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**FUNCTIONALIZED POROUS POLYMER SHEETS
AS MODELS OF THERMORESPONSIVE MEMBRANES FOR
WATER TREATMENT**

A final report

for the

**OFFICE OF NAVAL RESEARCH
CHEMISTRY DIVISION**

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Abstract.

A novel approach to thermoresponsive polymeric membranes based on molded monolithic sheets of macroporous polymers has been demonstrated. The macroporous sheet prepared from glycidyl methacrylate ethylene dimethacrylate is functionalized either by free-radical grafting of N-isopropylacrylamide, or, better, by copolymerization of N-isopropylacrylamide onto the vinylated surface of the pores of the polymer sheet. The macroporous polymers modified with poly(N-isopropylacrylamide) were shown to be thermoresponsive. Changes in the temperature of a flow system incorporating the modified macroporous material were accompanied by significant changes in the backpressure required to effect flow. This study confirms the feasibility of thermoresponsive membranes for water purification.

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Introduction

This one year feasibility study was aimed at the exploration of different designs of "smart" porous polymers, focusing on composite materials that exhibit size selectivity controlled by temperature. More specifically, the modification of porous polymeric sheets with grafted polymer chains which change their swelling in response to temperature was investigated. Whereas the solubility of most compounds increases with rising temperature, some polymers exhibit the opposite behavior; i.e. they are water soluble at lower temperatures, but precipitate at higher temperatures. The temperature at which the phase transition occurs is called the *lower critical solution temperature* (LCST), values of which vary in a broad range depending on the particular polymer. This phase transition is driven by entropic changes. The most often cited example of a LCST polymer is poly(N-isopropylacrylamide) (PNIPAAm).

Although polymers exhibiting a LCST have been known for more than three decades, they originally served as model compounds for studying phase separations in gels. It has only been in the last decade that a number of practical applications for these materials have emerged. Among others, these include the isolation and purification of biomolecules, immobilization of biocatalysts, dehydration of suspensions, biosensors, and the controlled delivery of drugs. The ability of these polymer molecules to undergo a phase transition from an extended, hydrated form below its LCST to a compact, hydrophobic coil above its LCST has also been used in the preparation of "membranes" with controlled permeability. These sheets of slightly crosslinked gels swell in water at low temperatures, but shrink at higher temperatures. Although these sheets exhibit a different permeability below and

above their LCST, the rate of change is slow, since the surface layer collapses first and prevents the exclusion of water from the bulk of the gel. In addition, the mechanical properties of lightly crosslinked, highly swollen gels are typically poor. Therefore, a few attempts have been made to support the soft hydrogel with a polymer film (microporous membrane) or controlled pore glass (CPG 30-nm) plate in order to improve the handling.

Grafted polypropylene membranes

Although the literature of LCST polymers is quite extensive, no reports exist as to the grafting of microporous polymer membranes with temperature sensitive polymers. Therefore, we used a typical polypropylene porous membrane (CELLGARD 2400, Hoechst Celanese) to demonstrate the concept of temperature controlled porosity. The thin membrane, which has an average pore size of 20 nm, a thickness of 25 mm, and a porosity of 38%, has an additional advantage in that it can be handled using typical membrane technology equipment (Amicon ultrafiltration stirred cell, model 8010). This allows the direct measurement of the flux through the membrane as a function of pressure in the cell.

The original polypropylene membrane is not permeable to water, as the excessively hydrophobic surface cannot be wetted directly. Therefore, water permeation through the CELLGARD membrane can only be achieved by first wetting the surface with methanol, followed by methanol/ water mixtures. Additionally, the surface of polypropylene is rather inert, and grafting can be achieved only after suitable functionalization. We chose an oxidation reaction with a 5-10% aqueous solution of potassium persulfate, which proceeded for 2-4 hours at 80°C. This surface functionalization of the membrane with hydroxyl

groups did not change its permeability, but did allow the membrane to be completely wetted with water due to the increase in the hydrophilicity of the surface.

NIPAAm was then grafted to the surfaces of the modified membranes. Generally, ammonium cerium nitrate (CAN) and nitric acid are used to activate the hydroxyl groups and initiate free radical graft polymerization. The typical grafting procedure involved mixing the CAN with 1 mol/ L nitric acid, dissolution of the NIPAAm in demineralized water, and purging the solutions with nitrogen for 15 min. Both solutions were mixed in a flask, and disks punched from the oxidized membrane were added. After an additional purging with nitrogen for 5 more minutes, the flask was sealed and the contents heated at 50°C for several hours. As expected, the grafting decreased the flux through the membrane. For example, the flow through the original oxidized 25 mm membrane at a pressure of 50 psi was 1.1 mL/min, while the same membrane grafted with PNIPAAm exhibited a flow of only 0.97 mL/min at a room temperature.

Figure 1 shows the effect of temperature on the permeability of the grafted polypropylene membrane. The flux through the pores doubles at higher temperature, at which the PNIPAAm chains are collapsed, thereby occupying less volume. The switching rate depends solely on the rate of temperature change that can be achieved in the relatively bulky measuring cell.

These preliminary experiments using a typical microporous membrane demonstrate that the proposed design of smart membranes is feasible.

