Published in final edited form as:

J Solgel Sci Technol. 2014 May ; 70(2): 278–285. doi:10.1007/s10971-013-3199-y.

Trapping and release of cargo molecules from a micro-stamped mesoporous thin film controlled by Poly(NIPAAm-co-AAm)

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Abstract

Materials that utilize the micropatterned structure of a mesoporous silica film to successfully load and release cargo using a thermal sensitive polymer are presented in this paper. Films with pore sizes of ~2 nm and ~5 nm aligned in the pulling direction were synthesized using evaporation induced self-assembly techniques. The pores are exposed using a new method of stamping micropatterns without the use hydrofluoric acid. A well studied temperature dependent polymer (poly(N-isopropylacrylamide-co-Acrylamide)) was grafted onto the surface of these films to act as a temperature activated gatekeeper. Below the lower critical solution temperature (LCST) the polymer is erect and can block the pore openings, trapping cargo inside the pores. When the temperature is above the LCST the polymer collapses and unblocks the pores, allowing cargo to escape. The loading capacities as well as the reusability of these films were studied.

Keywords

Mesoporous thin film; sol-gel process; on-command release; thermosensitive polymer; micro patterning

1 Introduction

Mesoporous silica materials, prepared by sol–gel methods, are of great interest because of their many attractive features such as stable mesoporous structures, large surface areas, tunable pore sizes, and the simplicity in modifying the inside pores with organic groups. [1-5] The nanopores exhibit narrow pore size distributions and can store a wide variety of molecules.[6, 7] Accordingly, these materials have been studied for many applications including catalysis,[8-10] medical drug delivery,[6, 11, 12] or separation technology.[2, 13, 14]

Mesostructured sol-gel thin films formed by evaporation induced self-assembly (EISA) during dip- or spin-coating are an important class of materials.[15-21] A sol containing a silica precursor and a template agent is deposited as a thin liquid layer onto a suitable substrate. The evaporation of the solvent drives the formation of surfactant micelles, which further assembles into a liquid crystal. At the same time the silica condenses around the

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micelles. By choosing a specific composition of the sol, environmental conditions, and the method of deposition, mesostructured films with highly-ordered hexagonal, lamellar, or cubic structures can be produced.[20, 22-27] The surfactant molecules can be removed from the pores of the film by solvent extraction or calcination, thus making it possible to fill the empty pores with nano-sized cargos. The controllable release of stored molecules from the nanopores is attracting increasing interest. Because a macro-substrate can be more easily handled and manipulated than nanospheres, thin films containing mesopores would be very convenient if the openings of the nanopores were accessible to molecules outside of the films.

Many efforts have been made to prepare films in which the pore openings are oriented towards the surface of the films.[28-32] Unfortunately such procedures remain complex, time-consuming and difficult, and the types of templating surfactants or polymers that can be used are limited.[28] An alternative approach consists of preparing a film with a well-known structure such as a 2D-hexagonal structure in which arrays of tubes in highly arranged stacks are aligned parallel to the upper surface of the films, then etching away selectively narrow regions of the film that are perpendicular to the nanopore orientation. This procedure allows for the creation and the exposure of pore openings. An example of such a film, with a thickness of ~ 300 nm and a pore diameter of 2.5 nm, has been reported. [33] Based on these patterned films, a molecular storage and on-demand release system was realized. In this paper, an improved material that allows more cargo to be stored inside the pores is presented. By changing the surfactant from CTAB to F127 the pore size is changed from ~2 nm to ~5 nm. This material could be useful in biomedical applications to deliver larger doses of drugs as well as the potential to deliver larger cargo molecules. In order to test the cargo trapping capacity of this material, a well studied synthetic temperature-responsive co-polymer, poly(N-isopropylacrylamide-co-Acrylamide) (poly(NIPAAm-co-AAm)) is used. It undergoes a sharp coil-globule transition in water at 41 C, changing from a hydrophilic state below this temperature to a hydrophobic state above it.[34-37] The temperature at which this change occurs is called the lower critical solution temperature (LCST). While this polymer has been used on silica to release cargo, the results have been materials that are either leaky or release cargo at room temperature.[38-40] The grafted polymer acts as a gate that controls the pore opening. At room temperature it stands erect in front of the pores, trapping the cargo inside. Above the LCST the polymer collapses allowing the cargo to diffuse freely out of the pores. Because the polymer is covalently attached to the surface of the film the system is not leaky at room temperature, and after an initial release the films can be re-loaded with cargo to perform a second release. The overall system is depicted in Fig. 1.

