Polymer Membranes

Negatively Thermoresponsive Membranes with Functional Gates Driven by Zipper-Type Hydrogen-Bonding Interactions**

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Membranes with porous substrates and functional gates that are responsive to environmental stimuli are attracting increasing interest from various fields. Their permeation properties can be controlled or adjusted by the gates according to the external chemical and/or physical environment, and they may find various applications e.g. in controlled drug delivery, bioseparation, chemical separation, water treatment, tissue engineering, and as chemical sensors. The functional gates for stimuli-responsive membranes serve as chemical valves, and have been reported to act in response to changes in environmental temperature,[1–5] pH,[5–10] ionic strength,[11] glucose concentration,[12,13] electric field,[14] light,[15] redox properties,[16] or different molecules.[17–19] There are many cases in which environmental temperature fluctuations occur naturally, and in which the temperature stimuli can be easily designed and artificially controlled; therefore much attention has recently been focused on thermoresponsive membranes.[2–5] Up to now, almost all of the thermoresponsive gating membranes have featured positively thermoresponsive characteristics, that is, the membrane permeability increases with increasing environmental temperature, because all of the thermoresponsive functional gates were constructed from poly(*N*-isopropylacrylamide) (PNIPAM).[1–5] In these cases, the membrane pores change from a "closed" to an "open" state when the environmental temperature increases from below the lower critical solution temperature (LCST) of PNIPAM to above the LCST, as a result of the swelling/shrinking conformational change of the polymer. In certain applications, however, an inverse mode of the thermoresponsive gating behavior of the membranes is preferred. Here we report a novel family of thermoresponsive gating membranes with negatively thermoresponsive gating characteristics, that is, "opening" of the membrane pores is induced by a decrease rather than an increase in temperature.

The concept of the proposed negatively thermoresponsive gating membrane and the fabrication procedure are schematically illustrated in Figure 1. The functional gates of the membrane are constructed from thermoresponsive interpenetrating polymer networks (IPNs) composed of polyacrylamide (PAAM) and poly(acrylic acid) (PAAC). It is known that PAAM and PAAC form complexes in solution through hydrogen-bonding interactions.[20] The resultant cooperative "zipping" interactions between the polymer chains indicate that the PAAM/PAAC-based IPN hydrogels have a thermoresponsive volume phase transition characteristic that is the reverse of that of PNIPAM, that is, the hydrogel swelling is induced by an increase rather than a decrease in temperature.[21–23] PAAC forms intermolecular hydrogen bonds with PAAM when the environmental temperature is lower than the upper critical solution temperature (UCST) of the

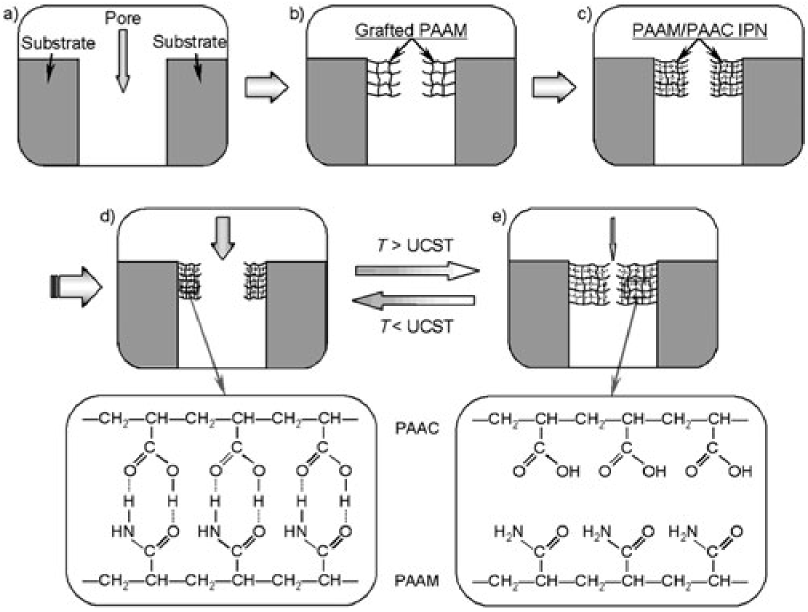

Figure 1. Schematic illustration of the concept of the proposed negatively thermoresponsive gating membrane and the fabrication procedure. The functional gates of the membrane are thermoresponsive interpenetrating polymer networks (IPNs) composed of polyacrylamide (PAAM) and poly(acrylic acid) (PAAC), in which the volume phase transition is driven by the cooperative "zipping" interactions between the molecules that result from hydrogen-bonding interactions. a) Porous membrane substrates. b) Membranes with grafted PAAM gates prepared by a plasma-graft pore-filling polymerization method. c) Membranes with PAAM/PAAC-based IPN gates prepared by sequential IPN synthesis. d) The pores of the membranes "open" because the functional gates are in their shrunken state at temperatures below the upper critical solution temperature (UCST) as a result of PAAM/PAAC complex formation by hydrogen-bonding interactions. e) The membrane pores "close" because the PAAM/PAAC-based IPN gates are in their swollen state at temperatures above the UCST as a result of complex dissociation by the breakage of hydrogen bonds.

