pH-Sensitive Permeability Control of Polymer-grafted Nylon Capsule Membranes[1]

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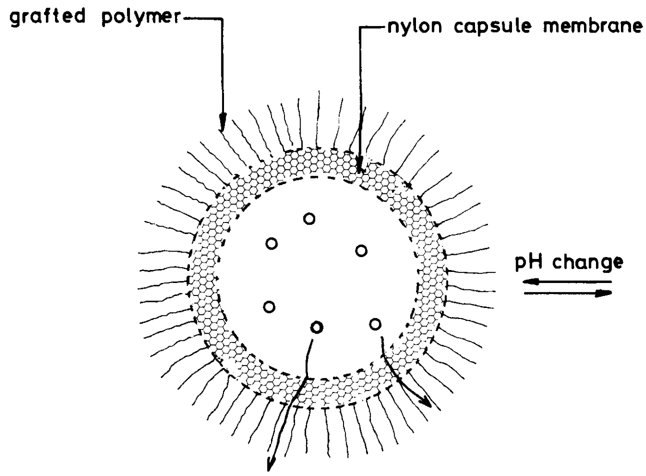
Poly(4-vinylpyridine) or poly(methacrylic acid) was grafted onto an ultrathin, porous nylon capsule membrane so that permeation across the capsule membrane of NaCl trapped in the inner aqueous phase could be reversibly controlled by ambient pH changes.

We have recently reported novel functional nylon capsules whose porous membranes were coated with bilayers of synthetic substances.[2—8] Permeation through the membranes of water-soluble substances trapped in the inner phase was reversibly controlled by outside effects such as temperature,[2,8] photoirradiation,[3,4] ultrasonic power,[6] and interaction with divalent cations.[5] Their signal-receptive permeability control is explained by changes in the physical state of the coated bilayers which act as ion 'gates'.

We report here that a nylon capsule membrane with surface-grafted polyelectrolyte can be used as a pH-sensitive capsule, whose permeability is reversibly regulated by pH



Scheme 1

changes in the outer medium. We expected the grafted polymer to act as a permeation valve for the capsule membrane. A schematic illustration of the polymer-grafted capsule is shown in Scheme 1.

Large, porous, ultrathin nylon capsules (diameter 2.5 mm; membrane thickness 1 μm) were prepared from ethylenediamine and 1,10-bis(chlorocarbonyl)decane by the method described in previous papers.[2—8] Graft polymerization of 4-vinylpyridine, methacrylic acid, or acrylic acid onto the capsule membranes was carried out in an aqueous solution of 0.1 M nitric acid and 0.01 M cerium(IV) ammonium nitrate at room temperature for 4 h with nitrogen bubbling, as in the described general procedure.[9—11] The polymer-grafted capsules obtained were washed with an excess of water to remove non-grafted polymers and unreacted monomers, and then dialysed against 0.2 M aqueous NaCl to give capsules containing NaCl as a permeant. Gel-permeation chromatography (g.p.c.) of the residual grafting polymer after hydrolysis of the nylon capsule membranes and direct ESCA analysis of the polymer-grafted capsules confirmed that 20—60 μg of linear polymers (average molecular weight 5×10^4) were grafted onto the surface of a capsule membrane (20 ± 2 μg).

The permeability of the capsule to NaCl was measured by detecting increases in the electrical conductance of the outer aqueous phase, after dropping one capsule into deionized water. pH changes in the outer medium were effected as follows; a capsule was removed from a cell immersed in a solution of definite pH for 1 min, and then returned to the cell. Figure 1(a) shows reversible changes in the permeation of NaCl when the polymer-grafted capsule was alternately dipped in aqueous solutions of pH 2 or pH 9. In the case of the ungrafted, original capsule membrane, the permeation was not affected by an ambient change of pH to 2 or 9.