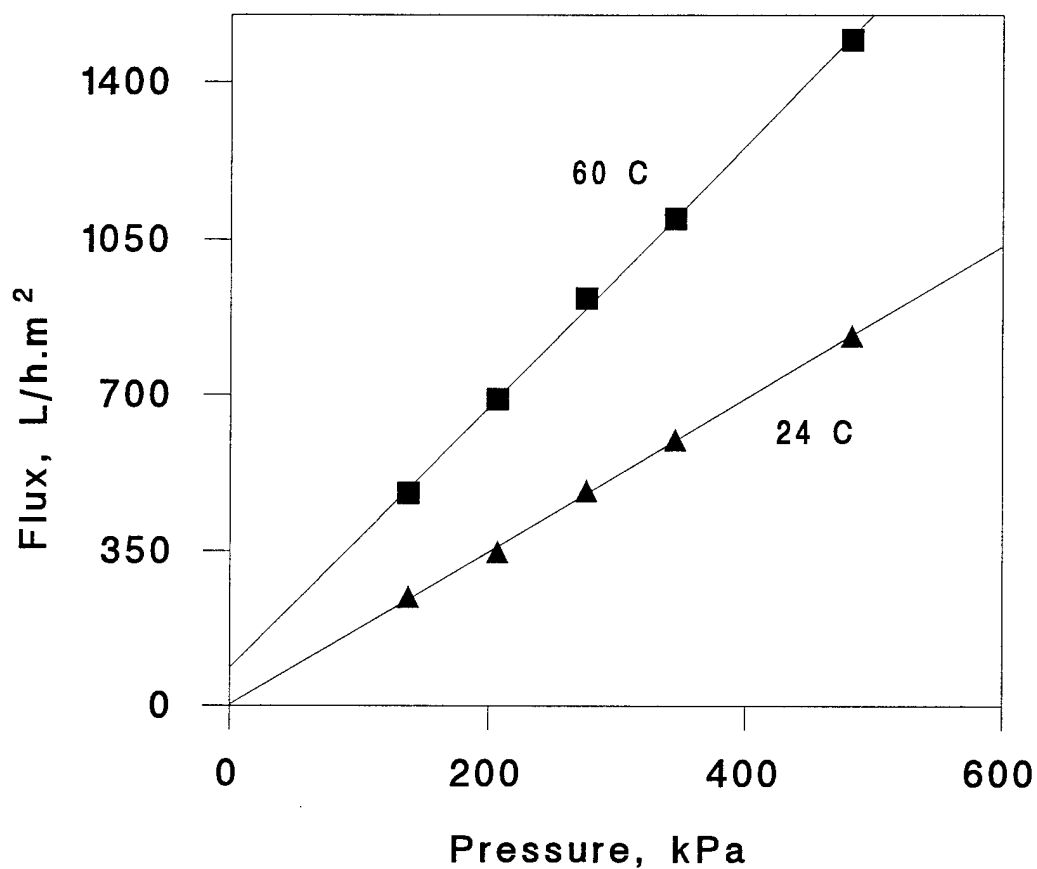


Figure 1. Effect of temperature on permeability of oxidized CELGARD membranes modified by grafting of NIPAAm.

Reaction conditions: Oxidation in 5% aqueous potassium persulfate for 4 h at 80 °C; Grafting in a solution of 0.0219 ammonium cerium nitrate, 0.4921 g 1 mol/L nitric acid, and 1 g NIPAAm in 9 mL water for 5 h at 55 °C; Permeation of water through 25 mm diameter membrane determined in Amicon Stirred Ultrafiltration Cell.

Preparation of reactive polymers with controlled porosity

Based on our previous experiments, glycidyl methacrylate was used throughout this work. This monomer is commercially available, copolymerizes well with a number of crosslinking monomers, and the resulting epoxide surface chemistry has sufficient reactivity. Ethylene dimethacrylate was used as a model crosslinker, and mixtures of cyclohexanol and dodecanol were used as the porogenic solvent. Two different approaches were explored for the physical production of molded porous monoliths with reactive surface functionality.

The simplest method involves performing the polymerization in a flat mold consisting of two parallel plates separated by a gasket. The thickness of the gasket determines the thickness of the resulting porous sheet. As this thickness is typically kept small (1.5 mm), the heat of polymerization generated is easily dissipated, and the temperature of the mixture inside the mold does not change very much during the reaction. Thus, large homogeneous sheets are easily produced.

A number of different variables can be used to tailor the porous properties of a molded polymeric monolith, including both the nature and amount of the porogen, the percentages of both the crosslinker and initiator, and the reaction temperature. However, the latter is the most convenient, as it does not require any change to the composition of the polymerization mixture. Figure 2 shows pore size distribution curves obtained by mercury intrusion porosimetry for flat sheets of porous poly(glycidyl methacrylate-*co*-ethylene dimethacrylate). With the exception of the sheet obtained at 55 °C, a general rule can be inferred: the higher the polymerization temperature, the smaller the pores.

