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Communications to the Editor

Thermoselective Permeation from a Polymer-Grafted Capsule Membrane[1,2]

Permeability of microcapsules has been investigated rather extensively because of its importance in the design and construction of sustained drug release devices and artificial cells.[3,4] In spite of its potential usefulness, the reversible, signal-receptive permeation control of the capsule has not been fully investigated.

We report here that the permeation of NaCl and dyes from a large nylon capsule membrane with a surface-grafted poly(*N*-isopropylacrylamide) can be reversibly regulated by ambient temperature changes, in which the grafted polymer is expected to act as a thermoselective permeation valve on the membrane. A schematic illustration of the capsule is shown in Figure 1.

Large, porous, ultrathin nylon capsules (diameter 2.5 mm, membrane thickness 5 μm) were prepared from ethylenediamine and 1,10-bis(chlorocarbonyl)decane by the interfacial polymerization method described in previous papers.[5–7] Graft polymerization of *N*-isopropylacrylamide onto the capsule membrane was carried out as follows. A small amount of ethylene glycol dimethacrylate was first grafted onto the capsule membrane in the presence of cerium(IV) ammonium nitrate in order to introduce vinyl groups onto the membrane surface, and then *N*-isopropylacrylamide (mp 64 °C) was grafted in aqueous solution using KPS–$NaHSO_3$ as a radical initiator at room temperature for 2 h with nitrogen bubbling.[6,7] The polymer-grafted capsules were washed with excess water and ethanol to remove nongrafted polymers and unreacted monomers. It was confirmed from gel permeation chromatography of the residual grafting polymer after hydrolysis of nylon capsules and weighing before and after polymerization that 2 μg of linear polymer (average molecular weight 5×10^4) was grafted onto the surface of a capsule membrane of dry weight 20 μg. Thus, one polymer chain is estimated to be grafted per 2×10^3 repeating units of nylon-2,12 capsules. The capsules were dialyzed against aqueous solutions of 0.2 M NaCl, 1×10^{-2} M benzenesulfonate, or 1×10^{-3} M naphthalenedisulfonate to give capsules containing the respective molecule as a permeant in the inner aqueous phase.

The permeability of the capsule to NaCl and dyes was measured at various temperatures by detecting increases in the electrical conductance and absorbance at 210 or 225 nm of the outer aqueous phase, respectively, after dropping one capsule into deionized water. Apparent permeation rates (*P*, cm s^{-1}) were obtained as described previously.[5–7]

Figure 2 shows Arrhenius plots of NaCl and dye permeation from the polymer-grafted and the ungrafted capsule membranes. In the case of the ungrafted capsule membrane, permeation of all probes had nearly the same rates and gave a straight Arrhenius plot in which permeability simply increased with increasing temperatures. On the contrary, permeability of the polymer-grafted capsule was remarkably reduced above temperatures near 35 °C, especially for permeation of the large naphthalenedisulfonate.

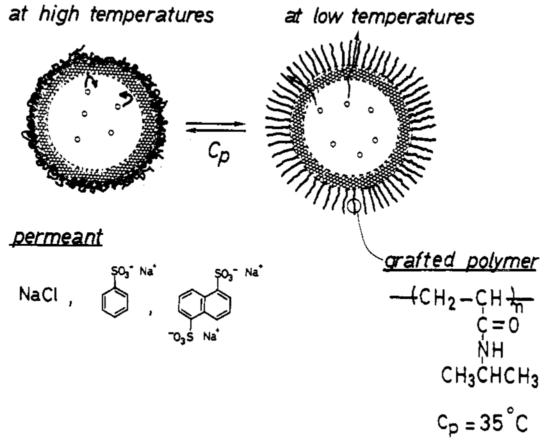

Figure 1. Schematic illustration of the capsule membrane grafted with polymers as a permeation valve.

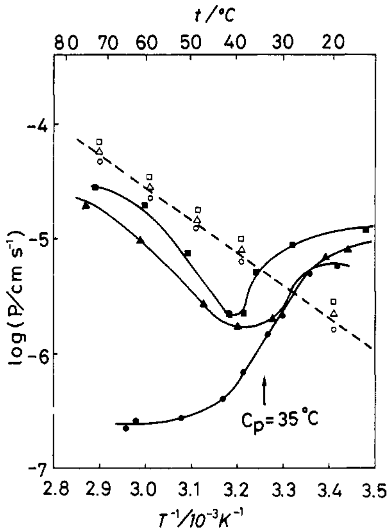

Figure 2. Arrhenius plots of permeation of NaCl (■), benzenesulfonate (▲), and naphthalenedisulfonate (●) from the poly(*N*-isopropylacrylamide)-grafted capsule membrane. The broken line with open symbols shows Arrhenius plots of the ungrafted capsule membrane.

