

Synthesis and Characterization of Silica–Poly(*N*-isopropylacrylamide) Hybrid Membranes: Switchable Molecular Filters

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Hybrid materials consisting of stimuli-responsive polymers (SRPs) in an inorganic matrix have the potential for use in a variety of applications as switchable or tunable membranes, coatings, adsorbents, and solute reservoirs. Poly(*N*-isopropylacrylamide) (PNIPAAm) is an SRP that exhibits inverse solubility behavior in water upon an increase in temperature through a transition from a hydrophilic to a hydrophobic state. In an earlier communication, we demonstrated that when PNIPAAm is encapsulated in a silica matrix by a sol–gel process, the resultant hybrid material can function as a switchable molecular filter. In this paper, we present detailed investigation and characterization of these membranes, which exhibit reversible on/off permeation behavior, above and below the transition temperature of PNIPAAm, respectively. Scanning and transmission electron microscopic studies show that the membranes are highly homogeneous, and phase separation of the polymers is not observed. Differential scanning calorimetry, contact angle, and permeation experiments indicate that the PNIPAAm in the hybrid materials retains its aqueous critical solubility transition. Nitrogen porosimetry measurements indicated that the dried hybrid materials are mesoporous with an average pore size of ~30 Å. Permeation of solutions of poly(ethylene glycols) (PEGs) varying in molecular weight through the hybrid membranes clearly demonstrates that they can function as switchable molecular filters. Under controlled pressure, the membranes are impermeable to water below the transition temperature. At the same pressures, above the transition temperature, membranes are permeable to PEGs with molecular weights below a threshold value. In the membranes studied, the molecular weight of PNIPAAm encapsulated in the silica did not dramatically affect the PEG molecular weight threshold for permeation.

Introduction

The development of hybrid functional nanosystems that incorporate polymers and inorganic components is a recent trend in materials synthesis.^{1,2} There has also been widespread interest in the research of smart or intelligent materials during the past decade.^{3–5} These materials respond to slight changes in the external medium such as pH, temperature, ionic strength, or electric field. Poly(*N*-isopropylacrylamide) (PNIPAAm), one of the most widely studied temperature-responsive polymers, exhibits a transition from a hydrophilic state to a hydrophobic state at a temperature known as the lower critical solution temperature (LCST). Below the LCST (typically ~32 °C), the polymer is in an extended

conformation and soluble in water; above the LCST, the polymer collapses and is insoluble in water.^{6–8} This interesting property was exploited in a variety of applications including bioseparations,^{3–6,8–10} control of biofouling,^{11,12} and enzyme and cell immobilization.^{13–15} PNIPAAm and other smart polymers have also been used to control fluid and molecular transport in materials and devices, for example, in drug delivery^{3,4,16–18} and microfluidic systems.¹⁹ In general, the methods by which

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PNIPAAm has been used to control permeation can be grouped into three distinct approaches: (1) as bulk cross-linked gels in which transition to the compact (dehydrated) conformation results in a decrease in permeability of the gel,^{6,16,17} (2) as immobilized chains on a porous support in which transition to the compact conformation results in a change in the permeability of the hybrid structure,^{20–22} and (3) as immobilized chains on a porous support in which the LCST transition results in a change in the polarity of a surface that influences transport through a chromatographic column.^{9,10}

Recently we described a sol–gel synthesis of a new type of smart hybrid material composed of silica and a thermoresponsive polymer (PNIPAAm).²³ The PNIPAAm is randomly dispersed in a silica matrix. The concentration of PNIPAAm is controlled above its percolation threshold.²⁴ By dispersing the PNIPAAm in an impermeable silica matrix, transition through the LCST results in the opening of a contiguous porous network of molecular dimensions.²³

In this paper, we present detailed investigation of the microstructure and function of these silica–PNIPAAm hybrid membranes. Structural information is obtained from scanning and transmission electron microscopy and nitrogen porosimetry; functionality of the hybrid membranes is probed by permeation measurements and differential scanning calorimetry. The effect of the molecular weight of the encapsulated PNIPAAm on the permeation behavior is also examined. We carried out permeation experiments using solutions of monodisperse poly(ethylene glycol)s of various molecular weights and demonstrated that the PNIPAAm in hybrid membranes can act as a molecular switch that can be used to control the selective molecular permeability of the membranes. We also demonstrate the functioning of the switchable molecular filters in a pressurized ultrafiltration cell and compare the permeation behavior observed with that obtained in centrifugal filters. In addition, contact angle measurements were also carried out to demonstrate the switchable behavior (from a hydrophilic to a hydrophobic state) of the surface of a smart coating upon an increase in temperature.