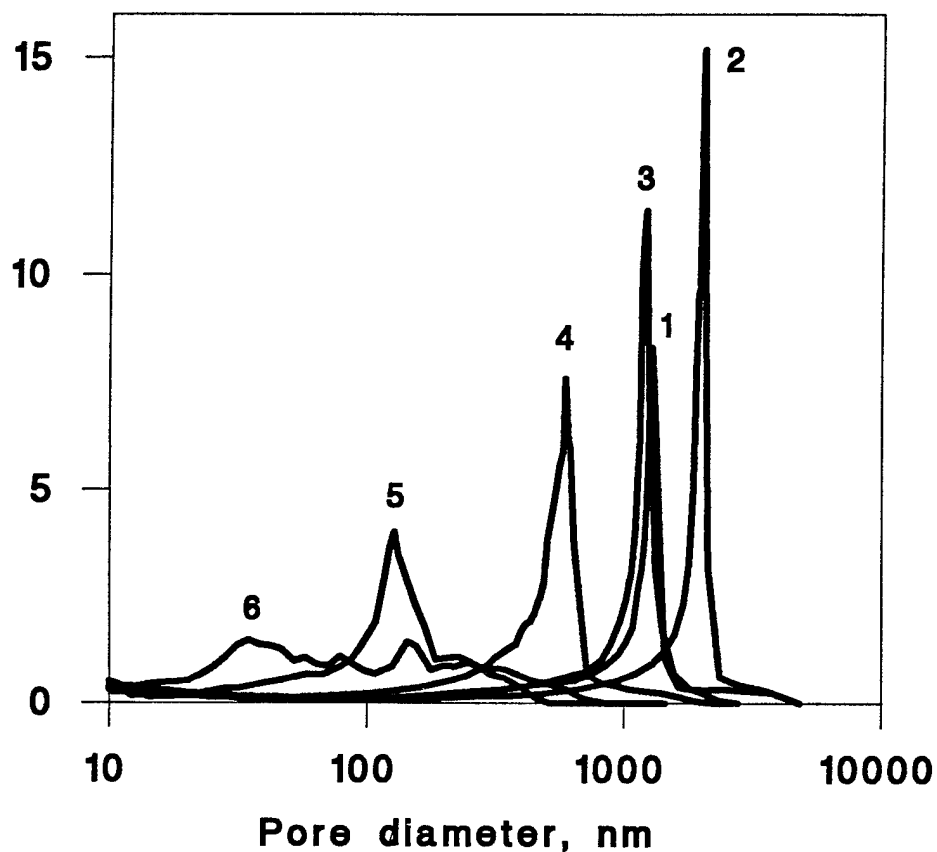


Figure 2. Differential pore size distribution curves of poly(glycidyl methacrylate-co-ethylene dimethacrylate) sheets prepared by polymerization at temperatures of 55 (1), 60 (2), 65 (3), 70 (4), 80 (5), and 90 °C (6).
Polymerization conditions: Polymerization mixture, glycidyl methacrylate 24 %, ethylene dimethacrylate 16 %, cyclohexanol 54 %, dodecanol 6 %, azobisisobutyronitrile (1% in respect to monomers); polymerization in a flat mold 15 x 30 cm consisting of two Teflon plates separated by 1.5 mm thick gasket; polymerization time 24 h.

The polymerization in flat molds is advantageous for the preparation of large square-shaped sheets. However, the punching of discs required for experiments on the laboratory scale from these sheets leads to excessive waste of material. Although disc-shaped molds are feasible, the production of a cylindrical rod in a tubular mold, followed by mechanical cutting, is more efficient. In contrast to flat molds, the heat evolved during polymerization, and its subsequent transfer and dissipation through the bulk of the polymerization mixture and mold walls, can be a real problem in molds with a diameter exceeding approximately 25 mm. Therefore, an alternate technique for the preparation of cylindrical monoliths with a diameter greater than 25 mm was developed. The polymerization is performed in a tubular mold, into which the polymerization mixture is gradually added over time using a syringe pump. This approach leads to a monolith with a completely homogeneous pore size distribution, as opposed to the typical distribution of large rods prepared by a one step bulk polymerization, which are characterized by a substantial, radial pore size gradient.

Materials with a pore size distribution shown in Figure 3, where the majority of pores are in the 1 mm range, were chosen for use throughout the entire study.

Preparation of “smart” composite materials

One of the aims of this research was the design of hybrid, porous membrane-like devices which allow both controlled permeability and the ability to absorb metal ions when used in the dead-end filtration mode. While the functionalization of the support with chelating groups is expected to be straightforward based on the substantial volume of literature, the “gate” behavior of large pore materials has never been studied. Therefore, our