When the capsule grafted with poly(4-vinylpyridine) (PVP) was soaked in the basic solution (pH 9), NaCl permeation was drastically reduced, below that of the ungrafted membrane. Upon dipping the PVP-grafted capsule into the acidic solution (pH 2), the permeability was immediately enhanced by a factor of 13—15, and reduced again almost to the same slow rate by returning the capsule to the solution of pH 9. In the case of the capsule grafted with poly(methacrylic acid) (PMA) the reverse occurred, the permeability was reduced in the acidic medium (pH 2) and increased in the basic medium (pH 9), and the magnitude of variations in permeability with changes in pH was not as large as those in the PVP-grafted capsule. This permeability regulation of the PVP- and PMA-grafted capsules in response to pH changes could be repeated more than 10 times without damaging the capsules. The capsule grafted with poly(acrylic acid) (PAA), however, did not show pH-sensitive permeation behaviour and NaCl permeation was very fast at both pH 2 and 9.

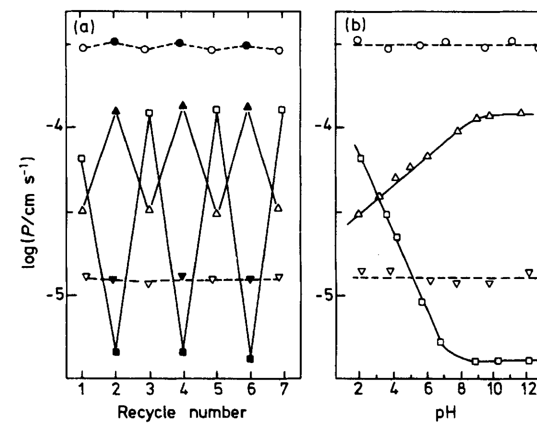


Figure 1. NaCl permeation across polyelectrolyte-grafted capsule membranes at 25 °C. ○,●: the ungrafted capsule, □,■: the PVP-grafted capsule, △,▲: the PMA-grafted capsule, ▽,▼: the PAA-grafted capsule. (a) Reversible permeability control by pH changes in the outer medium. Filled symbols: pH 9, open symbols: pH 2. (b) pH–Rate profile of the NaCl permeation.

Figure 1(b) shows pH–rate profiles of the NaCl permeation. The PVP-grafted capsule membrane formed a high barrier to NaCl permeation in the neutral pyridine form of the grafted polymer (above pH 7), but not in the pyridinium cationic form (below pH 6), relative to that of the ungrafted capsule. The permeability of the PMA-grafted capsule was decreased when the polymer was in the neutral carboxylic acid form (below pH 7) and increased for the carboxylate anionic form (above pH 8). The permeability of the PAA-grafted capsule did not change over the whole range of pH 2—12.

The pH–rate profiles clearly show that ionisation of the grafted polymers on the capsule membrane plays an important role in the observed pH-sensitive permeation. When the grafted polymer is in the ionized form (PVP cation below pH 7; PMA anion above pH 8), the polymer chains may be repelled by charge repulsion between the ionic side chains, and NaCl would then permeate smoothly through the charged, hydrophilic membrane as shown on the left hand side of Scheme 1. On the other hand, when the grafted polymer is in the neutral form (PVP above pH 7; PMA below pH 7), the entangled, relatively hydrophobic polymer covers the porous capsule membrane, and NaCl permeation is significantly reduced, especially in the more hydrophobic PVP-grafted capsule (see the right hand side of Scheme 1). In the case of the PAA-grafted capsule, since the neutral PAA is not hydrophobic enough to entangle and cover the membrane surface, the permeability is hardly affected by pH changes.

The pH-sensitive capsule membrane can also be used in controlling the permeation of other water-soluble substances such as uncharged glucose and relatively hydrophobic fluorescent probes.

In conclusion, the grafted polymer on the capsule membrane acts as a kind of valve which responds to pH changes in the outer medium. The valve of these grafted polymers can also be opened or shut by effects outside the capsule such as chelation with heavy metal ions or polymer complexation by hydrogen bonding with poly(ethylene oxide).[12]

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