Experimental Section

Materials. We used the following chemicals: tetraethyl orthosilicate (TEOS) (Aldrich), PNIPAAm (weight average $M_w = 349\,000$; $M_w/M_n = 3.64$ from Polysciences, Inc), carboxyl PNIPAAm (M_w of 70, 26, 14, and 7000 with $M_w/M_n \sim 1.1$ from Polymer Source), ethyl alcohol

(Aaper), crystal violet ($M_w = 408$, Fischer Scientific), poly(ethylene glycol) (PEG) of polymer standard grade with molecular weights (M_w) of 100, 1000, 2200, 2700, 5000, 6000, 7850, 9000, and 15 000 with $M_w/M_n 1.1$ (Polysciences and Polymer Source), and PEG ($M_w = 400$, Aldrich). All chemicals were used as received. Deionized water whose resistivity was greater than 18.2 MΩ·cm was used for all the experiments.

Silica sol was prepared by a standard sol–gel process by mixing TEOS, ethanol, water, and HCl in a molar ratio of 1:3:1:0.0007 followed by a reaction at 60 °C for 90 min.^{23,25} The resulting stock sol was stored at –20 °C until use. For each membrane prepared, 0.25 mL of stock sol was diluted with 0.043 mL of water and 0.6 mL of ethanol and stirred well to yield a sol with final proportion TEOS:ethanol:water:HCl = 1:20:5.02:0.0007. Aliquots (1 mL) of PNIPAAm solutions (4.5 mg/mL) in pH 4.0 were prepared, added to the diluted stock sol, and stirred to obtain a clear, transparent hybrid sol. The concentration of PNIPAAm in precursor solution is 20 vol % to that of silica. The hybrid sols were coated on Millipore Microcon centrifugal filter units (diameter 1.23 cm, active membrane area 0.32 cm²) with 30 000 (YM-30), 50 000 (YM-50) and 100 000 (YM-100) molecular weight cutoff membranes at 1500–2000 rpm using a spin coater. Sols were also coated on YM-30 disk membranes (2.5-cm diameter) that were used in pressurized ultrafiltration experiments. To obtain bulk gels, the sol was aged at room temperature until gelation. Gels were washed thoroughly with water prior to characterization.

Characterization. Uncoated and silica–PNIPAAm coated filters were sputter coated with platinum and characterized by scanning electron microscope (SEM) (Hitachi S-800). Transmission electron microscopy (TEM; JEOL 2010 HRTEM) studies were carried out on the hybrid films. The membranes were scraped and collected on a carbon-coated copper grid. Point-to-point resolution of the HRTEM is 0.19 nm. Silica–PNIPAAm hybrid gels were subjected to thermal analytical studies to determine the LCST of PNIPAAm in the silica gel matrix. Differential scanning calorimetric (DSC) studies were carried out using a Universal V2.5H TA instrument. A total of 40–50 mg of sample was used for the measurements. Experiments were carried out in a nitrogen atmosphere with a heating rate of 1 K/min. Silica gel prepared without the PNIPAAm was used as a reference.

Surface area and pore size distribution studies were carried out using nitrogen adsorption and desorption at 77 K on washed and dried gels using a Micromeritics ASAP 2000 porosimeter (Micrometrics Inc., Norcross, GA).²⁴ Samples were outgassed at 80 °C for 12 h under ultrahigh-purity helium.

Silica–PNIPAAm sols were also spin coated on gold-coated glass substrates. The films thus obtained were used for contact angle measurements using a Ramé–Hart model 100 contact angle goniometer. The sample was placed inside an environmental chamber saturated with water vapor and heated by circulating water from the temperature-controlled water bath. The tempera-

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ture inside the chamber was measured with a thermocouple. The sample was equilibrated at a specified temperature for 20 min, and then the contact angle values were measured using a sessile drop method.

