REVERSE-SELECTIVE GAS-SEPARATION MEMBRANES PREPARED BY ATOM TRANSFER RADICAL POLYMERIZATION

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ABSTRACT

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About 95% of the H₂ synthesized in the United States is produced by steam reforming of hydrocarbons followed by the water gas shift reaction. However, this process gives ~25 mol% CO₂ as a byproduct, and the energy and capital-intensive pressure swing adsorption (PSA) procedures for CO₂ removal exhibit some unavoidable H₂ loss. Membrane separations, especially those with reverse-selective membranes that selectively permeate CO₂ from H₂ streams, are a promising alternative to pressure swing adsorption. The purified H₂ on the high-pressure feed side of the membrane could directly go to storage and transportation without re-pressurizing.

This research aims to develop reverse-selective membranes containing thin poly(ethylene oxide) (PEO)-based polymer films grown from porous substrates via surface-initiated atom transfer radical polymerization (ATRP). PEO has an excellent CO_2 solubility, but crystallization of PEO chains leads to low CO_2 permeability and minimal CO_2/H_2 selectivity. To prevent crystallization, we copolymerized poly(ethylene glycol)methyl ether methacrylate (PEGMEMA) monomers containing PEO side chains with 23-24 (PEGMEMA-1100) and 8-9 (PEGMEMA-475) PEO unites. The shorter PEO chains

prevent crystallization, and the copolymer membranes still exhibit a CO_2/H_2 selectivity of 12 with a CO_2 permeability of about 20 Barrers.

Cross-linking of poly(PEGMEMA) films may slightly decrease CO₂ permeability and CO₂/H₂ selectivity, but it should also enhance the membrane's chemical and physical durability. Cross-linked copolymer films prepared by polymerization of PEGMEMA-1100, PEGMEMA-475 and poly(ethylene glycol)diacrylate (PEGDA-700) on RC membranes showed CO₂/H₂ selectivities ranging from 6.5 to 19.9, but a CO₂ permeability of 5-15 Barrer. Efforts to increase permeability included embedding SiO₂ nanoparticles into the cross-linked poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) film to increase fractional free volume (FFV). Unfortunately, nanoparticles didn't enhance the CO₂ permeability, perhaps because the non-rigid chains.

During the course of membrane preparation, growth of poly(PEGMEMA-1100-*co*-PEGMEMA-475) films in water resulted in an exceptionally rapid polymerization (200 µm-thick films in just 30 min of polymerization). The remarkable thickness does not stem from precipitation, but seems to arise from a unique increase in catalyst activity in the presence of water and PEO side chains.

Future work should include further examination of the kinetics of the very rapid polymerization as well as studies of nanoparticle-containing membranes made with glassy, reverse-selective polymers. The nanoparticles embedded in glassy polymer should give more FFV, and finally increase the permeability and selectivity of the membrane. To My Husband

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LIST OF ABBREVIATIONS

ATRP	Atomic Transfer Radical Polymerization		
BiBB	2-bromoisobutyryl bromide		
b.p.	Boiling Point		
bpy	2,2'-bipyridine		
DMAEMA	2-(dimethyl amino) ethyl methacrylate		
DMF	dimethylformamide		
FFV	Fractional Free Volume		
GC	Gas Chromatography		
GMA	glycidyl methacrylate		
HEMA	2-hydroxyethyl methacrylate		
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine		
MES	2-(methacryloyloxy) ethyl succinate		
MMMs	Mixed Matrix Membranes		
MMA	methyl methacrylate		
MWCOs	Molecular Weight Cut-offs		

NMR	Nuclear Magnetic Resonance		
NMDG	N-methylglucamine		
PAA	poly(acrylic acid)		
PALS	Positron Anihilation Lifetime Spectroscopy		
PDI	Polydispersity Index		
PDMAEMA	poly(2-dimethylamino)ethyl-methacrylate		
PEG	poly(ethylene glycol)		
PEGDA	poly(ethylene glycol diacrylate)		
PEGMA	poly(ethylene glycol methacrylate)		
PEGMEMA	poly(ethylene glycol methyl ether methacrylate)		
PEO	poly(ethylene oxide)		
PES	poly(ether sulfone)		
PET	poly(ethyleneterephthalate)		
PGMA	poly(glydicyl methacrylate)		
РМА	poly(methyl acrylate)		
PMMA	poly(methyl methacrylate)		
PMP	poly(4-methyl-2-pentyne)		