2 Experimental Section

2.1 Preparation of Mesoporous Silica Films

Three types of porous silica films with different pore diameters were synthesized using different silica templates. Large pore films (pore size 5.5 nm) were prepared using triblock copolymers as templates, while small pore films (pore size 2.5 nm) were produced by

surfactant templating. Additionally, microporous films (pore size < nm) were created without using a templating agent.

Mesostructured silica films were synthesized according to a two-step process as previously reported.[22, 41] First, a stock solution was prepared by mixing TEOS, absolute ethanol, water and HCl (mole ratios 1 : 3.8 : 1 : 5×10^{-5}), and heating at 60 °C for 1.5 hrs. Then, a 7.5 mL sample of this initial solution was cooled to room temperature and mixed to 1 mL of 0.07 M HCl and 0.35 mL of water. After stirring for 15 min, the mixture was allowed to age for 15 min. without stirring, followed by dilution with two equivalents of absolute ethanol. Finally, after the sol was aged for 3 days, triblock copolymer poly(ethyleneoxide₁₀₆-propyleneoxide₇₀-ethyleneoxide₁₀₆) (Pluronic F127) or cetyltrimethylammonium bromide (CTAB) was added. The surfactant/TEOS mole ratios were 0.007 for Pluronic F127 and 0.1 for CTAB, respectively. An additional mixture was prepared without adding surfactant into the silica sol.

The as-prepared mixtures were dip-coated on silicon or glass substrates at a constant pulling speed of 3 mm/sec to yield the mesostructured films. Before deposition, the substrates were soaked in a 1M HNO₃ solution overnight, then rinsed with water, ethanol and acetone to remove contaminants. The entire film-pulling apparatus was placed inside a controlled-humidity chamber. The relative humidity was fixed to $35 \pm 5\%$ when using Pluronic F127, and $55 \pm 5\%$ when using CTAB. This procedure results in several hundred nanometer thick crack-free films. For the studies reported in this paper, only one side of the substrate consists of the mesostructured film as the other side was cleaned using dilute HF.

Stamp Preparation and Micropatterning—An AFM calibration grating (Mikromasch TGZ04) was used as a source of the pattern. The pattern consists in lines 1.5 μm wide, 1 μm high, with 3 μm pitch. A poly(dimethylsiloxane) (PDMS, Sylgard 184) mixture was poured onto the grating and heated at 100 °C until it solidified. The PDMS stamp was then removed from the grating surface, rinsed with ethanol and dried in air. The micropatterned films were prepared by gently pressing the PDMS stamp onto the surface of the as-synthesized films immediately after the dip-coating. The films covered with the stamp were heated at 100 °C for 30 min and then allowed to cool at room temperature. The stamp was delicately peeled off using tweezers. A successful pattern transfer leaves a visible indication as a diffraction effect is observed at the film surface. The micropatterned mesostructured films were heated at 100 °C overnight to consolidate the silica network. Finally, the films were calcined at 500 °C for 5 hrs. in air to remove the template, and stored in a vacuum sealed desiccator. The mesoporosity of the films was verified by XRD and TEM.