Permeation Experiments. Permeation experiments were carried out using an IEC Centra CL3R centrifuge at various temperatures ranging from 25 to 40 °C with a controlled temperature of ± 1 °C. Solutes (100–300 μ L aliquots of crystal violet (0.1 wt % aqueous solution) and PEGs (1–3 wt % aqueous solutions)) were centrifuged through uncoated, silica-coated, and silica-PNIPAAm-coated YM-30, -50, and -100 centrifugal filters. Unless otherwise indicated, permeation experiments were done at 1000 rpm, equivalent to an estimated centrifugal force of 200g for 3 min. Initially, the samples were equilibrated to the test temperature in an oven for 10–20 min and transferred to the centrifuge, which was maintained at the set temperature, and the samples were again equilibrated at that temperature for 5 min before the centrifugation was carried out. The concentration of crystal violet in the filtrate was determined from UV spectrophotometric measurements at 591 nm. For PEG experiments, the concentration of the filtrate was determined from refractive index measurements using a Kernco refractometer by comparing to a calibration curve obtained by measuring the refractive index of known concentrations of PEG. The minimum concentration of PEG, which can be measured using our refractometer, was determined to be 0.3 wt %.

Permeation experiments were also carried out using a standard Amicon stirred ultrafiltration 8003 cell with a capacity of 3 mL. Silica-PNIPAAm-coated YM-30 membranes were mounted in the ultrafiltration cell, and nitrogen gas was used to pressurize the cell at various set pressures (20–60 psi). The amount of filtrate collected was weighed and used to estimate the flow of filtrate per minute. Refractive index measurements were carried out at room temperature to determine the concentration of PEG in the filtrate.

Results and Discussion

Scanning electron microscopy was used to ensure that the spin-coating process produces defect-free overlayers of hybrid silica-PNIPAAm membrane over the macroporous membranes used as supports (Figure 1). Uncoated YM-100 membranes have very large pores connected as channels. YM-100 membranes are molecular weight cutoff filters; under an appropriate pressure, globular proteins whose molecular weight is less than 100 000 pass through these membranes but proteins with molecular weight greater than 100 000 do not.²⁶ According to specification of the manufacturer of YM-100 membranes, the rejection of a globular protein above MW 100 000 through a YM-100 membrane is 5%. Random coil polymers higher than MW 100 000 may also snake through the pores of the membranes.²⁶ Scanning electron micrographs of dried silica-PNIPAAm membranes indicate that the surface of the membranes is smooth and devoid of any defects, and the thickness of the hybrid membrane is ~ 2 μ m. Similar results are obtained for membranes coated on YM-30 and YM-50

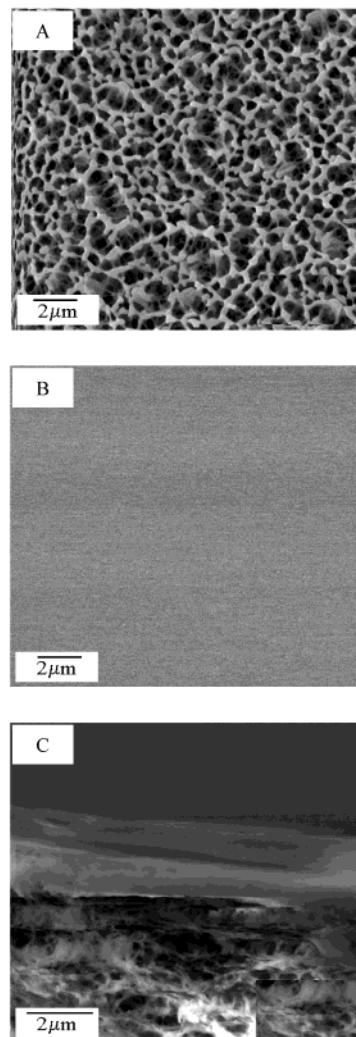


Figure 1. Scanning electron micrographs of (A) uncoated YM-100 membrane, (B) silica-PNIPAAm (MW 40 000) illustrating absence of pinholes, and (C) cross section of the membrane showing the thickness of the membrane (~ 2 μ m).