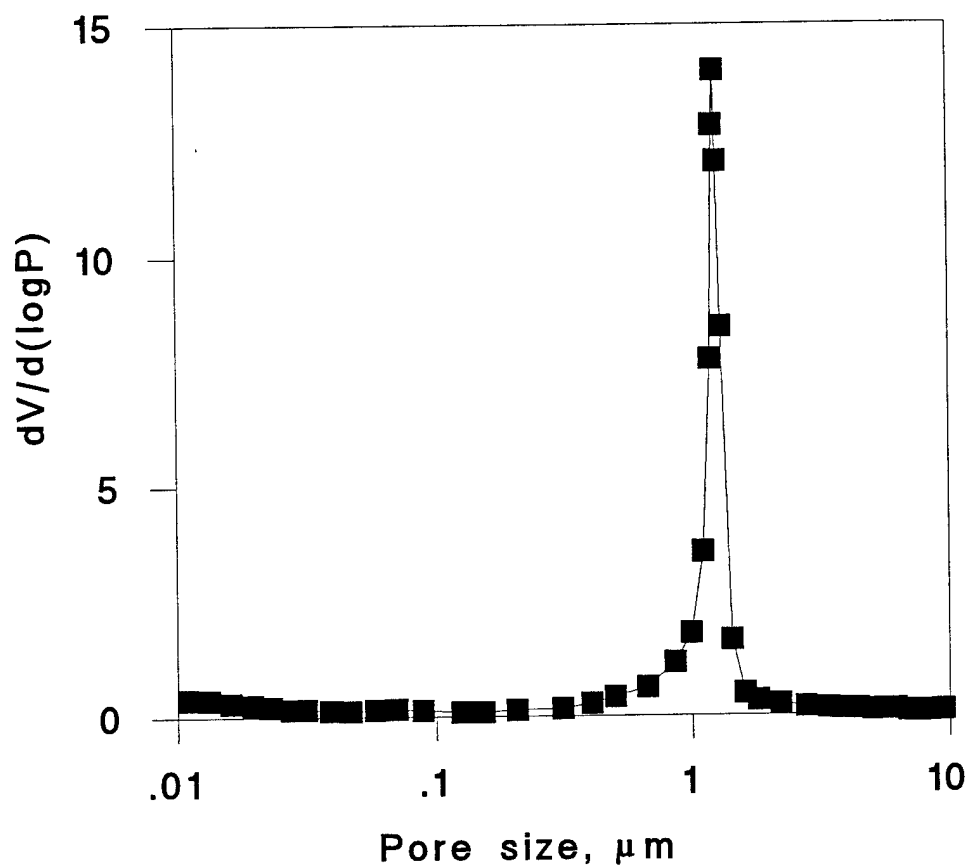


Figure 3. Differential pore size distribution curve of the poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolith.
Polymerization conditions: Polymerization mixture, glycidyl methacrylate 24 %, ethylene dimethacrylate 16 %, cyclohexanol 60%, azobisisobutyronitrile (1% in respect to monomers); polymerization in a tubular mold 100 x 8 mm i.d.; polymerization time 24 h at 55 °C.

efforts concentrated on the latter area. Experimentally, a closed system similar to a chromatographic column was attached to a pump. After modification, the back pressure of the system was measured with respect to temperature. Significant changes in back pressure at different temperatures served as a good indication that the desired functionalization had occurred. The majority of experiments were done with monoliths polymerized *in situ* in tubular devices 10 and 50 mm long.

Functionalization with aminogroup terminated PNIPAAm

Semitelechelic poly(N-isopropylacrylamide)

The epoxide functionalities of the porous glycidyl methacrylate copolymer react readily with amines. This can be used advantageously for the attachment of LCST polymers to the solid support. Based on methods reported in the literature, several NIPAAm polymers were prepared in the presence of various amounts of 2-aminoethanethiol, which remains attached to the PNIPAAm molecules through the sulfur atom as a result of a chain transfer reaction during free radical polymerization. The average molecular weight of semitelechelic PNIPAAm produced in this manner ranged from 1100 to 2700, as determined by MALDI TOF-MS.

Initially, the reaction of semitelechelic PNIPAAm with porous epoxide-containing polymer was performed in vials. Pieces of the crushed monolith were mixed with a 10% solution of PNIPAAm in 1-propanol, and reacted at 70 °C for various times. The appearance of small bands at 3400 and 1650 cm^{-1} , characteristic of the amide N-H stretch and

C=O stretch respectively, confirmed the functionalization of the surface. This reaction was repeated in 10 mm long porous monoliths imbibed with PNIPAAm solutions.

Upon completion of the reaction, the monoliths were placed into a 10 mm jacket, and attached to a chromatographic pump. In contrast to expectations, no changes were observed in the back pressures of the columns when measured at both ambient temperature and 50°C. This indicates that the PNIPAAm chains were too small to close the pores. Because we were unable to prepare semitelechelic NIPAAm polymers with much higher molecular weight, this approach was abandoned.

Cerium (IV) initiated free-radical grafting to the support

The second approach investigated for the desired modification of the porous monoliths involved the use of CAN in nitric acid to initiate the grafting polymerization of NIPAAm, a technique which was successful in the modification of polypropylene membranes. According to the literature, this technique is most efficient with compounds containing isolated hydroxyl groups, as vicinal diols could lead to a surface partially modified with aldehyde groups, resulting from cleavage of the diol carbon-carbon bond.

Our preliminary attempts to prepare a monolith with isolated hydroxyl groups using 2-hydroxyethyl methacrylate as the primary monomer completely failed. In addition, the attempted *in situ* reduction of the epoxide groups to a primary alcohol on the polymer monolith using sodium cyanoborohydride in the presence of boron trifluoride proved technically impractical. Therefore, despite its potential lower efficiency, we hydrolyzed the

epoxide functionalities of glycidyl methacrylate to the diol in order to produce the hydroxyl-modified surface required for the cerium (IV) salt-initiated polymerization.

Model experiments were run in closed vials in order to optimize grafting conditions for the molded material, with the extent of grafting being assessed by the weight gain exhibited by the polymers. Grafting experiments were then performed on 50 mm long monoliths. In an example reaction, the column exhibited a back pressure of 100-200 psi at a flow of 1 mL/ min of water when immersed in a 60 °C bath. However, the back pressure rose steeply when the device was removed from the bath and left at room temperature. When the pressure approached the operating limit of the pump, the column was reimmersed in the heated bath, resulting in a nearly immediate drop in the column back pressure. When the solvent was switched to methanol, sharp back pressures increases were seen regardless of the temperature to which the column was exposed. Table 1 summarizes the results of some of the grafting experiments.

