Novel Thin Film with Cylindrical Nanopores That Open and Close Depending on Temperature: First Successful Synthesis

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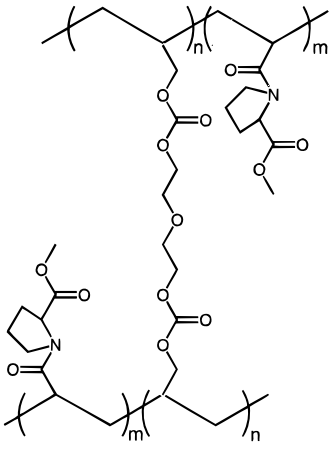
Received August 8, 1996
Revised Manuscript Received November 4, 1996

Recently, much attention has been focused on thin films developed from organic and inorganic molecules with micro- and mesopores.[1] These films have many useful functions in the selective transportation or absorption of specific molecules with sizes of those of the pores.[2] With the additional ability to open and close in response to an external stimulus, these pores can serve as an intelligent channel for the transportation of substances of molecular size. We describe the first successful synthesis of a novel thin film with a pore structure that opens and closes in aqueous solution depending on the temperature. The synthetic process for a film with pores that open and close involves four steps: (1) preparation of a thin core film made from a new polymer with specific characteristics sensitive to subsequent treatments; (2) irradiation of the film with a high-energy to form latent tracks through the film; (3) treatment of the film with an alkaline aqueous solution to develop cylindrical pore structures through the film; and (4) grafting of a polymer with a thermoresponsive swelling and shrinking capability. The film thus obtained was demonstrated to have open pores at temperatures above 16 °C and closed pores at temperatures below 12 °C by atomic force microscopy (AFM).



The 50 μm thick film was prepared by a cast polymerization technique involving copolymerization of diethylene glycol diallyl carbonate (DEBA, 1.8 g, 6.56 mmol) and acryloyl-L-proline methyl ester (A-Pro-OMe, 0.2 g, 1.09 mmol) initiated by diisopropyl peroxydicarbonate (0.06 g, 0.29 mmol) at 70 °C for 24 h between two glass plates spaced 50 μm apart by a spacer made from poly(ethylene terephthalate). DEBA is a comonomer which makes the film sensitive to the heavy ion beam irradiation,[3] and A-Pro-OMe contributes to the homogeneity of the subsequent grafting of the thermoresponsive polymer.[4] The film was irradiated with a ^{84}Kr ion beam with an energy of 6.19 MeV/n at a fluence of 10^7 ions/cm^2 under a high vacuum of 10^{-7} Torr (1 Torr = 133.3 Pa) with the Azimuthally Varying Cyclotron at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA). The film with latent ion tracks was treated with an aqueous 6 M NaOH solution at 60 °C for 1 h for etching of the ion tracks. Scanning electron microscopy (SEM) of the resulting film demonstrates that this treatment resulted in cylindrical pores of 1.3 μm diameter traversing the film whose thickness decreased to 48.4 μm by the alkaline etching of its surfaces.[5] The film was then immersed into an aqueous A-Pro-OMe solution (5% w/w) and irradiated with γ-rays at an irradiation dose of 30 kGy from a ^{60}Co source at 25 °C to give homogeneous graft-polymer chains on the surface of the film as well as that of the cylindrical pores. The yield of grafting was 1.1% as determined by gravimetry. The A-Pro-OMe polymer grafted onto the core film forms a gel layer 300 nm in thickness in an aqueous solution at 30 °C,[6] which swells and shrinks according to the temperature of the solution.[7] The end result was a synthesized thin film with cylindrical pores 700 nm in diameter covered with a thermoresponsive gel layer.

