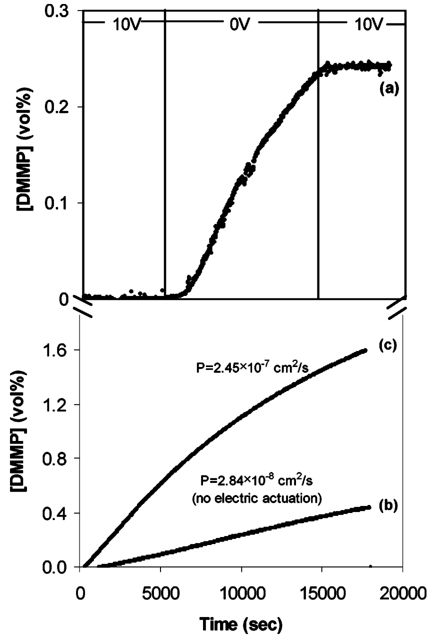
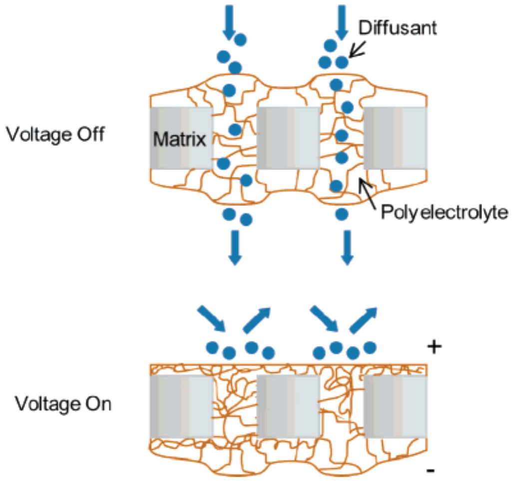


Figure 2. DMMP permeability of the PAMPS gel-*g*-PETE nanocomposite membrane (with 15 wt % PAMPS gel) (a) with and (b) without acutation and (c) the original (unfilled) PETE membrane (50 nm pore diameter).

Scheme 1. Electrosensitive Permeability in PAMPS Gel-*g*-PETE Nanocomposite Membranes



membrane, where the electric signal had no impact on the permeability of DMMP (Figure 2c). The effect of the electric field on the network structure of the PAMPS gel in the nanocomposite is schematically shown in Scheme 1. Without voltage, the PAMPS gel in the pores swells in water,[10] and this swollen network allows for the diffusion of molecules. With voltage, the PAMPS gel on the surface and in the pores of the membrane asymmetrically contracts (due to hydronium ion transport to the cathode),[2] resulting in increased diffusion resistance. The significant difference in the wet and dry thickness of the membrane supports these results.[8]

Table 1. Mechanical Properties[a] of PETE, PAMPS, and PAMPS Gel-*g*-PETE Nanocomposite Membranes

sample	breaking strength (MPa)	breaking elongation (%)	modulus (MPa)
	Dry Samples		
PETE	87 ± 9	21 ± 3	762 ± 203
PAMPS gel-*g*-PETE	67 ± 19	16 ± 4	467 ± 120
PAMPS gel[b]	72 ± 15	3.2 ± 0.3	3108 ± 420
	Hydrated Samples		
PETE	77 ± 9	19 ± 1	788 ± 77
PAMPS gel-*g*-PETE	21 ± 5	9.8 ± 0.4	121 ± 4
PAMPS gel[c]	0.012	40	0.03

[a] Tensile tests were conducted on Instron 4200/4300/4400 as described previously.[8] [b] Containing 5 wt % BisA cross-linker. [c] 98% swelling.[11]

Tensile tests show that the pure PAMPS gel membrane is more rigid and brittle than PETE matrix in the dry state (Table 1). As expected, the hydrophobic PETE membrane showed no obvious changes in mechanical properties after being exposed to water. However, the PAMPS gel lost its strength by many orders of magnitude after hydration. By grafting PAMPS gel within the pores of the PETE matrix, the resulting composite showed a similar breaking strength and elongation in the dry state and a slightly lower strength in the hydrated state compared to the original PETE membrane. However, unlike the pure PAMPS gel, the mechanical properties of the composite membranes were on the same order of magnitude as the matrix.

In summary, this study demonstrates that nanocomposite membranes consisting of a hydrophobic matrix with oriented polyelectrolyte nanodomains grafted within possess electrosensitive permeability, while still maintaining mechanical stability on the same order of magnitude as the matrix. Further experiments are underway to determine the effect of pore size, cross-linking density, and voltage on electrosensitive permeability.

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