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PAAM/PAAC-based IPN gel, and the IPN hydrogels have a shrunken state as a result of the interaction between two polymer chains, which is the so-called chain–chain zipper effect. However, when the environmental temperature is higher than the UCST of the IPN gel, intermolecular PAAM–PAAC hydrogen bonds are disrupted and the IPN hydrogels become swollen. Therefore, the proposed membrane gates shrink at temperatures below the UCST as a result of PAAM–PAAC complex formation by hydrogen-bonding interactions, and swell at temperatures above the UCST as a result of PAAM–PAAC complex dissociation. Consequently, the membrane pores change from an "open" gate to a "closed" gate when the temperature increases from below the UCST above the UCST.

Thermoresponsive membranes with PAAM/PAAC-based IPN gates were prepared by a method of sequential IPN synthesis, in which cross-linked PAAM grafted in the pores of porous nylon 6 (N6) membranes and PAAC gels were synthesized as an initial gel matrix and as secondary gels, respectively (see Supporting Information). Briefly, plasma-graft pore-filling polymerization was employed to graft cross-linked PAAM gates in the pores of the substrates according to the method described previously.[3,10,13,17] The PAAM-grafted N6 membranes were swollen, immersed in aqueous acrylic acid (AAC) solution containing initiator and cross-linker, and the AAC monomer was polymerized and cross-linked within the grafted PAAM matrix gels in the pores to form PAAM/PAAC-based IPN gates. Scanning electron microscope (SEM) images and X-ray photoelectron spectroscopy (XPS) were used to confirm the structure of the membrane and the IPN synthesis. Pressure-driven filtration experiments were carried out to determine the temperature dependence of the hydraulic permeability of membranes with PAAM/PAAC-based IPN gates.

Figure 2 shows SEM images of the cross-sectional views of the virgin porous N6 substrate and membranes with grafted PAAM gates and PAAM/PAAC-based IPN gates. The parameters Y_{PAAM} and Y_{PAAC} are the mass increase ratios of the membrane after PAAM grafting and PAAC synthesis, respectively. It can be seen from the cross sections of the virgin (Figure 2a), PAAM-grafted (Figure 2b), and PAAM/PAAC-based IPN-gated (Figure 2c) membranes that the structures are quite different. After grafting of PAAM onto the inner pore surfaces of the porous N6 membrane, a significant gating layer with a thickness of about 2 μm was formed near the membrane surface. On synthesis of the PAAM/PAAC-based IPN, the gating layer under the membrane surface clearly became denser than that of the PAAM-grafted membrane, while the thickness of the gating layer was almost the same. These microstructures indicate that the PAAM/PAAC-based IPNs were only synthesized in the initial PAAM gel matrix.

Figure 3 shows the XPS O_{1s} core-level spectra of the virgin N6 membrane, the membrane with grafted PAAM gates, and the membrane with PAAM/PAAC-based IPN gates. The spectrum of the N6 membrane can be curve-fitted with a single peak of binding energy (BE) of 531.7 eV for the C=O species. For the membrane with grafted PAAM gates, the peak area of the C=O species is larger than that of the N6 substrate, as a result of the contribution of C=O groups of the grafted PAAM. The O_{1s} core-level spectrum of the membrane with PAAM/PAAC-based IPN gates can be curve-fitted by using two peak components with BEs of 531.8 eV for the C=O species and 533.2 eV for the O–H species. The new peak component at BE 533.2 eV is assigned to the O–H species of the synthesized PAAC polymers in the PAAM/PAAC-based IPN. These experimental observations confirm that the prepared gates of the porous membranes have the expected PAAM/PAAC-based IPN architecture.