Although the first two experiments demonstrated the exact behavior expected of a NI-PAAm-grafted monolith, there are several problems with the cerium-initiated grafting technique. First, despite a relatively high extent of grafting as evidenced by the level of nitrogen, the gate effect was never successfully demonstrated on the shorter monolith, which is closer to the ultimate goal of producing a thin, "gate" layer at the top of a larger, adsorption active region. Another significant drawback of this approach is its poor reproducibility, as evidenced by the variation in both the nitrogen content of three identical polymerizations, and in the columns' responses to external stimuli.

Table 1. Effect of reaction conditions on grafting of acrylamide (AAm) and NIPAAm onto hydrolyzed poly(glycidyl methacrylate-co-ethylene dimethacrylate) monoliths

Reaction conditions: 10 % aqueous solution of monomer, CAN 2.5 mmol/L, nitric acid 25 mmol/L, reaction time 5 h.

Monomer	Monolith length, mm	Polym. temp., °C	N content % ^a	Grafted polym., % ^b	Temper. effect ^c
NIPAAm	50	60	0.23	1.86	yes
NIPAAm	50	60	0.33	2.66	yes
NIPAAm	10	60	0.70	5.65	no
NIPAAm	50	60	0.18	1.45	no
NIPAAm	50	25	0.12	0.97	no
AAm	50	60	1.03	5.22	-
AAm	10	60	1.73	8.85	-

^a Determined by elemental analysis; ^b Calculated weight percentage of nitrogen containing polymer with respect to the total weight of the polymer sample; ^c Indicates a reversible change in back pressure depending on the temperature of the environment

Several experiment were performed in an attempt to understand the inconsistent results. It was hypothesized that the molecular weight of the grafted polymer was limited by the precipitation of the growing chains, as the reaction temperature used was above the LCST of PNIPAAm. However, the corresponding reaction performed at room temperature showed no improvements. Also, several experiments were performed under identical conditions with acrylamide, the grafting of which onto hydroxyl-containing substrates by the Ce(IV) technique is well documented. The polymerization of this monomer proceeds far more readily, suggesting that the Ce(IV) mediated polymerization of NIPAAm is not well suited for the production of large graft chains. As a result, this approach was also abandoned.

Free radical polymerization of NIPAAm in vinylized pores

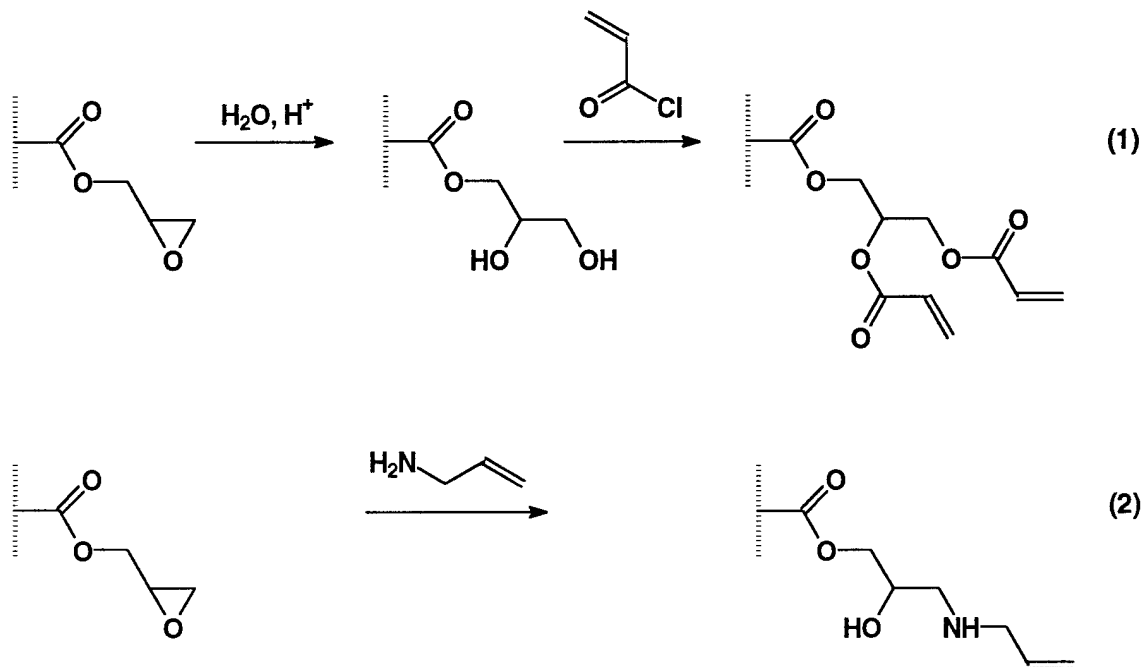
The third approach to the desired modification involved the free radical polymerization of NIPAAm using more traditional initiators within the pore structure of a polymer monolith, the surface of which had been functionalized with vinyl groups. Upon being incorporated into a growing chain, these vinyl residues bind the newly formed macromolecule to the column's surface.

Vinylization of porous polymer surface

Several methods can be designed to functionalize the surface of poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) with pendant double bonds. Scheme 1 illustrates the two methods investigated.

The first was the reaction of the hydroxyl groups of hydrolyzed poly(glycidyl methacrylate-*co*-ethylene dimethacrylate) with acryloyl chloride (reaction 1 -- "ester" derivative). Typically, this acylation is performed in the presence of a weak base such as pyridine, which traps the liberated hydrogen chloride. The ammonium salt thus formed is insoluble in the reaction medium, and precipitates from solution. Such a precipitation during an *in situ* reaction on a monolith could plug the pores of both the monolith and the end frits. Therefore, this reaction was performed with a solution of acryloyl chloride in THF. Normally a facile reaction, a significant decrease in the intensity of the hydroxyl band at 3500 cm^{-1} was observed only upon heating the sealed tube imbibed with the reaction solution at $60\text{ }^{\circ}\text{C}$ for 12 hours.