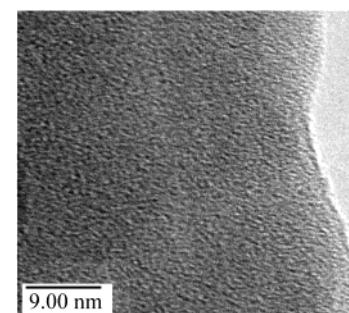


Figure 2. Transmission electron micrograph of silica-PNIPAAm (MW 300 000) membrane showing the homogeneity of the membrane.

filters. Bulk hybrid gels prepared similarly are transparent, indicating that PNIPAAm is highly dispersed in the silica matrix and there is no phase segregation. Transmission electron micrographs of the dried hybrid membranes did not show any evidence of heterogeneity in the structure of the membranes (Figure 2), further indicating the absence of segregation of PNIPAAm in the hybrid material.

Figure 3A presents adsorption and desorption isotherms of the dried hybrid gels that indicate that these

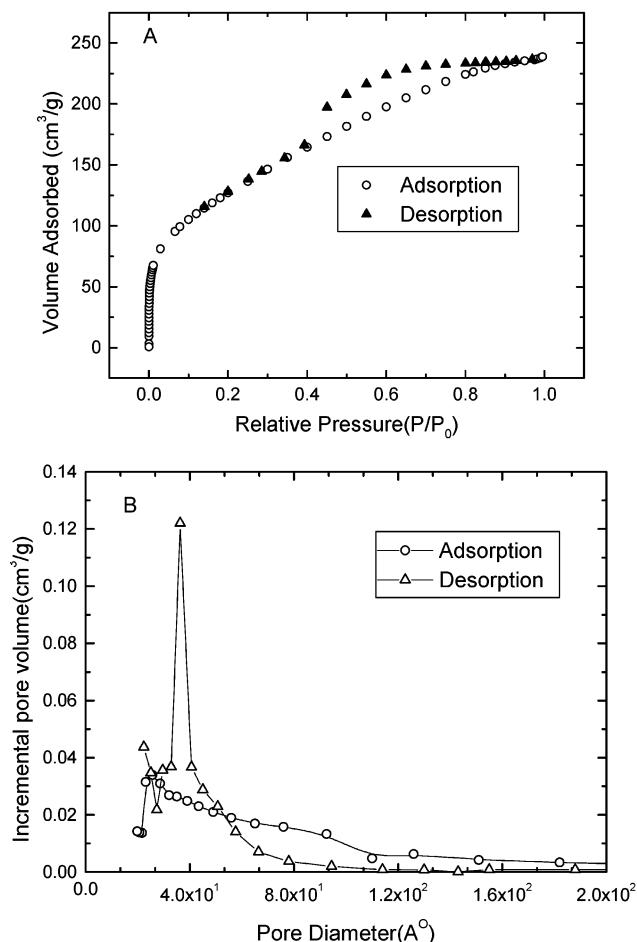


Figure 3. (A) Nitrogen adsorption and desorption isotherms at 77 K of silica–PNIPAAm (MW 300 000) gel samples. Hysteresis is a characteristic of mesoporous material. (B) Pore size distribution of hybrid material.

hybrid materials are mesoporous (presence of hysteresis at higher pressures).²⁷ During drying of the gels, PNIPAAm is in a collapsed state, which forms pores in the silica matrix. Pore size distributions are evaluated from both adsorption and desorption branches and are illustrated in Figure 3B. The average pore diameters estimated from adsorption and desorption isotherms are 35 and 34 Å, respectively.

Data from differential scanning calorimetry of silica–PNIPAAm bulk gels prepared with various molecular weights of PNIPAAm are presented in Figure 4. The transition temperature is determined from the intersection of the baseline and the leading edge of the peaks in the thermograms.²⁸ A strong endotherm around 30 °C corresponding to the LCST of PNIPAAm is observed, which is in good agreement with the literature value reported for aqueous PNIPAAm solutions. Unlike other smart polymers (e.g., elastin-like polypeptides²⁹), the effect of polymer molecular weight on LCST is negligible, even though the thermogram corresponding to 300 000 is more pronounced than lower molecular weight polymers.