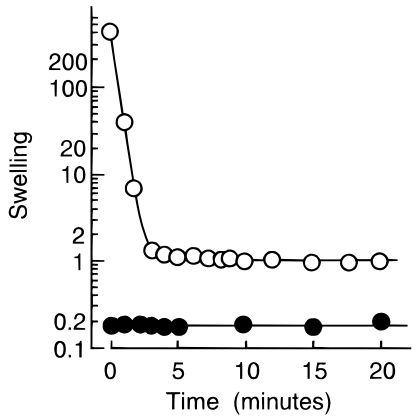


Figure 1. Shrinking profiles of a hard-core film consisting of DEBA/A-Pro-OMe (●) and a gel layer of poly(A-Pro-OMe) grafted onto the core film (○) after a temperature jump from 0 to 30 °C.

The thermoresponsive character of the film is shown in Figure 1. The rate of swelling (Sw) was determined by the equation $Sw = (W - W_0)/W_0$, where W is the weight of the sample immersed in water at a specific temperature and W_0 is that of the dried one. The core film has a consistent rate of Sw of 0.2 in the temperature range 0−30 °C. This suggests that the diameter of the cylindrical pores through the core film does not vary with on the temperature. In contrast, the Sw for the gel layer decreases rapidly from 440 to 1.1 when the temperature increases from 0 to 30 °C. This means that the gel layer swells by taking up water at 0 °C and shrinks to a thin layer by eliminating water molecules at 30 °C.

It can be expected from the swelling characteristics of the components of the film that cylindrical pores 700 nm in diameter consisting of a surface layer of poly(A-

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S0024-9297(96)01194-1 CCC: $12.00