MEH-PPV Incorporation—First, the inner pore surface of the patterned films was made hydrophobic to aid in incorporation of the fluorescent polymer (MEH-PPV). The films were treated with a solution of dimethyldichlorosilane in dry toluene in the presence of triethylamine as an activating base. After reaction, the films were washed with ethanol and water, and cured at 100°C for 1 hr. To incorporate the polymer MEHPPV (average Mn = 40 000 – 70 000 Da) into the pores, the hydrophobic films were soaked in a 1% solution of MEH-PPV in chlorobenzene for 48 hrs. at 80 °C. The samples were extensively washed

with chlorobenzene and chloroform, dried in air, and stored under a nitrogen atmosphere in the dark.

2.2 Synthesis of Thermo-Responsive Silica Films

NIPAAm (3.66 g), AAm (0.26 g), N,N,N',N',N'-pentamethyldiethylenetriamine (PMDETA) (35 μ l), 2-bromo-2-methyl propionic acid (0.01 g), deionized water (36 ml) and methanol (24 ml) were mixed in a Schlenk flask and degassed by freeze-pump-thaw cycles. While the mixture was frozen, CuBr (0.01 g) was added. The flask was then filled with argon and the mixture was left to melt at room temperature. The reaction solution was magnetically stirred overnight at room temperature. After evaporation of the solvent, the crude product was dissolved in water and purified by dialysis to yield poly(NIPAAm-co-AAm) with an LCST of 41 °C.

Surface Modification of Films—The films were soaked in a 0.01 M solution of 3-aminopropyltriethoxysilane (APTES) in dry toluene under nitrogen and stirred at reflux overnight. Finally the surface was extensively rinsed with dry toluene and dried in vacuum. 50 mg of poly(NIPAAm-co-AAm) was dissolved in 10 ml of deionized water. 50 mg of 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDAC) was added and the amine modified silica film was immediately added afterwards. The solution was stirred overnight at room temperature. After the reaction, the films were removed from the solution, extensively rinsed with deionized water and dried in vacuum. The surface modification was confirmed by FTIR and AFM.

Dye Loading and Release Studies—Poly(NIPAAm-co-AAm)-modified patterned films were loaded with the fluorescent dye propidium iodide. The film was submerged in a 2 mM propidium iodide solution (10 mL), heated to 50 °C (> LCST), and left stirring for 24 hrs. Afterwards, the loaded film was removed from the solution, thoroughly rinsed with room temperature water, and used for release studies immediately to avoid propidium iodide degradation.

The operation of the thermo-responsive films was monitored using fluorescence spectroscopy. A small 1 cm $\times$ 1 cm film (size of micropattern 0.8 cm $\times$ 0.8 cm) was placed on the bottom of a cuvette. 6 mL of deionized water and a small stir-bar were added. The sealed cuvette was placed on a temperature-controlled plate. The emission of propidium iodide in the solution above the film was measured as a function of time by using a 377 nm excitation beam (10 mW) to excite the dye molecules as they are released from the film. The emission spectrum was recorded as a function of time at 1 second intervals. The release profiles were obtained by plotting luminescence intensities of propidium iodide at the emission maximum (650 nm) as a function of time. The release of the cargo dye was activated by increasing the aqueous media temperature from room temperature (< LCST) to 45 °C (> LCST).

2.3 Characterization Methods

The structure of mesostructured silica films was investigated by powder X-ray diffraction (PXRD) experiments in Bragg-Brentano geometry (θ -2 θ) on a Philips X'Pert Powder

