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14. ABSTRACT Stimuli-responsive functional polymeric membranes with controlled structures and properties have applications for the military as well as civilians in a range of fields. In this project, polymeric films with arrays of nanoscale and thermal-switchable pores based on self-assembling of block copolymer are formed. The block formed the matrix is random copolymer of styrene and 4-vinylbenzocyclobutene (4-VBCB) (4:1 molar ratio). The other block is the random copolymer of bis- and tris(ethylene glycol) methacrylate [(EO)2,3MA] with a tuned lower critical-solution					
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Report Title

Functional Polymeric Membranes Based on Self-Assembling of Synthetic Stimuli-Responsive Polymers

ABSTRACT

Stimuli-responsive functional polymeric membranes with controlled structures and properties have applications for the military as well as civilians in a range of fields. In this project, polymeric films with arrays of nanoscale and thermal-switchable pores based on self-assembling of block copolymer are formed. The block formed the matrix is random copolymer of styrene and 4-vinylbenzocyclobutene (4-VBCB) (4:1 molar ratio). The other block is the random copolymer of bis- and tris(ethylene glycol) methacrylate [(EO)₂,3MA] with a tuned lower critical-solution temperature (LCST) at ~38°C (the LCST of 1 wt % PEO₂MA in water is 24 °C, 1wt % PEO₃MA in water is 48 °C). These P[(St-r-4-VBCB)-b-(EO₂MA-r- EO₃MA)] copolymers were synthesized by controlled atom transfer radical polymerizations. Polymeric membranes were prepared by casting blends of P[(St-r-4-VBCB)-b-(EO₂MA-r- EO₃MA)] and poly(N-vinylpyrrolidone) (wt of PVP: 16-22%). The as-casted films were annealed at 180°C for 5 days and 220°C for two hours under argon. After rinsing the films with THF/methanol (8:2), membranes with arrays of thermal-switchable pores were formed. Preliminary tests of water filtration using these films proved the proposed concept of principle. Much better performance is expected when the block copolymer compositions, the composition of blend, and membrane preparation conditions are optimized.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Number of Papers published in peer-reviewed journals: 0.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations:

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

One is prepared for the upcoming ACS meeting (Polymer Preprint)

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 1

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Patents Submitted

Patents Awarded

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>

Total Number:

Names of personnel receiving PhDs

<u>NAME</u>

Total Number:

Names of other research staff

<u>NAME</u>

<u>PERCENT SUPPORTED</u>

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Functional Polymeric Membranes Based on Self-Assembling of Synthetic Stimuli-Responsive Polymers

Final Report

Investigators: Kunlun Hong⁽¹⁾ and Jimmy W. Mays^{(1),(2)}

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Functional Polymeric Membranes Based on Self-Assembling of Synthetic Stimuli-Responsive Polymers (CBT)

Abstract: Stimuli-responsive functional polymeric membranes with controlled structures and properties have applications for the military as well as civilians in a range of fields. In this project, polymeric films with arrays of nanoscale and thermal-switchable pores based on self-assembling of block copolymer are formed. The block formed the matrix is random copolymer of styrene and 4-vinylbenzocyclobutene (4-VBCB) (4:1 molar ratio). The other block is the random copolymer of bis- and tris(ethylene glycol) methacrylate [(EO)_{2,3}MA] with a tuned lower critical-solution temperature (LCST) at ~38°C (the LCST of 1wt % PEO₂MA in water is 24 °C, 1wt % PEO₃MA in water is 48 °C). These P[(St-r-4-VBCB)-b-(EO₂MA-r-EO₃MA)] copolymers were synthesized by controlled atom transfer radical polymerizations. Polymeric membranes were prepared by casting blends of P[(St-r-4-VBCB)-b-(EO₂MA-r-EO₃MA)] and poly(N-vinylpyrrolidone) (wt of PVP: 16-22%). The as-casted films were annealed at 180°C for 5 days and 220°C for two hours under argon. After rinsing the films with THF/methanol (8:2), membranes with arrays of thermal-switchable pores were formed. Preliminary tests of water filtration using these films proved the proposed concept of principle. Much better performance is expected when the block copolymer compositions, the composition of blend, and membrane preparation conditions are optimized.