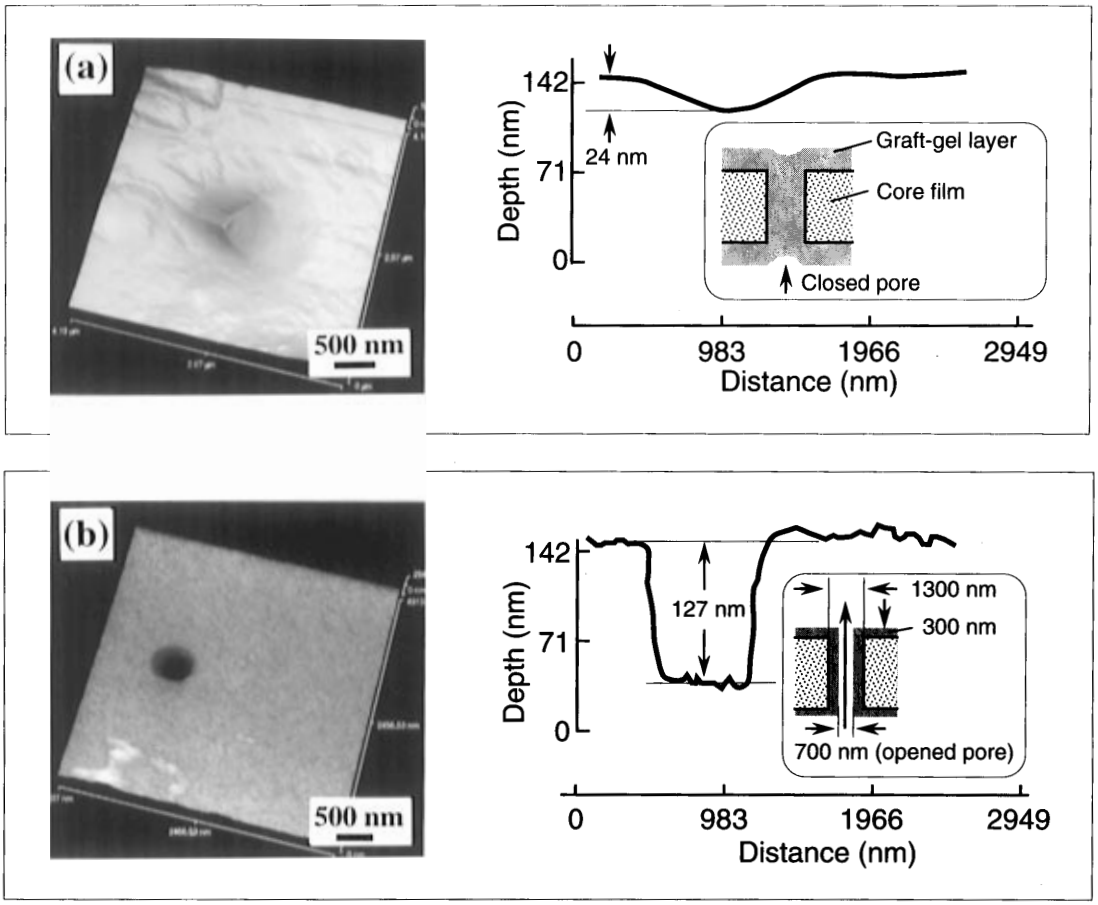

Figure 2. AFM photographs and line profiles of a thin film having cylindrical nanopores at 0 (a) and 30 °C (b).

Pro-OMe) grafted onto a core film should be completely closed by swelling of the surface layer at 0 °C and fully opened by shrinking of it at 30 °C. AFM observations showed that the cylindrical pores were fully opened at temperatures above 16 °C and fully closed at temperatures below 12 °C. This result is expected when taking into account the volume phase transition of the surface layer at 14 °C.[8] Direct evidence of opened and closed pores is illustrated by the AFM photographs in Figure 2.[8] At 0 °C (Figure 2a) the AFM photograph shows no evidence of any open pores in the films and a craterlike dent at the location where the cylindrical pores are present. The AFM photograph at 30 °C (Figure 2b), however, clearly shows evidence of fully opened pores. The line profiles obtained with AFM suggest that the dent formed by closing the cylindrical pore at 0 °C has a depth of 24 nm in the center. The open cylindrical pore at 30 °C can be estimated as having a diameter of 700 nm and a depth of 127 nm. The depth reaches the limit for what can be determined with the AFM used. The SEM photographs shown in Figure 3 support the results obtained by the AFM observations. Figure 3a represents the fully closed pores with a uniform size of 1.3 μm diameter at 0 °C, and Figure 3b represents the opened pores with 700 nm diameter at 30 °C.

The on−off switch function of pores opened and closed fully between two temperatures was also confirmed by studying the permeation of *p*-nitrophenol through the A-Pro-OMe-grafted and the ungrafted films having cylindrical nanopores, using a modified Franz cell,[9] and the result is shown in Figure 4. The apparent permeability constant (P) was calculated from the equation $P = \kappa V/AC$, where κ is the slope of the release-time curve, V is the volume of the outer water phase (receiver chamber), and A is the concentration of *p*-nitrophenol trapped in the donor chamber.[10] In the case of the ungrafted film, the permeability simply increased with increasing temperature. On the contrary, the permeability of the A-Pro-OMe-grafted film showed a marked change around a lower critical solution temperature of 14 °C,[5] where the permeability of *p*-nitrophenol at temperatures below 14 °C was found to be 8.2×10^{-6} cm/min, as the pores are fully closed, roughly 1/217 of the open-state value at 16 °C. This finding suggests the results obtained from both the AFM and the SEM observations.

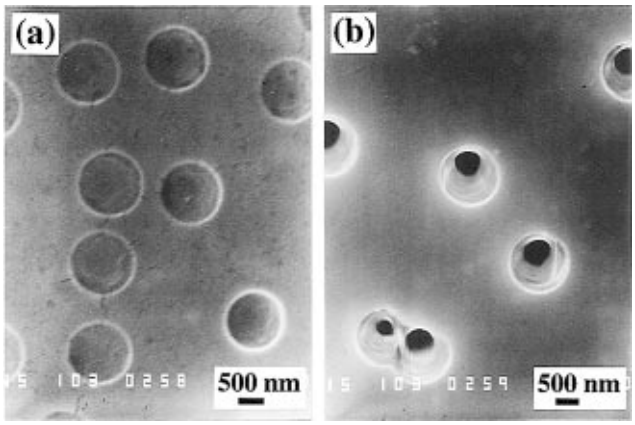

Figure 3. SEM photographs of a thin film having cylindrical nanopores covered with a gel layer of A-Pro-OMe at 0 (a) and 30 °C (b).