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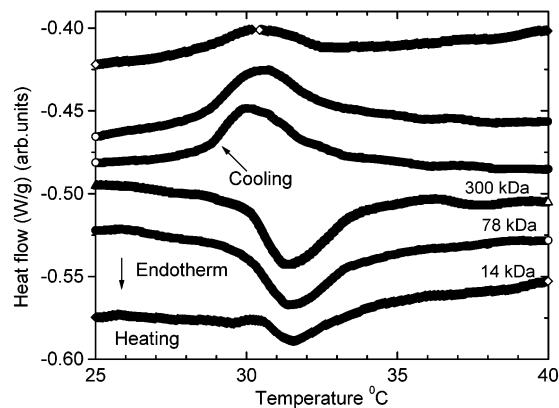


Figure 4. DSC thermograms of silica–PNIPAAm bulk gels prepared with various molecular weights of PNIPAAm. The endotherms (~30 °C) correspond to the hydrophilic-to-hydrophobic transition of PNIPAAm in the silica matrix.

Initial permeation studies investigated the permeation characteristics of crystal violet and PEG-400 through silica–PNIPAAm membranes coated on centrifugal filters. At room temperature, all the membranes were impermeable to crystal violet and PEG solutions when centrifuged at 200g for 3 min. In contrast, when the membranes were centrifuged under similar conditions at 40 °C, they were permeable to both solutions, and the concentrations of crystal violet and PEG in the filtrate and feed solutions were similar. Thus, the solubility transition of the smart polymer results in an increase (above LCST) or decrease (below the LCST) of the permeance of the hybrid membranes. To determine the permeation transition temperature, the membranes were tested at various temperatures using crystal violet in the permeating solution. The permeation transition was found to be 32 °C (data not shown) for all of the silica–PNIPAAm membranes tested, independent of the molecular weight of PNIPAAm in the hybrid.

The permeation measurements clearly indicate that silica–PNIPAAm membranes exhibit switchable behavior at the LCST. Thermal cycling on the membranes between room temperature and 40 °C was used to investigate the reversibility and stability of the membranes. As control experiments, pure silica membranes (without any PNIPAAm) were also tested and these membranes withstood more than 15 cycles, with no permeation observed either at room temperature or at high temperature. This confirms that membranes formed from silica alone are defect free and do not exhibit temperature-dependent permeation. In contrast, Figure 5 shows that silica–PNIPAAm membranes are thermally responsive and impermeable to crystal violet solution at room temperature and permeable at 40 °C. To retain the reversibility of the membranes, however, a gradual reduction in centrifugal force is required (from 800 to 200g), and at 200g, the membranes withstood at least 15 cycles. Similar trends were observed for all the hybrid membranes prepared with different molecular weights of PNIPAAm. Incomplete reversibility of the membranes at higher forces is attributed either to fatigue of the membrane or to incomplete closure of the pores due to slow relaxation of PNIPAAm chains.³⁰

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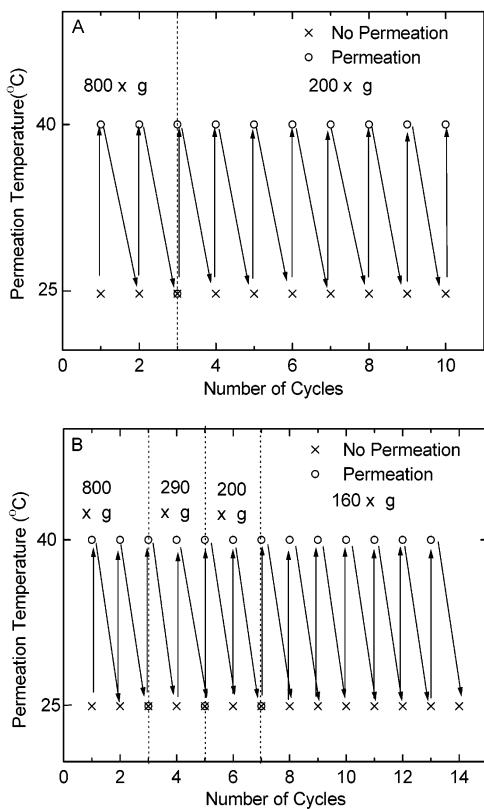


Figure 5. Permeation data for crystal violet solutions (100 μ L) through silica-PNIPAAm membranes. (A) Membrane prepared with PNIPAAm of molecular weight 300 000 and (B) membranes prepared with MW 78 000 PNIPAAm. “Permeation” indicates that the solution permeated through the membrane and the concentration of the filtrate and the feed were measured to be the same. “No permeation” indicates that not even a trace of water was observed to permeate through the filter. Each data point was obtained after 3 min of centrifugation at the indicated centrifugal force.