Proposed Research Objectives

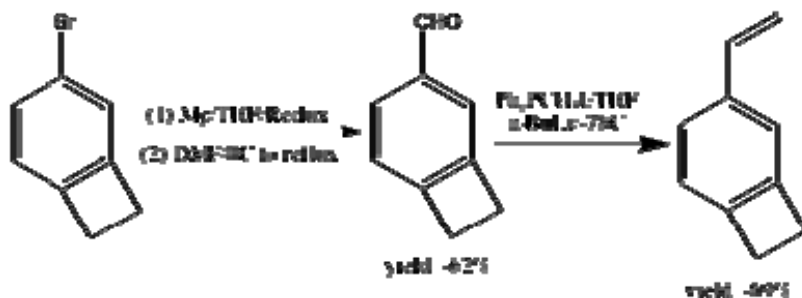
The overall objective of this proposed work is to prepare functional polymeric membranes with **controlled** sizes and **thermally responsive switches** from the self-assembly of well-defined block copolymers. Specifically, we synthesized and characterize styrene/4-vinylbenzocyclobutene (4-VBCB) and bis or tris(ethylene glycol) methacrylate [(EO)_{2,3}MA] block copolymers, P(S/4-VBCB)-b-P((EO)₃MA), via controlled atom transfer radical polymerizations. The copolymer is then blended with poly(N-vinylpyrrolidone) (PVP) homopolymers to form film (membrane precursors). The 4-VBCB moieties are then crosslinked by annealing of the film at 180°C for 5 days. PVP, which is miscible with oligo(ethylene glycol) methacrylate block, functions as a sacrificial pore template, and is removed after crosslinking of the 4-VBCB moiety through rinsing with THF/methanol mixture. The pore size is tuned by the amount of PVP used.

The resulted membranes have good mechanical strength and contain a thermal responsive layer [poly(tris(ethylene glycol) methacrylate)] that exhibits low critical-solution temperature (LCST) inside the pores. The membranes are evaluated by passing water through it at different temperatures.

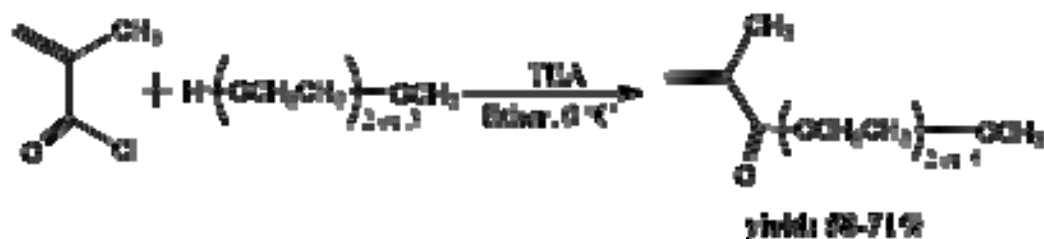
Highlighted Results

(1) **Synthesis of 4-VBCB, (EO)_{2,3}MA monomers and its block copolymers:** 4-VBCB was synthesized according to **Scheme 1** and the overall yield is around 40%. (EO)_{2,3}MA were synthesized according to **Scheme 2** and the yield is typical about 60-70% after column purifications. The block copolymers based on these monomers are synthesized by atom transfer radical polymerization using according to **Scheme 3**. The synthesized polymers are reasonable well-defined and the total molecular weight is around 33K according to GPC (calibrated with