The evidence presented here shows that we have successfully synthesize a film with cylindrical pores of 700 nm diameter which fully opens at temperatures above 16 °C and fully closes at temperatures below 12

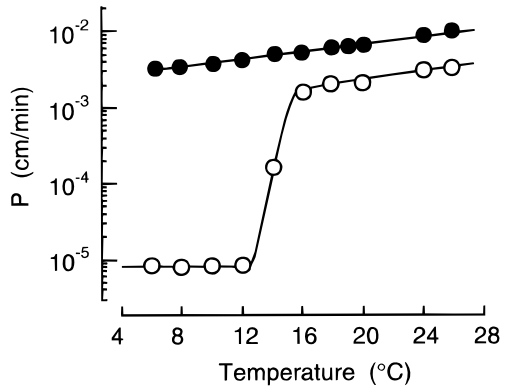

Figure 4. Temperature dependence of the permeability of *p*-nitrophenol from (○) A-Pro-OMe-grafted and (●) ungrafted films having cylindrical nanopores.

°C in an aqueous solution. Since the grafted polymer, A-Pro-OMe, which controls the opening and closing of the pores has been shown to have a specific rate of swelling of more than 1.1 at a specific temperature between 12 and 16 °C,[6] the film synthesized in this study could have cylindrical pores with a diameter of less than 700 nm at a specific temperature between these temperatures.

Acknowledgment. We are especially grateful to Dr. Michiko Hasemi (Nissei Sangyo Co., Japan) for her assistance in the AFM observations.

References and Notes

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(4) Graft-polymerization of A-Pro-OMe onto a film of poly(DEBA) without comonomer residues of A-Pro-OMe gave a heterogeneous grafting.

(5) For scanning electron microscopy, a sample was cut along the cylindrical pores. The cross section was coated by goal with a Giko IB-3 ion coater and then observed with a JEOL JXA-733 scanning electron microscope.

(6) Radiation-induced polymerization of A-Pro-OMe in an aqueous solution gives polymer chains with cross-linkings to lead a so-called "self-bridged polymer gel": Yoshida, M.; Safranj, A.; Omichi, H.; Katakai, R. *Macromolecules* **1996**, *29*, 2321.

(7) The gel based on poly(A-Pro-OMe) in aqueous solutions shows a phase transition at 14 °C with an abrupt volume change from a swollen state to a collapsed one: Safranj, A.; Yoshida, M.; Omichi, H.; Katakai, R. *Langmuir* **1993**, *9*, 3338.

(8) For AFM observation, the film in a vial was treated first at −78 °C to fix the structures established at 0 or 30 °C followed by lyophilization. The AFM photographs were obtained with a TopoMetrix TMX-2100 atomic force microscope.

(9) The A-Pro-OMe-grafted and ungrafted films having cylindrical nanopores cut into 1.9 cm diameter were sandwiched between two diffusion cells, 3 mL for donor chamber and 39 mL for the receiver chamber. The effective film area was 2.83 cm^2. The Franz cell was immersed in water kept at the prescribed temperature. Three milliliters of aqueous *p*-nitrophenol solution (695 μg/mL) maintained at the previously prescribed temperature was charged into the donor chamber immediately before the permeability measurement. Aliquots of the receiver chamber were collected from a side arm at various intervals. The concentration of permeated *p*-nitrophenol was assayed spectrophotometrically at 317.5 nm: Franz, T. J. *J. Invest. Sci.* **1975**, *64*, 190.

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