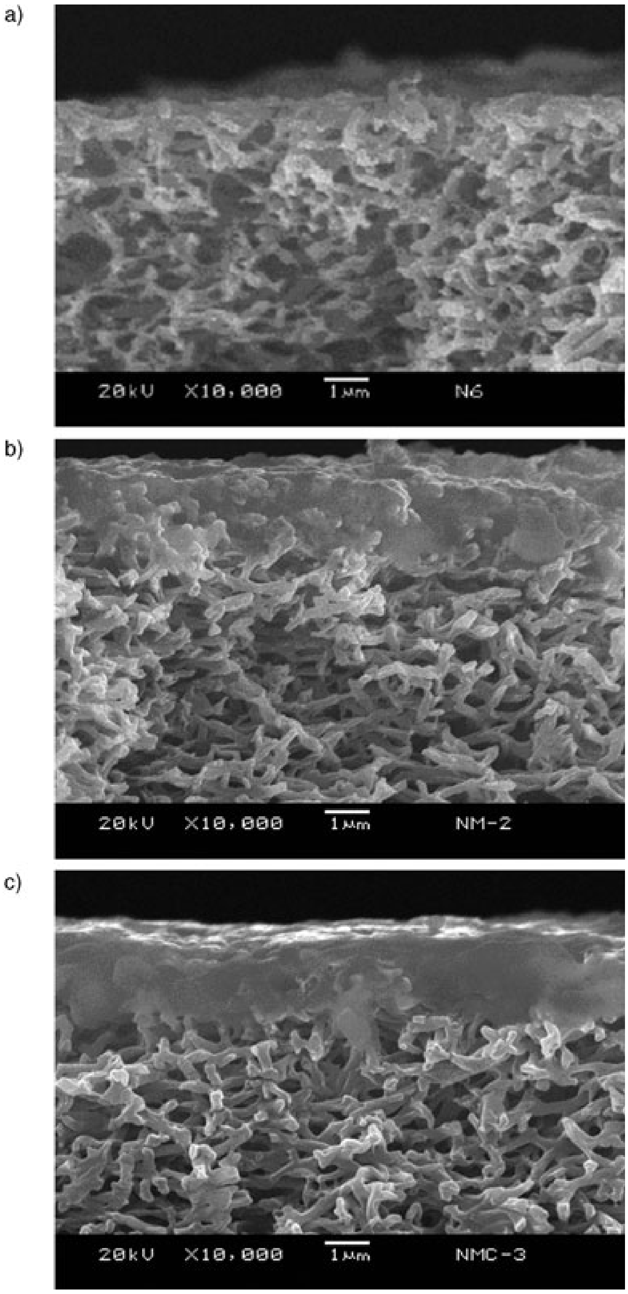

Figure 2. SEM images of the cross sections of a) virgin nylon 6 (N6) substrate membrane, b) membrane with grafted PAAM gates ($Y_{\mathrm{PAAM}} = 4.61\,\%$), and c) membrane with PAAM/PAAC-based IPN gates ($Y_{\mathrm{PAAM}} = 4.25\,\%$ and $Y_{\mathrm{PAAC}} = 2.20\,\%$). Scale bar 1 μm.

Figure 4a–c shows the temperature dependence of hydraulic permeability through the virgin N6 substrate membrane and the membranes prepared with PAAM/PAAC-based IPN gates. The water flux of the virgin N6 substrate simply increased with increasing environmental temperature, as a consequence of the decreasing viscosity of water with increasing temperature. However, under the same experimental conditions, the temperature-dependent water flux curves of membranes with PAAM/PAAC-based IPN gates were quite different. These membranes exhibited negatively thermoresponsive characteristics, such that the membrane permeability decreased with increasing environmental temperature. The water flux in the temperature range from 10 to 15 °C was much larger than that in the range from 30 to 40 °C. A sharp transition of the hydraulic permeability occurred on going from 20 to 25 °C, which corresponded to the UCST of PAAM/PAAC-based IPN hydrogels.[21–23] The water flux of the membrane dropped rapidly with formation of PAAM/PAAC-based IPN gates in the pores or with increasing Y_{PAAM} and Y_{PAAC} values in the synthesis of IPN gates, which arose from the decrease of the effective mean diameter of the membrane pores. According to Hagen–Poiseuille's law, the water flux of a porous membrane is governed by the fourth power of the pore diameter.[3e,13a] Thus, the conformational change of PAAM/PAAC-based IPN gates constructed on the inner surfaces of membrane pores greatly affects the water flux. Below the UCST, PAAM/PAAC intermolecular complexes are formed by hydrogen-bonding interactions and the chain–chain zipper effect leads to collapse of the IPN and opening of the membrane pores; as a result the hydraulic permeability was large. In contrast, the IPN was in its swollen state at temperatures above the UCST because of PAAM–PAAC complex dissociation due to disruption of hydrogen bonds; therefore, the pores in the membrane were closed by the IPN gates, which resulted in a smaller hydraulic permeability (Figure 1). The thermoresponsive gating characteristics of the prepared membranes were complementary to those of membranes constructed with PNIPAM gates.[1–5]

To verify the reversibility of the IPN gates, pressure-driven filtration experiments were carried out by changing the environmental temperature across the UCST; the temperature was alternately kept at 10 and 40 °C. The reversible thermoresponsive gating characteristics of the membrane with PAAM/PAAC-based IPN gates are shown in Figure 4d. The thermoresponsive permeability of the membrane was satisfactorily reproducible, which suggests that the IPN gates retained their thermal swelling/shrinking properties intact, even though they underwent repeated temperature changes across the UCST. Thus, reversible thermoresponsive permeation was effectively achieved.