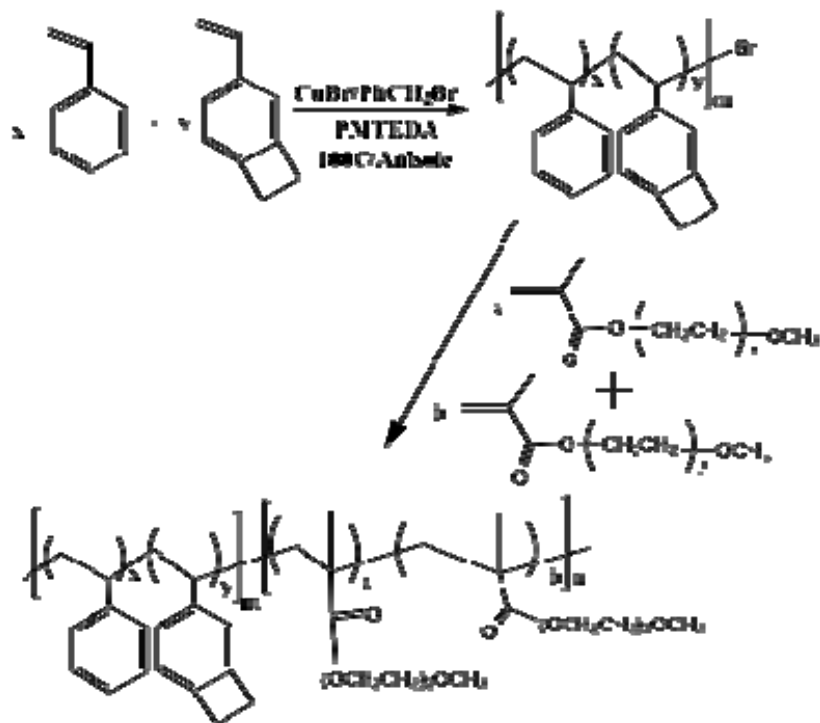
polystyrene standards) and the data is listed in Table 1. We used the random copolymerization of bis or tris(ethylene glycol) methacrylate to tune the LCST temperature of the thermal-sensitive block. Controlled experiment showed the LCST is around 38C (Table 1). Their homopolymer are also listed in table 1. for comparison.



Scheme 1 Synthesis of 4-VBCB



Scheme 2 Synthesis of (EO)_{2,3}MA



Scheme 3 Synthesis of the block copolymer

Table 1 Characteristics of the block copolymers

Polymer	MW (Kg/mol)	PDI	Composition	LCST (°C) (1.0 % in water)
P(EO ₂ MA)	7.1	1.23	-	24
P(EO ₃ MA)	8.4	1.26	-	48
P(EO ₂ MA-r-EO ₃ MA)	11.9	1.22	EO ₂ MA: EO ₃ MA (mol: 47/53) ^a	38
P(St-r-4VBCB)	12.5	1.19	St/4-VBCB (mol: 87/13) ^b	-
P[(St-r-VBCB)-b-(EO ₂ MA-r-EO ₃ MA)]	17.4	1.32	-	-

^a: from feed ration; ^b: from NMR

(2) Membrane from the self-assembly of the block copolymer and preliminary evaluation The synthesized P[(St-r-VBCB)-b-(EO₂MA-r-EO₃MA)] block copolymers was blended with polyvinylpyrrolidone (PVP, MW ~6K, with wt: 16% and 22%) by co-dissolving in THF (~8%). Precursor of the membranes was formed by casting the solution inside a Teflon breaker (diameter 2.5cm). The as-casted films (about 2mm thick) were annealed at 180°C for 5 days and 220°C for two hours under argon. The films apparently have good mechanical strength. After rinsing the films with THF/methanol (8:2) (pure water was not effective), the membrane was transfer inside a custom made tube with coarse frit glass filter (frit diameter ~19mm). Then the film was rinsing with THF to make sure good contacts and dry in convention oven at 35C under vacuum.

The proof of principle tests was done in a Marathon 21000R centrifuge (used as temperature control unit). The amount of water passed through the membrane at certain temperature in ~ 6 minutes is listed in Table 2.

Table 2 Preliminary evaluation of the membranes (tested time 6 min)

Membrane	PVP wt%	Water passed at 25°C	Water passed at 46°C
1	15.7	0.26 gram	8.13 grams
2	22.4	0.43 grams	10.05 grams

Summary and future outlook

We have successfully prepared polymeric membranes based on P[(St-r-4-VBCB)-b-(EO₂MA-r-EO₃MA)] copolymers. These membranes should have the advantages of controllable morphology (pore) and wide selections of thermal-responsive layers. Preliminary tests showed the membrane were thermal-responsive. They have potential applications for the military as well as civilians in a range of fields. Due to the funding scope, the membranes are far from optimized. Their morphologies are also need to be examined if further funding is available.