Diffractionmeter operated at 40 kV, 40 mA using CuK α radiation ($\lambda=1.54 \text{ \AA}$). For the observation of the mesoporous films with transmission electron microscopy (TEM), the films were detached from the substrates and dispersed in ethanol, then deposited and dried on a carbon Cu grid. Micrographs were recorded on a JEM1200-EX (JEOL) electron microscope operating at 50 kV. Infrared (FTIR) measurements were acquired on a Jasco Model 420 spectrometer after the samples were dehydrated under vacuum for 5 hrs. at room temperature. The thickness and the surface morphology of the patterned films were determined by atomic force microscopy (AFM) on a Dimension 5000 instrument in contact mode. For fluorescence polarization measurements, mesoporous films treated with MEH-PPV polymer were illuminated using the 407 nm line of a Coherent I302C krypton ion laser (10 mW). A polarizer was used to select out parallel and perpendicular emission components. A 420 nm filter was placed in front of the polarizer to block stray laser light. The photoluminescence spectra of the samples were collected throughout the visible region using an Acton 2300i monochromator and a Princeton Instruments CCD detector. Fluorescence microscopy images of poly(NIPAAmco-AAm) derivatized patterned films were acquired on a Leica confocal SP2 MP-FLIM microscope. The films were loaded with Rhodamine B, then the pores were closed, sealing the dye inside the pores. The excess dye on the surface was washed off.

The LCST was measured spectrophotometrically with a polymer solution being heated 1°C every three minutes. The LCST is defined as the temperature at which the light transmittance is 90% of the original transmittance (at 450nm). The average molecular weight (M_n) and polydispersity index (PDI) of the polymer was measured by Gel Permeation Chromatograph (GPC) using a Waters 515 Differential Refractometer with Waters 410 HPLC pump and two styragel HR 5E columns in THF (0.1 mg/L) as an eluent at 42°C , calibrated with polystyrene standards.

3 Results and Discussion

3.1 Micropatterned Nanoporous Silica Films

A simple dry-stamping method is used to prepare mesoporous films with a significant accessibility to the pore openings. While the nanopore orientation can easily be controlled in the plane of the film,[42-44] it is difficult to synthesize films in which the pores are perpendicular to the film surface. Only a few reports show a successful orientation of the pore openings toward the upper surface,[28-31] A limited number of surfactants can be used and thus the range of pore sizes that can be studied is restricted. To make the interior pores of the films accessible, a dry-stamping procedure that compresses regions of a film that are perpendicular to the pore orientation was implemented. The films consist of highly ordered arrays of tubes aligned in the plane of the films.

The first step consists of preparing the organized nanostructured films with different pore sizes. They were prepared by EISA techniques.[21, 22] Ordered mesostructured films were obtained using F127 or CTAB as templates. Dip-coating was used to deposit the films rather than spin-coating in order to obtain preferential orientation of the pores (along the direction of the pull). The XRD patterns of the as-synthesized films are consistent with a 2D-hexagonal mesostructure with lattice spacings of $114 \text{ \AA}$ for F127 and $39.4 \text{ \AA}$ for CTAB

templates (Fig. S1). The structure is confirmed by TEM characterization (Fig. S2). The micrographs show straight mesochannels regularly arrayed parallel to the substrate with a wall-to-wall distance estimated to be about 10 nm and 6 nm for F127 and CTAB, respectively. Additional films were prepared without using a template. No structure was recorded by XRD and no pores were observed by TEM. The porosity of such films is expected to be sub-nanometric.[45, 46]

The second step consists of micro-patterning the as-prepared films. Molecular transport is extremely limited in the 2D-hexagonal structure as the nanopore openings are only present at defects or at each end of the films. To create pore accessibility, a PDMS stamp is pressed on the continuous films, thus allowing the creation of surface defects according to a known pattern. This procedure has to be done immediately after the deposition while the silica network is soft. As the stamp is placed on the silica material, the film regions that are in physical contact with the highest parts of the patterned stamp are constricted. After heating at 100 °C for 30 min to consolidate the framework, the stamp is removed. The pattern leaves strips of mesoporous silica 1.5 μm wide and 600 nm high, that approximately corresponds to the thickness of the films. Profiles remain similar regardless of the pore sizes. The stamp is pressed in a way such that the strips run perpendicular to the nanopore orientation. Therefore the nanopores that are inside the strips are exposed and open along the vertical sides of these strips.