Scheme 1



A simpler approach was the direct opening of the epoxide ring with allyl amine (reaction 2 -- "allyl" derivative). When imbibed with a 50% aqueous solution of the allyl amine, a tube sealed at 60°C for 8 hours yielded the ring-opened polymer, as measured by FT-IR.

Polymerization in pores

Two approaches to the production of high molecular weight PNIPAAm grafted to the vinylized surface were investigated. The first involved a redox-initiated polymerization in an aqueous medium. Since the polymerization is done at a temperature below the polymer's LCST, the growing chains will not precipitate. The second involved free radical polymerization in non-aqueous solvents. Typical free radicals initiators such as azobisisobutyronitrile could be used, since NIPAAm chains only exhibit a LCST in water.

The redox polymerization of acrylamide and its derivatives, including NIPAAm, often use an initiator combination of potassium persulfate and sodium metabisulfite. However, polymerization proceeds rapidly at room temperature, making it difficult to imbibe the column. An induction period can be introduced by not performing the standard nitrogen purging of the polymerization mixture, allowing the dissolved oxygen in the system to act as a "natural" inhibitor. Using this approach, a 10 mm long modified monolith was produced, which exhibited different back pressure profiles at temperatures above and below the LCST. However, the "gate" was not completely closed at the higher temperature. Clearly, more work on this system is required to define polymerization conditions that allow the effective and reproducible imbibing of the column, while still producing grafted chains of the required size.

Table 2. Effect of reaction conditions on grafting of NIPAAm onto vinylized poly(glycidyl methacrylate-co-ethylene dimethacrylate) monoliths

Reaction conditions: 10 % solution of monomer in a solvent, AIBN 1% in respect to monomer, crosslinker methylenebisacrylamide 1 % based on total weight of monomers, temperature 60 °C, reaction time 20 h.

Vinylized derivative	Solvent	Crosslinker	N content % ^a	Grafted polym., % ^b	Temper. effect ^c
Allyl	2-Propanol	yes			no
Ester	2-Propanol	yes			no
Allyl	Benzene	yes			yes
Ester	Benzene	yes			no
Allyl	Benzene	no			yes

^a Determined by elemental analysis; ^b Calculated weight percentage of nitrogen containing polymer with respect to the total weight of the polymer sample; ^c Indicates a reversible change in back pressure depending on the temperature of the environment

The second approach involved the use of traditional thermal initiators in non-aqueous systems. Table 2 summarizes the results of some experiments that were performed in 50 mm long monoliths.

These results clearly demonstrate that 2-propanol is not a suitable solvent for the grafting polymerization, and that the acryloylated surface of the solid support as produced did not provide sufficient anchoring for the PNIPAAm chains. In contrast, the polymerization of NIPAAm in benzene within the pores functionalized with allyl amine always led to a monolith which exhibited the desired "gate" behavior.

The back pressure profiles shown in Figure 4 reflect the rates of the phase transition of the grafted PNIPAAm chains from their "swollen" hydrated state to their shrunken state over several cycles. In all cases, the rate is very fast, allowing the columns to respond rapidly to environmental changes. However, a significant difference exists between the monoliths modified with PNIPAAm in either the presence or absence of the crosslinker. Specifically, the phase transitions of the crosslinked polymer are slower, as the more confined chains require a longer time to completely change their conformation. Additionally, the back pressure does not return to its baseline value even after 5 minutes at a temperature of 60°C, indicating that the initial fast collapse of the swollen gels occurs in such a manner that some of the chains are prevented from reaching their fully shrunken state. By contrast, the phase transitions of the chains prepared without the addition of any crosslinker are quicker, and always return to the same baseline value.

Since the "gate" portion of the final hybrid column should ideally be as thin as possible, the polymerizations were repeated in 10 mm monoliths under the same conditions.