It is known that the solubility of poly(*N*-alkylacrylamide) in aqueous solution is reduced with increasing temperatures, having a critical clouding point (C_p).[8–11] Poly(*N*-isopropylacrylamide) was reported to have C_p near 31–35 °C in water from viscosity, light scattering, and differential scanning calorimetry (DSC) studies.[9–11] This is explained by the fact that the solubility is decreased due to a weakening of the ordering effect of the water–amide hydrogen bonds and an increasing of the nonpolar, intermolecular hydrogen bonds between polymers as the temperature is raised.[8] This solubility change is reversible and was recently utilized for acrylamide gel with thermally reversible swell/shrinkage properties.[11]

The grafted poly(*N*-isopropylacrylamide) on the capsule membrane was also confirmed to have C_p at 35 °C by DSC measurements in water. This indicates that the solubility of the grafted polymer drastically changes at C_p = 35 °C as does that of the homopolymer. The polymer of the capsule may be solubilized and repelled in water at temperatures below C_p, and permeants smoothly pass through the porous capsule membrane. On the contrary, at temperatures above C_p, the insoluble, entangled polymer covers the porous capsule membrane, and permeation is significantly reduced, depending on the molecular size of

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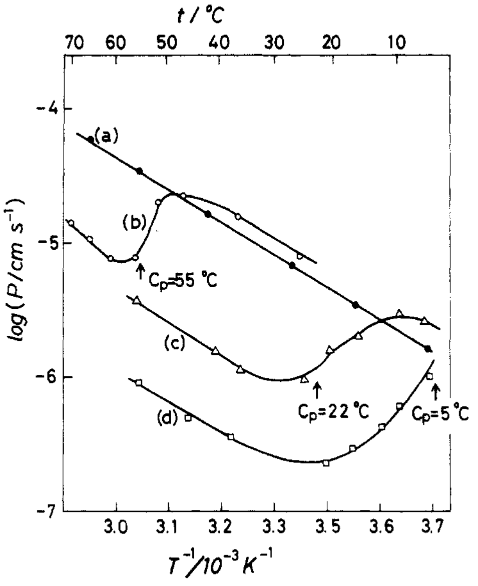
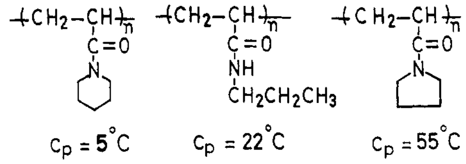


Figure 3. Arrhenius plots of permeation of naphthalenedisulfonate from polymer-grafted capsules: (a) ungrafted capsule; (b) poly(*N*-acryloylpyrrolidine)-grafted capsule (C_p = 55 °C); (c) poly(*N*-*n*-propylacrylamide)-grafted capsule (C_p = 22 °C); (d) poly(*N*-acryloylpiperidine)-grafted capsule (C_p = 5 °C).

Chart I



the permeants. Thus, the permeability of the large naphthalenedisulfonate was decreased 12–15 times above C_p = 35 °C relative to that below C_p and 100 times lower than that of the ungrafted capsule. This thermosensitive permeation is reversible: the permeability of naphthalenedisulfonate can be changed repeatedly in the range of 12 within 30 s when the temperature of the outer medium is changed between 25 and 40 °C. Although the permeation of relatively small molecules such as NaCl and benzenesulfonate was decreased to some extent near 35 °C, it was gradually increased as the temperature was raised beyond C_p. Thus, the entangled, corked polymer moves thermodynamically at high temperatures and the permeation of small molecules is hardly suppressed at temperatures beyond C_p.

The temperature region of the thermosensitive permeation of the polymer-grafted capsule can be selected when the poly(*N*-alkylacrylamides) in Chart I having C_p at 5, 22, and 55 °C are employed as grafting polymers. Arrhenius plots of the permeation of naphthalenedisulfonate from polymer-grafted capsules are shown in Figure 3. The permeability decreased at temperatures beyond the corresponding C_p compared with that of the ungrafted capsule.

In conclusion, although nylon capsule membranes are simply semipermeable in proportion to temperature, the poly(*N*-alkylacrylamide)-grafted capsule membrane can reversibly regulate permeability by temperature changes depending on the molecular size of the permeants, in which the grafted polymer acts as a reversible thermovalve. The valve of the grafted polymer can also be opened or shut by pH changes[6] or redox reactions[12] when polyelectrolytes or viologen-containing polymers were employed for a permeation valve, respectively.

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References and Notes

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Yoshio Okahata,* Hiroshi Noguchi, and Takahiro Seki

Department of Polymer Chemistry
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152, Japan

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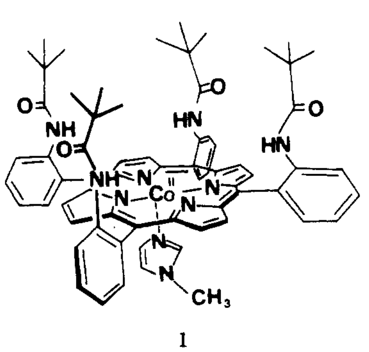
Highly Selective Transport of Molecular Oxygen in a Polymer Containing a Cobalt Porphyrin Complex as a Fixed Carrier

We describe herein the preparation of a polymer membrane containing [$\alpha,\alpha',\alpha'',\alpha'''$-*meso*-tetrakis(*o*-pivalamidophenyl)porphinato]cobalt(II) 1-methylimidazole (CoPIm) complex (1) through which molecular oxygen permeates with high selectivity ($P_{O_2}/P_{N_2} > 10$) and discuss the transport mechanism of the penetrant in the membrane containing the fixed carrier.



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Metal complexes such as iron–porphyrin derivatives and cobalt–Schiff base complexes form oxygen adducts reversibly and have been successfully applied to an oxygen-transporting fluid[1] and to an oxygen-separating liquid membrane.[2] These metal complexes bind oxygen according to a Langmuir isotherm. A polymer membrane containing the metal complex as a fixed carrier is expected to sorb and transport oxygen selectively by the Langmuir mode. From this viewpoint, a polymer membrane was

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