The patterned films contain template molecules that are removed by calcination at 500 °C. The silica films conserve the 2D-hexagonal mesostructure, as shown by XRD and TEM. After calcination, the pore diameters were estimated to be about 5.5 ± 1.0 nm and 2.5 ± 0.5 nm for F127 and CTAB, respectively. The resulting films patterned by F127, CTAB, and no template will be referred to as large pore films, small pore films and micropore films, respectively.

The method developed here is an alternative to usual printing techniques such as soft lithography[47-49] and reactive wet-stamping methods (r-WETS).[50, 51] Our procedure is a one-step technique based on a mechanical compression that does not require surface preparation or layer deposition and does not use fluoride, which makes it easy-to-use and inexpensive. In addition, it should be noted that reactive wet-stamping techniques could not be used for our large pore films. Attempts were made to etch a pattern into films by having them come into a contact with a micro-patterned hydrogel stamp. The stamp was soaked in a buffered hydrofluoric acid (BHF) solution, as described by Klichko et al.[33] Although this method was successful for CTAB-templated films (pore size 2.5 nm), it systematically failed for F127-templated films (pore size 5.5 nm) as BHF drastically infiltrates the porosity and quickly diffuses into the silica framework to destroy the film.

3.2 Nanopore Alignment and Accessibility

To explore the ability of external molecules to enter the porosity of the films, fluorescence polarization of a long-chain linear polymer (MEH-PPV) incorporated into the pores of a patterned film was investigated by polarized fluorescence spectroscopy. In addition, a film was infiltrated with a small dye molecule, Rhodamine B, and was characterized by confocal microscopy.

A fluorescent polymer MEH-PPV was infiltrated into the pores of a large pore film. It is known that the conformation of the polymer chains controls the polymer photophysics.[52] Emission polarization is affected by the orientation, the degree of aggregation and the surrounding environment of the polymer chains.[53-55] In a homogeneous solution, polymer strands are randomly oriented and free to move, which leads to a non-polarized fluorescence. Inside the pores of a patterned film, the polymer chains are forced to stretch out and align in the direction of the nanopores. This preferential alignment gives rise to polarized fluorescence. Any parts of the polymer that are not inside the pore have random orientations and give rise to non-polarized fluorescence.

Fluorescence emission spectra of infiltrated materials are shown in Fig. 2a. Both the polarization of the emitted light and the peak shifts in the polymer emission are examined. When the sample is not washed, three main peaks are observed at 492 nm, 568 nm, and 625 nm. A difference in the intensities measured with analyzer polarizer aligned parallel and perpendicular to the pore direction is observed and is particularly pronounced for the peak at 492 nm. This peak corresponds to polymer chains aligned preferentially inside the nanopores while the other peaks correspond to polymers at the surface. In fact, the polarization effect is the greatest at the 492 nm peak that corresponds to the behavior of aligned chains in the direction of the nanopores. In contrast, the emission peaks of the polymer on the outside of the film are only slightly polarized, probably caused by the tail of the 492 nm polarized band. In addition, a polymer chain that is confined in a nanopore and surrounded only by silica or silane is expected to result in a blue shift in emission, compared to polymer chains surrounded by other polymers.[55, 56] This effect accounts for the shift from 568 nm for surface polymers to 492 nm for the aligned polymers in pores, and has been observed by Klichko and coworkers for mesoporous CTAB-templated silica films infiltrated by MEH-PPV.[33] Finally, when the sample is extensively washed only the peak at 492 nm remains (Figure 2a). That is additional evidence that the peak at 492 nm corresponds to polymers that infiltrated the nanopores. After the sample is washed, aggregated polymer chains are removed from the surface while polymer strands remain inside the pores.

A patterned mesoporous large pore film was derivatized with poly(NIPAAm-co-AAm), as described in the next section and loaded with Rhodamine B. The polymer chains blocked the pore openings, sealing in the dye inside the pores, and the excess dye on the surface was washed off. Fluorescence confocal microscopy revealed the presence of the dye inside the material (Fig. 2b). The patterned film surface appears as parallel fluorescent lines, while regions where the silica was constricted are dark (the larger dark areas are defects). This is evidence that molecules of Rhodamine B entered the pores and were retained inside by the polymer.