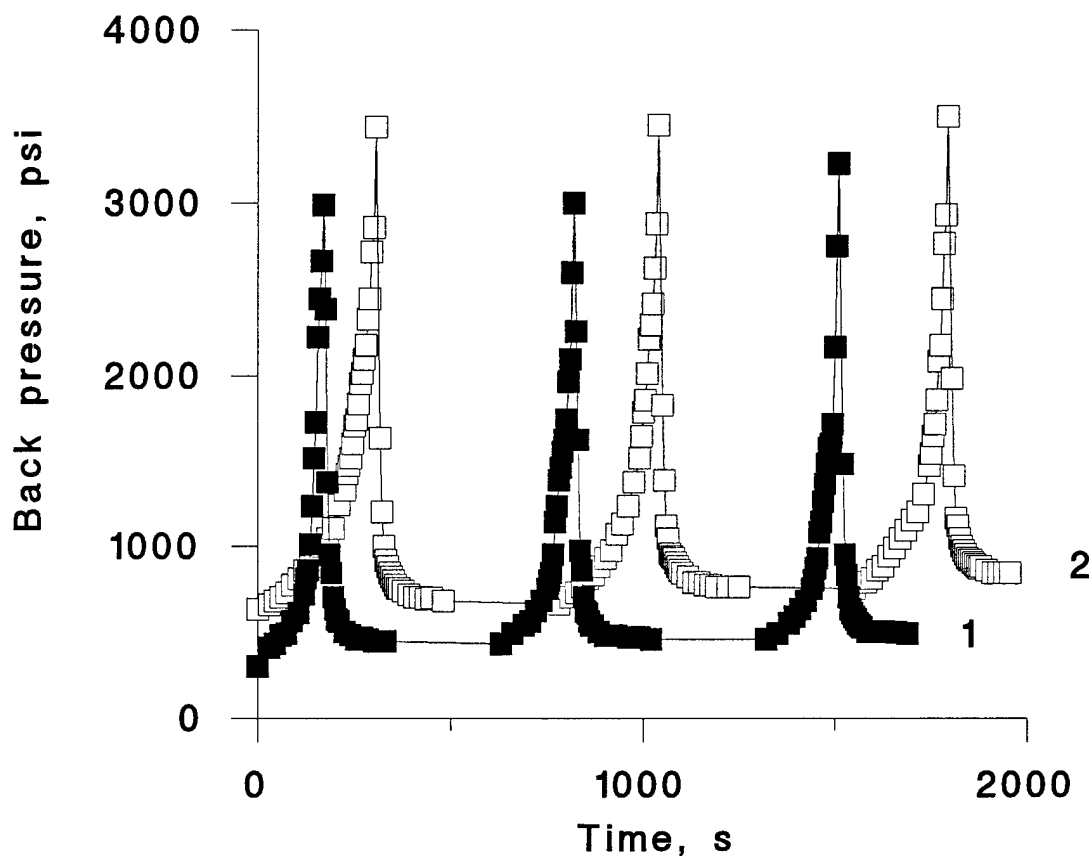


Figure 4. Back pressure changes in 50 x 8 mm poly(glycidyl methacrylate-co-ethylene dimethacrylate) monoliths modified by reaction with allylamine and grafting of NIPAAm (1) and NIPAAm-methylenebisacrylamide (99:1)(2) as a function of temperature variation.

Reaction conditions: Vinylization, 50% aqueous solution of allylamine, temperature 60 °C, time 8 h; Grafting, 10 % solution of monomers in benzene, azobisisobutyronitrile (1% in respect to monomers), reaction time 20 h, temperature 60 °C; Permeation through a 50 x 8 mm i.d. monolith measured at a flow rate of 1.0 mL/min of water using a chromatographic pump; flow through starts at 25 °C, and after the back pressure reaches a value of 3000-3500 psi, the holder with the monolith is immersed into a water bath thermostated to 60 °C and kept there for 5 min, and then removed.

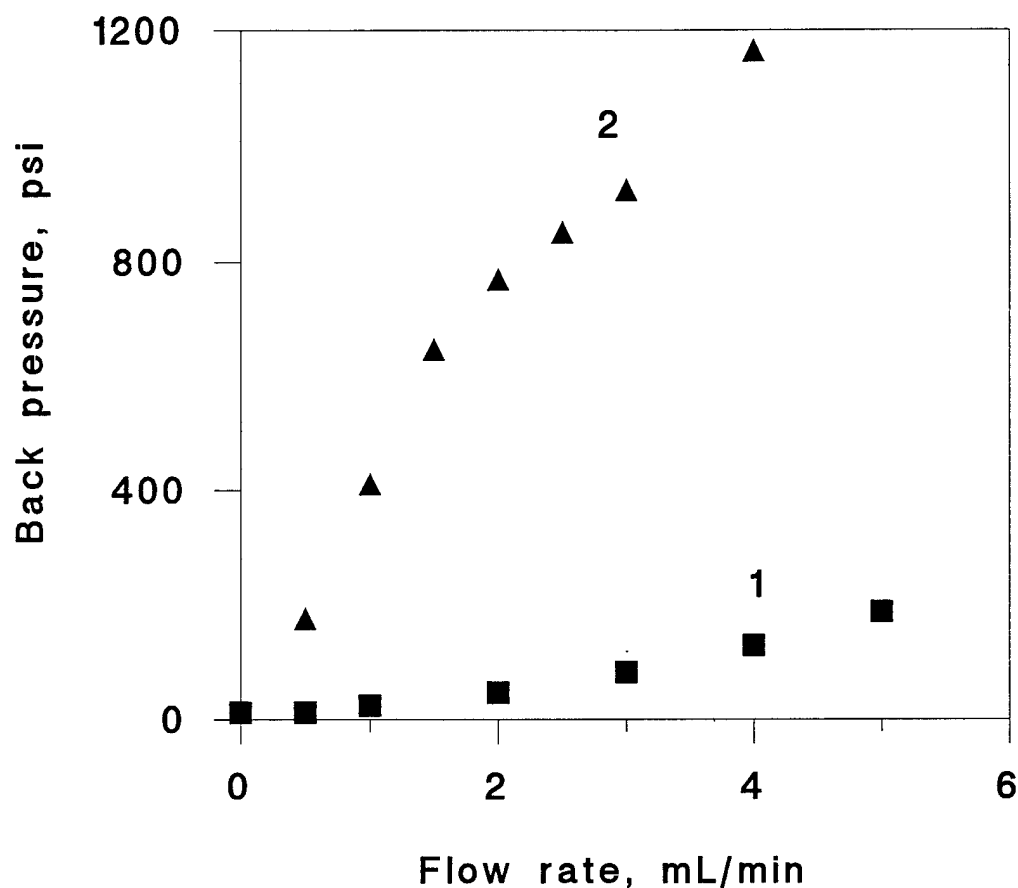


Figure 5. Back pressure profile of 10 x 10 mm poly(glycidyl methacrylate-co-ethylene dimethacrylate) monolith modified by reaction with allylamine and grafting of NIPAAm-methylenebisacrylamide (99:1) measured at temperatures of 25 (1) and 60 °C (2).

