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Poly(*N*-isopropylacrylamide)-grafted Thermosensitive Anodized Aluminum Oxide Membrane

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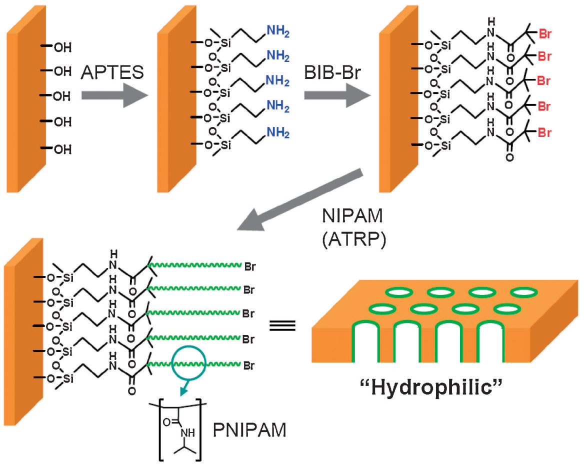
Thermosensitive membrane is prepared by surface-initiated atom-transfer radical polymerization of *N*-isopropylacrylamide (NIPAM) from initiator-attached anodized aluminum oxide (AAO) membrane to formulate smart membrane which can control mass transport through membrane by temperature control. PNIPAM-grafted AAO membrane with partially open pores shows accelerated water transport on heating above lower critical solution temperature (LCST). Pore widening effect might suppress increased hydrophobicity of PNIPAM brush on the pores of AAO membrane above LCST.

Membrane engineering has received increasing research interest because precise control of active mass transfer through membrane layers is essential not only in most biological systems but also in many smart micro devices such as sensors and valves. Light-induced wettability change, light-induced nanopore size variation, and electric field-induced nanopore modulation have been reported to efficiently control the chemical and dimensional properties of nanopores inside membranes.[1–4] Temperature is an excellent and versatile controlling parameter which renders precise engineering of nanomaterials or nanostructures possible.[5] Poly(*N*-isopropylacrylamide) (PNIPAM) is a well-known temperature-responsive material which can impart temperature-driven reversible wettability change on surfaces. PNIPAM is hydrophilic and water soluble at ambient temperature but loses its hydrophilicity above its lower critical solution temperature (LCST) around 38 °C shifting to hydrophobic, and finally precipitation occurs due to strong interchain aggregation.[6–9] When PNIPAM is used as a form of polymer brush on a surface, interchain polymer aggregation cannot happen because all PNIPAM chains are covalently linked with the surface. Instead every polymer chain shrinks by itself and then this shrinkage makes the PNIPAM brush layer thinner above LCST.[10,11]

In this communication, we report the preparation of thermoresponsive PNIPAM-grafted membrane which can precisely control water-transfer rate through membrane by temperature variation (Scheme 1). Commercially available anodized aluminum oxide (AAO) membranes with pore size of 0.2 µm were used for the experiments.[12] After intensive cleaning with water, methanol, and acetone, bare AAO membranes were dried over 120 °C under vacuum. Then, amine functionalities were introduced on the surface of AAO membrane via self-assembled monolayer (SAM) formation with 3-aminopropyltriethoxysilane (APTES). For surface-initiated atom-transfer radical polymerization (ATRP),[13] initiating bromine functionalities were introduced on the surface of AAO membrane by esterification of amine-functionalized AAO with 2-bromoisobutyryl bromide (BIB-Br). Finally, surface-initiated ATRP of *N*-isopropylacrylamide (NIPAM) was carried on using the above initiator-functionalized AAO membrane in argon using CuBr and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) as catalyst and ligand, respectively, in ethanol at room temperature.[14] After enough polymerization, PNIPAM-attached AAO membranes were extensively washed with water, methanol, and acetone to remove any physically adsorbed reagents. The molecular weights of PNIPAM brushes on AAO membrane were estimated by GPC measurement of molecular weights of free PNIPAM in polymerization medium.



Scheme 1. Schematic illustration of the preparation of PNIPAM-grafted "hydrophilic" AAO membrane.

To confirm the presence of initiators and PNIPAM chains on the surface of AAO membrane, energy-dispersive X-ray (EDS) analysis was performed. EDS analysis of initiator-attached AAO membranes showed the presence of corresponding C, Si, and Br atoms (3.73, 0.48, and 0.71 atom %, respectively) while atomic composition was mainly Al and O (27.31 and 66.58 atom %, respectively). Nitrogen was not significantly observed possibly due to its weak signal intensity. After ATRP of NIPAM for 12 h, PNIPAM-grafted AAO membrane shows significant peaks from C and N atoms (11.27 and 6.45 atom %, respectively), confirming that surface-initiated ATRP of NIPAM on initiator-attached AAO membrane was successful. To determine the molecular weights of grafted PNIPAM chains, molecular weights of free PNIPAM chains in polymerization medium were monitored by GPC depending on the polymerization time with the use of sacrificial initiator.[14] After 6 and 12 h, M_w's of 5×10^4 and 3×10^5 Da and polydispersity index (PDI) (M_w/M_n) of 1.3 and 2.8 were observed, respectively. Increased termination processes such as radical coupling might contribute the high PDI in prolonged ATRP of PNIPAM. Polymerization for 24 h produced partially insoluble product in polymerization medium. Next, FE-SEM images of PNIPAM-grafted AAO membrane were monitored after polymerization time of 6, 12, and 24 h, respectively. While the initial bare AAO membrane just shows typical pore