3.3 Thermoresponsive Poly(NIPAAm-co-AAm) modified Films

The synthesis of poly(NIPAAm-co-AAm) is depicted in Fig. S3.[36] 2-Bromo-2-methylpropionic acid reacts with N-isopropyl acrylamide and acrylamide in the presence of copper bromide to form long polymer chains ($M_n = 102,000$ g/mol, $M_n/M_w = 1.42$ through

atom transfer radical polymerization. The LCST of the polymer was determined to be 41 °C by plotting the percent transmittance vs. temperature at 450 nm (Fig. 3).

The poly(NIPAAm-co-AAm) is chemically grafted onto the films. The patterned silica films are submerged in dry toluene after which APTES is added to the solution and then refluxed for 24 hrs. under nitrogen (Fig. 4). The films are then thoroughly rinsed and left to dry. Poly(NIPAAm-co-AAm) is dissolved in water and immediately after adding EDAC the amine modified films are carefully placed in the solution. After 24 hrs. the long polymer chains are grafted onto the stamped silica surface. Fig. 5 is an AFM image of the film before and after the polymer grafting. The channels of the pattern are well defined before the polymer is grafted. Afterwards, the polymer fills the insides of the channels as well as the top surface of the film.

3.4 Release Studies

The loading of cargo molecules into the pores, trapping them by the polymer and releasing them by increasing the temperature are illustrated in Fig. 1. Below 41 °C, the polymer strands stand erect due to hydrophilicity and blocks the pores. To load the film, the film is placed in a solution containing the desired cargo molecules and heated above 41 °C. The polymer changes from hydrophilic to hydrophobic, collapsing the polymer and exposing the pore openings. The solution is then cooled to room temperature allowing the polymer to once again block the pores. The film is then washed to remove excess dye. The cargo molecules are allowed to exit the unblocked pores “on command” when the film is heated above 41 °C, again due to the polymer changing to a hydrophobic state.

The operation of the thermo responsive films was monitored in an aqueous solution using luminescence spectroscopy. Fig. 6 depicts the release profiles of propidium iodide for polymer-coated films and non-polymer coated films, respectively. The polymer-coated large, small, and microporous films were loaded with cargo by submerging them in 2 mM propidium iodide solution heated to 50 °C and stirred for 24 hrs. The films were then cooled and thoroughly washed. The emission intensity was monitored for 1 hr. at room temperature before the solution was heated to 45 °C. The decrease in the baselines is caused by the photodegradation of propidium iodide that was absorbed onto the silica film.

In order to confirm that the large pore film can contain more cargo than the small pore film release studies were conducted using six different films; large pore, small pore, and microporous films with and without polymer. Fig. 6a shows the release profiles for the films with polymer. The large pore film's intensity increases the most and the microporous film's intensity increases the least. The small pore film released only half as much propidium iodide than the large pore film. This indicates that more cargo can be contained due to the larger sized pores, as expected. The small release on the microporous film is caused by dye trapped solely by the polymer, which is roughly 15% of the amount the large pore can release. Therefore, 85% of dye is being released from the pores of the large pore film. The data imply that the larger the pore the greater the amount of dye or cargo that can be trapped and released.

A small amount of the cationic propidium iodide cargo molecules adhere to the anionic silica surface even after extensive washing. Films without the polymer coating thus exhibit a small but observable amount of cargo release upon heating (Fig. 6b). The large-pore non-polymer coated film has a slightly higher intensity than that of the small-pored non-polymer coated film, and the microporous non-polymer coated film has a negligible increase. Comparing Figs 6a and 6b shows that in all three cases the films with the polymer coating trap and release more dye than the films without polymer coating. For the large and small pore film, this shows that the polymer is blocking the pore opening and is successfully trapping the dye inside. The release from the polymer coated microporous film shows that a small amount of dye is also trapped in the polymer itself.