Reaction conditions: Vinylization, 50% aqueous solution of allylamine, temperature 60 °C, time 8 h; Grafting, 10 % solution of monomers in benzene, azobisisobutyronitrile (1% in respect to monomers), reaction time 20 h, temperature 60 °C; Permeation through a 10 x 10 mm i.d. monolith measured at varying flow rates of water using a chromatographic pump.

Again, a significant difference was seen between materials produced in the presence and in the absence of crosslinker. Figure 5 shows the back pressure profile with changing flow rate for a monolith produced with 1% crosslinker. This experiment, along with the redox-initiated example, demonstrates that the level of pore closure can be controlled through the choice of polymerization conditions. In contrast, Figure 6 compares the back pressure profiles with changing temperature of 10 and 50 mm long columns produced with no crosslinker, demonstrating that the rapid and reversible plugging of a 1 μm pore system can be easily accomplished within a 1 cm length monolith layer.

Conclusion

The development of a "smart" polymer system targeted towards the construction of a hybrid device, which will eventually combine both sensitivity to an external stimulus and a specific sorption selectivity, was successfully completed. Specifically, we developed a reproducible technique that allows the permanent incorporation of a temperature sensitive polymer within a porous medium, where it is able to effect the reversible closing of pores even with sizes on the order of micrometers. Further, the extent of swelling, and therefore the resulting decrease in the pore size, can be controlled by judicious choice of the reaction conditions.

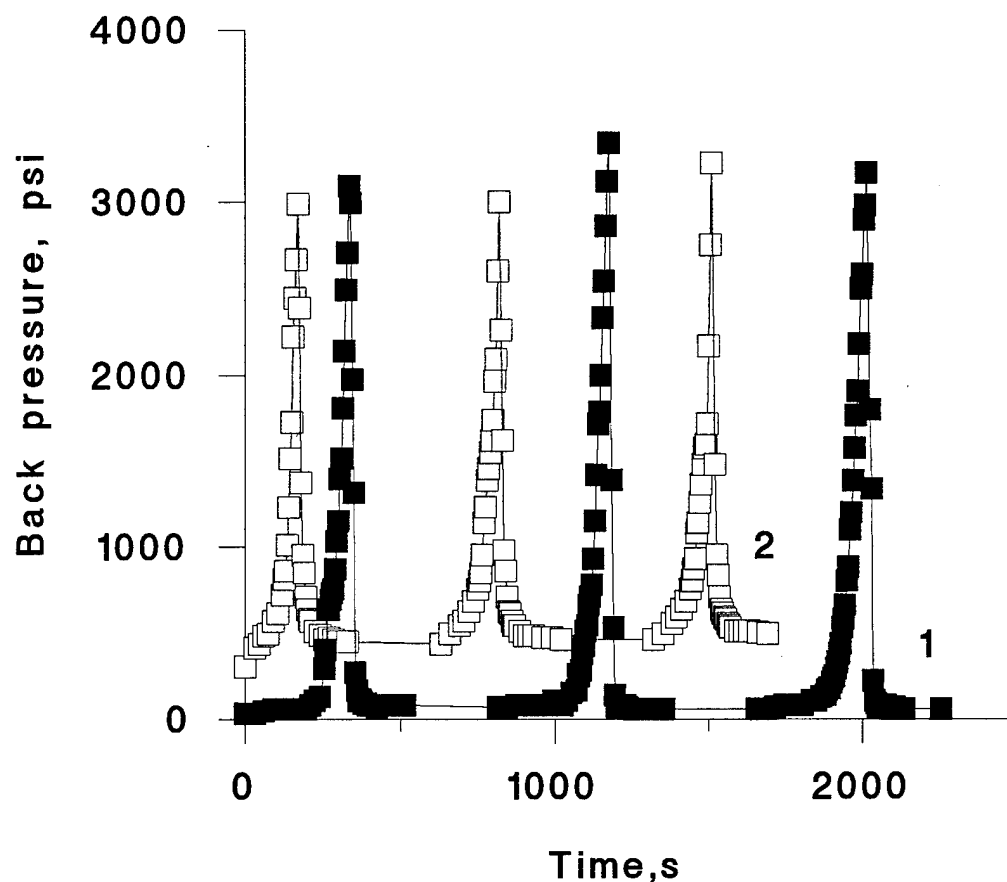


Figure 6. Back pressure changes in 10 x 10 mm (1) and 50 x 8 mm (2) poly(glycidyl methacrylate-co-ethylene dimethacrylate) monoliths modified by reaction with allylamine and grafting of NIPAAm as a function of temperature variation.

Reaction conditions: Vinylization, 50% aqueous solution of allylamine, temperature 60 °C, time 8 h; Grafting, 10 % solution NIPAAm in benzene, reaction time 20 h, temperature 60 °C; Permeation through the monoliths measured at a flow rate of 1.0 mL/min with water using a chromatographic pump; flow through starts at 25 °C and after the back pressure reaches a value of 3000-3500 psi, the holder with the monolith is immersed into a water bath thermostated to 60 °C and kept there for 5 min, and then removed.