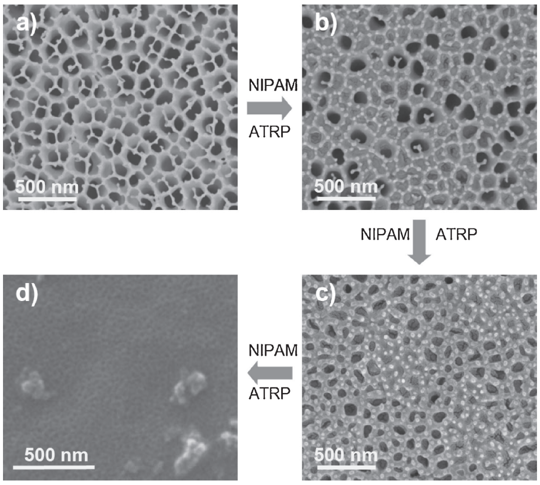


Figure 1. FE-SEM images of a) bare AAO membrane, b), c), and d) PNIPAM-grafted AAO membranes after polymerization time of 6, 12, and 24 h, respectively.

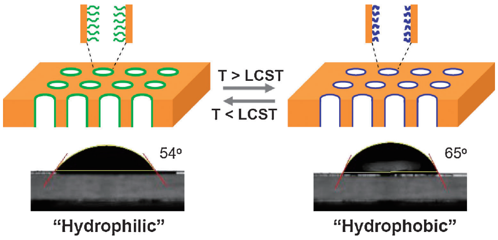


Figure 2. Illustration of thermoresponsive wettability change of PNIPAM-grafted AAO membrane and photo images of water droplets on above membrane below and above LCST.

structures with pore sizes around 0.2 µm (Figure 1a), PNIPAM-modified AAO membrane shows certain PNIPAM layers around pores of membrane. While polymerization for 6 and 12 h produces partially opened AAO membrane surface structures (Figures 1b and 1c), polymerization for 24 h shows completely closed pore structures (Figure 1d). Next, contact angles of water droplets were monitored on prepared PNIPAM-grafted AAO membrane while changing temperature. On heating over 40 °C, membrane surface showed decreased contact angle of 65° compared with original contact angle of 54° at room temperature (Figure 2). This wettability change results from hydrophilic–hydrophobic phase transition of PNIPAM chains above LCST. This wettability switching of PNIPAM-grafted membrane is reversible for more than 30 operation cycles.

Thermoresponsive wettability change of PNIPAM-grafted membrane prompted us to evaluate PNIPAM-attached AAO membrane as a *nanovalve* for water transport through thermoresponsive membrane. Heating above LCST will produce narrower and hydrophobic pores compared with wider and hydrophilic pores of membrane below LCST (Figure 2). Initially, on/off switching of water transport through thermoresponsive membrane was attempted by inserting the PNIPAM-grafted membrane (Figure 1d, after polymerization for 24 h) into a glass membrane filtration unit. The water-transport rate was, however, too slow regardless of temperature probably due to the dense structures of PNIPAM layer on the AAO membrane. Next, membranes having partially opened pores (Figures 1b and 1c, after polymerization for 6 and 12 h, respectively) were tested. Because membrane pores are still in *open* states, water can pass through the modified membranes through partially opened pores. When hot water above LCST was passed through PNIPAM-grafted membranes (after 12 h of polymerization), acceleration of water transport was observed [from 1.0 (below LCST) to $1.8\,\mathrm{mL\,s^{-1}}$ (above LCST)]. Actually, there are noticeable changes in both wettability and pore size. While heating over LCST induces *pore widening* due to aggregation of PNIPAM chains, hydrophobicity of membrane also increases. Pore-widening effect seems to suppress the increase of hydrophobicity, and finally water-transport rate significant increases on heating above LCST using PNIPAM-grafted membranes having partially opened pores. For comparison, water-transport rate was monitored using bare AAO membrane, and there was much weaker increase in water-transport rate (from 1.1 to $1.3\,\mathrm{mL\,s^{-1}}$) probably due to the slightly decreased viscosity of water on heating.

In summary, thermoresponsive PNIPAM-grafted AAO membrane was prepared via surface-initiated ATRP on surface of AAO membrane. Acceleration of water transport was demonstrated through pore-widening effect of PNIPAM-grafted membrane having partially opened pores above LCST. This formulation of thermoresponsive membrane can be helpful for the formulation of thermoresponsive nano devices.

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