To test the reusability of the films, the large pored film was used. The film was loaded with propidium iodide using the same method as before. After the first release experiment, the film was reloaded with propidium iodide and a second release experiment was conducted. Fig. 7 shows the results of the experiment. The reloaded film does not hold as much dye as a fresh film, as seen from the data, but the sharp increase in intensity indicates that the polymer on the film is still able to trap and release dye. The data shows that the films can be reused, but degradation occurs.

4 Summary

Mesoporous silica films with pore diameters of ~2 nm and ~5 nm aligned in the pulling direction were synthesized. The thickness of the films were determined to be ~600 nm and the patterned features were 1.5 μm wide strips oriented perpendicular to the direction of the nanopores which are separated from each other by 1.5 μm gaps. The patterned features were obtained using a PDMS stamp without the need for hydrofluoric acid. Loading the films with a fluorescent polymer and measuring the emission and polarization of the polymer inside the pores confirmed the nanopores accessibility and orientation.

Poly(NIPAAm-co-AAm) was grafted onto the surface of the films. The films with the polymer grafted on the surface were able to trap more dye than the films with no polymer. The large-pored film contained more dye than both the smaller pored and the micro-pored films. Release of the dye was only observed when the temperature reached the polymers LCST. While less dye was released, the films proved that when the pattern stays intact the film can be re-loaded with dye and a second release can be obtained. These smart materials utilize the micropatterned structure to successfully load and release cargo using a thermal sensitive polymer under external thermal.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by a grant from the NIH R01 CA133697, NIH fellowship to T.M.G.-A. (CA133697)

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Figure 1.

The operation of the temperature-activated opening of the nanopores. A side view of one of the stamped channels is illustrated. When heated past the polymer's LCST, the polymer chains collapse allowing cargo molecules to enter the pores. Washing with cool water below the LCST causes the chains to go back to their extended conformation, blocking the pore openings. Heating the water again causes the polymer to collapse, releasing the cargo.

Figure 2.

(a) Polarized fluorescence spectra of MEH-PPV incorporated into a patterned large pore film. When the sample is not washed (blue lines), multiple peaks are observed which correspond to polymers in the pore interiors (492 nm) and on the exterior surface (peak at 585 nm and tail to the red). After the sample is washed extensively (green lines), the peak at 585 and the tail decrease in intensity. The emission intensity of the 492 peak is polarized parallel to the orientation of the pores (solid) but the randomly oriented surface polymer emission is not polarized. (b) Fluorescence confocal microscopy image of a micro-patterned Rhodamine B dye-doped F127-templated mesoporous silica film after derivatization with poly(NIPAAm-co-AAm).

Figure 3. Temperature dependence of the transmittance at 450 nm of the polymer dissolved in water. The lower critical solution temperature (LCST) is 40.8 C

Figure 4.

Attachment of the polymer onto the stamped silicon film. APTES is attached to the film in dry toluene. The polymer is then grafted to the film using EDC as the linker.

Figure 5.

AFM images of a patterned mesoporous silica film prepared using Pluronic F127 (a) before and (b) after derivatization with poly(NIPAAm-co-AAm). The scanned area is $10 \times 10 \mu\text{m}$. The patterned features are strips $1.5 \mu\text{m}$ wide, 500 nm high, with a $3 \mu\text{m}$ pitch.

Figure 6.

a) Release of propidium iodide from the pores of films modified with the polymer. The baseline was taken at room temperature for an hour. Release of the propidium iodide from the pores into solution occurred when the temperature was increased to 45 C. b) Release of propidium iodide from films without the polymer modification. The profiles are on the same scale as those in Fig. 6a.

Figure 7. Release profile of propidium iodide from the large pore film (blue). The release profile from the same film after it was re-loaded with cargo is shown by the red trace.