Having established the switchability of the silica-PNIPAAm membranes, experiments were carried out to examine the filtration characteristics of the membranes. A series of PEGs (with $M_w/M_n \sim 1.1$) with M_w ranging from 1000 to 10 000 were used to determine the size-dependent permeation behavior of these membranes as a function of temperature. As expected, permeation experiments with uncoated YM filters showed facile passage of each PEG solution. Prior to high-temperature permeation, the silica-PNIPAAm membranes were found to be impermeable to all PEG solutions when centrifuged at 800g for 1 h at 25 °C. Permeation data for silica-PNIPAAm on YM-30 centrifugal filters are presented in Table 1. The data indicate that hybrid membranes with 300 000 PNIPAAm are permeable to PEGs of molecular weight less than 7850 and are impermeable to PEGs of molecular weight 7850 and above. Similar results are obtained for YM-50 and YM-100 filters. These results indicate that silica-PNIPAAm membranes are switchable, thermo-responsive molecular filters. Permeation measurements were also carried out by varying the concentration of PNIPAAm (data not shown). The best permeability results were obtained for the concentrations of 10–20 vol % PNIPAAm to that of silica.

Table 1. Permeation of PEG Solutions (200 μ L) at 40 °C through Silica-PNIPAAm (MW 300 000) Membranes Coated on YM-30 Centrifugal Filters

M_w	R^a (Å)	M_w/M_n	wt % (feed)	refractive index (± 0.0002)		% rejection
				ofeed	filtrate	
100	3	1.10	1.9	1.3350	1.3350	0
1000	9	1.10	2.8	1.3364	1.3365	0
2200	13	1.10	2.0	1.3350	1.3350	0
2700	15	1.10	2.0	1.3352	1.3352	0
4000	20	1.10	2.0	1.3354	1.3352	0
5000	22	1.10	1.6	1.3351	1.3350	0
7850	30	1.09	1.7	1.3347	1.3332	100
9000	40	1.10	2.8	1.3364	1.3330	100
15 000	55	1.10	1.6	1.3350	1.3330	100

^a Hydrodynamic radius of PEGs.³¹

Table 2. Effect of M_w of PNIPAAm on the Permeation of PEGs through Silica-PNIPAAm Membranes Coated on Centrifugal Filters

M_w of PNIPAAm	M_w cutoff of PEG
300 000	7850
78 500	5000
40 000	5000
14 000	5000
7 000	2700

The hydrodynamic radii of PEGs used in the present study are presented in Table 1.³¹ The size of the PEG corresponding to the molecular weight of cutoff is 30 Å for silica-PNIPAAm (MW 300 000) membranes, which is qualitatively consistent with the pore size data obtained from nitrogen adsorption and desorption studies.

The molecular weight cutoffs for the membranes obtained with various molecular weights of PNIPAAm are presented in Table 2. We initially expected that the molecular weight cutoff values due to the LCST transitions of hybrid silica-PNIPAAm membranes would be higher for higher molecular weight of PNIPAAm than those with lower molecular weight polymer. Even though there is a slight trend in the cutoff values of the membranes (Table 2), the difference in the cutoff values is not dramatic. This may be because the polymers are surrounded by rigid silica matrix that prevents their full collapse.

Permeation experiments for silica-PNIPAAm (MW 300 000) membranes were also carried out in a pressurized ultrafiltration cell (which allows enhanced filtrate flow rates) operating at 20 psi (Table 3). The cutoff value obtained (i.e., MW < 7850) is the same as that obtained in centrifugation experiments. Experiments are also carried out at higher pressures (40 and 60 psi) in the ultrafiltration cell, and similar molecular weight cutoff values were observed. Data obtained at 60 psi is presented in Table 4 (data for 40 psi is not shown). While the same PEG molecular weight cutoff is obtained at these higher pressures, a difference was observed that water was able to permeate at room temperature at these higher pressures. This may be due to (1) the presence of very fine pores in the membranes that are capable of permeating water at higher pressures or (2) the transport at higher pressures of water that is hydrating the PNIPAAm.