In summary, a novel family of thermoresponsive gating membranes composed of a porous substrate membrane and PAAM/PAAC-based IPN polymers in the pores, which act as thermoresponsive gates, has been successfully developed. The hydraulic perme-

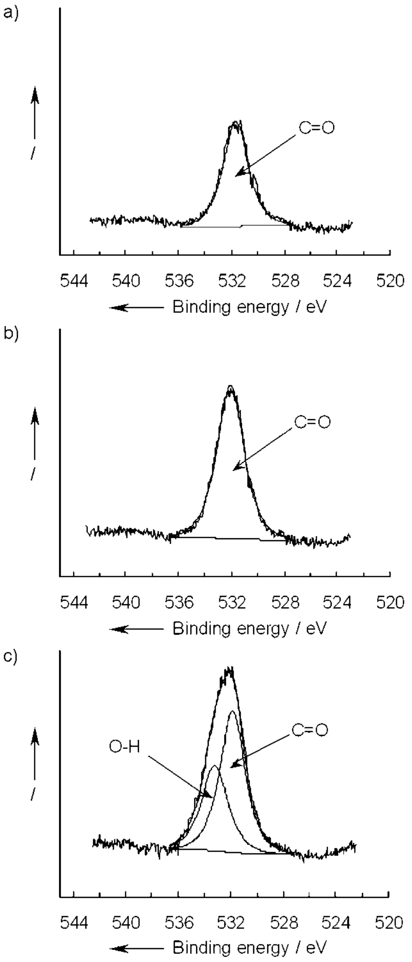

Figure 3. XPS O_{1s} core-level spectra of a) virgin N6 membrane, b) membrane with grafted PAAM gates ($Y_{\text{PAAM}} = 7.57\%$), and c) membrane with PAAM/PAAC-based IPN gates ($Y_{\text{PAAM}} = 6.94\%$ and $Y_{\text{PAAC}} = 7.53\%$).

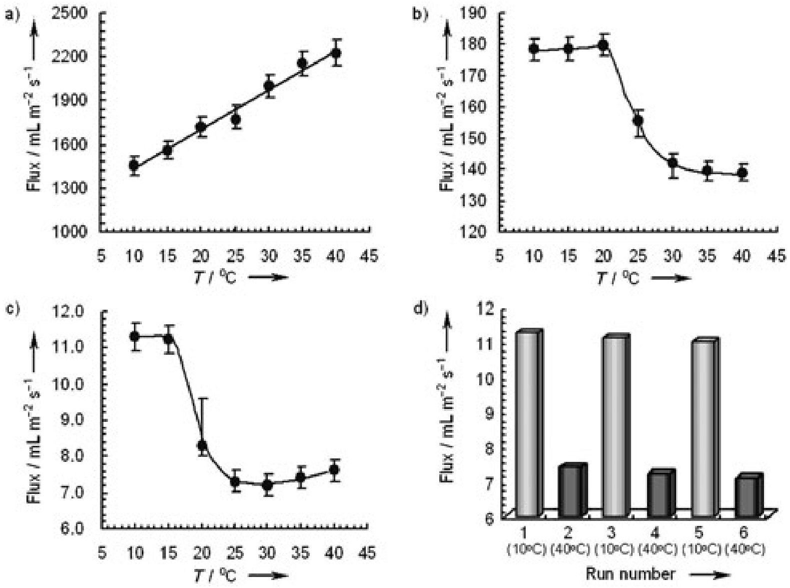

Figure 4. Temperature dependence and reversible thermoresponsive gating characteristics of hydraulic permeability through membranes with PAAM/PAAC-based IPN gates. a) Virgin N6 membrane and b–d) membranes with PAAM/PAAC-based IPN gates. b) $Y_{\text{PAAM}} = 2.94\%$ and $Y_{\text{PAAC}} = 4.12\%$; c, d) $Y_{\text{PAAM}} = 5.01\%$ and $Y_{\text{PAAC}} = 4.64\%$.

ability of the membranes exhibits significant negative gating characteristics, that is, the "opening" of the membrane pores is induced by a decrease rather than an increase in the environmental temperature. The membranes with PAAM/PAAC-based IPN gates show satisfactorily reversible and reproducible thermoresponsive permeation characteristics. These gating membranes provide a new mode of behavior for thermoresponsive "smart" or "intelligent" membrane actuators, which is highly attractive for targeting drug delivery systems, chemical separations, and sensors.

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