Table 3. Permeation of PEGs through Silica–PNIPAAm (MW 300 000) Membranes Coated on YM-30 Disk Membranes in an Ultrafiltration Cell (Operating Pressure 20 psi)

PEG MW ($M_w/M_n \sim 1.1$)	refractive index of feed	filtrate flow rate at RT	filtrate flow rate at 40 °C (mg/min)	refractive index of filtrate obtained at 40 °C	% rejection
1000	1.3355	no flow	9	1.3353	0
2200	1.3352	no flow	7	1.3348	0
5000	1.3353	no flow	5	1.3355	0
7850	1.3358	no flow	4.5	1.3330	100
10000	1.3355	no flow	3.5	1.3330	100

Table 4. Permeation of PEGs through Silica–PNIPAAm (MW 300 000) Membrane Coated on YM-30 Disk Membranes in an Ultrafiltration Cell (Operating Pressure 60 psi)

PEG MW ($M_w/M_n \sim 1.1$)	refractive index of feed	filtrate flow rate at RT	refractive Index of filtrate obtained at RT	filtrate flow rate at 40 °C (mg/min)	refractive index of filtrate obtained at 40 °C	% rejection
1000	1.3355	12	1.3329	25	1.3352	0
2200	1.3352	10	1.3330	20	1.3348	0
5000	1.3353	8.5	1.3330	16	1.3355	0
7850	1.3358	7	1.3330	12	1.3330	100
10 000	1.3355	5.5	1.3330	9	1.3330	100

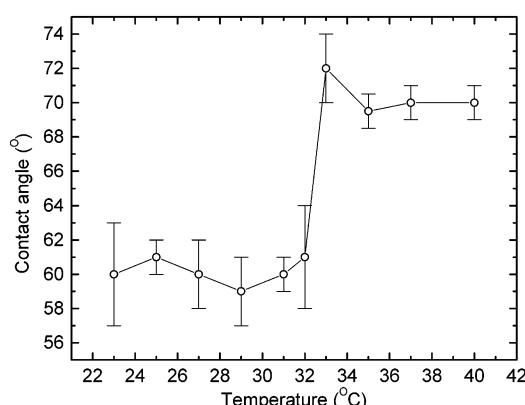


Figure 6. Contact angles of water (sessile drop) measured as a function of temperature for silica–PNIPAAm (MW 300 000). The sharp change in the contact angle at 33 °C corresponds to the hydrophilic-to-hydrophobic transition of PNIPAAm in the silica matrix. The reported values are averages of a minimum of six independent measurements.

In addition to creating membranes with thermally dependent permeation behavior as shown here, the presence of PNIPAAms at the surface of the hybrid membranes can also be exploited to create an interface with switchable properties. The transition from a hydrophilic to a hydrophobic surface can be conveniently studied through contact angle measurements.^{32–34} Figure 6 shows water contact angle data for the silica–PNIPAAm films. A discontinuity in the contact angle is observed at 33 °C for these samples. Below the LCST of the PNIPAAms, the surface is hydrophilic and contact angle with water is low (~60°), and above LCST, the

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PNIPAAms collapse, thereby increasing the hydrophobicity of the surface resulting in higher contact angles (~70°). The transition temperatures obtained from contact angle measurements are in good agreement with those obtained from DSC and permeation measurements.

Conclusions

We prepared temperature-sensitive hybrid membranes that contain uniformly dispersed PNIPAAm of varying molecular weights in a silica matrix by the sol–gel process. Calorimetry and contact angle studies revealed that the LCST behavior of the PNIPAAm can be maintained when it is encapsulated in a silica matrix. Temperature-dependent permeation was observed and is thought to be through pores that are formed due to hydrophilic-to-hydrophobic transition of the polymer. The hybrid membranes showed reversible permeability with good stability. Variation of the molecular weight of PNIPAAm did not have a dramatic effect on the permeation behavior of membranes studied. Permeation experiments with PEGs in centrifugation and ultrafiltration cells clearly demonstrated that silica–PNIPAAm hybrid membranes can function as switchable molecular filters and that the permeation at high temperatures through the hybrid membranes is due to the LCST behavior of PNIPAAm.

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