PPEGMA	poly[poly(ethylene glycol methacrylate)]		
PPEGMEMA	poly[poly(ethylene glycol methyl ether methacrylate)]		
PS	poly styrene		
PSA	Pressure Swing Adsorption		
PVDF	poly(vinylidene fluoride)		
RO	Reverse Osmosis		
SEM	Scanning Electron Microscopy		
SI-ATRP	Surface-Initiated Atomic Transfer Radical Polymerization		
tBMA	tert-butyl methacrylate		
TCD	Thermal Conductivity Detector		
TEA	triethylamine		
TEM	Transmission Electron Microscopy		

Chapter 1 Introduction and Background

This dissertation reports the growth of polymer brushes on porous supports to create membranes that allow selective permeation of CO₂ from CO₂/H₂ mixtures. Specifically, atomic transfer radical polymerization (ATRP) of poly(ethylene glycol methyl ether methacrylate) (PEGMEMA) monomers, sometimes in the presence of silica nanoparticles, yields selective membrane skins. My research investigates both film formation and gas-permeation properties of these films. To put the work in perspective, this chapter describes related previous studies and recent developments. First I introduce the potential 'Hydrogen Economy' and the need to develop cheaper methods to remove CO₂ from H₂. Second, I discuss membrane-based gas separations with a focus on reverse-selective separations, where larger gases permeate through a membrane more readily than smaller gases. Flory-Huggins theory provides a guide for selecting materials for reverse-selective membranes. Third, I present our method to develop the thin skins of membranes through surface-initiated ATRP (SI-ATRP). This includes discussion of the mechanism and successful examples of ATRP. Finally, I give a brief summary of the following chapters of this dissertation.

1.1 Hydrogen as an Energy Carrier.

Despite being the most abundant element in the universe, hydrogen does not exist on earth as H_2 in significant quantities. Instead, hydrogen reacts with oxygen, carbon and other elements to form molecules such as water. The molar mass of diatomic H₂ is only 2 g/mol, but the H-H bond energy is 436 kJ/mol,¹ making H₂ one of the most weightefficient energy carriers. Moreover, because combustion of H₂ yields only water, delivery of energy via H₂ is environmental friendly. The concept of a 'hydrogen energy economy' emerged in the 1970's, but numerous barriers currently limit such an economy.

The production of H_2 requires large quantities of compounds that contain releasable hydrogen. Currently, fossil fuels, water and biological matter are the main resources for H_2 production. As of 2010, annual H_2 production in the United States was nine million tons.² However, over 95% of this H_2 comes from fossil fuels, mainly through steam reforming of natural gases, crude oil and coal. Electrolysis and other H_2 production methods provide the other 4% of H_2 production.³ Reactions (1.1) and (1.2) show the steps in H_2 production from hydrocarbons. In the first step (steam reforming), hydrocarbons react with steam to yield CO and H_2 .

$$C_nH_m + nH_2O \rightarrow nCO + (m/2+n)H_2$$
(1.1)

$$CO+H_2O \rightarrow CO_2+H_2 \tag{1.2}$$

The second step, the water gas shift reaction provides additional H₂ and generates CO₂.

The above reactions demonstrate that *n* moles of CO₂ result from a hydrocarbonbased synthesis of (2n+m/2) moles of H₂. Even for the most hydrogen rich hydrocarbon resource, CH₄, 20% of the final product is CO₂. Considering this high CO₂ percentage along with the current annual H₂ production and the possible hydrogen economy of the future, even small improvements in H₂/CO₂ separations could save a huge amount of energy and capital.

If the H₂ produced from reactions (1.1) and (1.2) delivers energy by its reaction with oxygen, the amount of CO₂ released to the environment during H₂ production is equivalent to the amount of CO₂ produced from direct combustion of the hydrocarbon. Moreover, some energy is lost during H₂ synthesis. Thus, with current techniques, a hydrogen economy would not reduce CO₂ emissions. The potential benefit of a hydrocarbon-based hydrogen economy is that CO₂ and other pollutants could be sequestered at H₂ production plants.

1.2 Hydrogen Purification Techniques

The most common H_2 purification processes are: (1) pressure swing adsorption (PSA), (2) fractional/cryogenic distillation, and (3) membrane separations. Combinations of these processes are also possible.⁴

PSA operates in large vessels packed with materials that selectively adsorb CO₂. Initially CO₂ adsorbs to the packing and purified H₂ exits the vessel. When the amount of adsorbed CO₂ approaches the packing binding capacity, the high pressure feed is switched off, and the adsorbing vessel releases CO₂ and small amounts of H₂ at a much lower pressure to regenerate the packing. In PSA plants, a number of adsorbing vessels work alternatively to allow continuous separation (Figure 1.1), because one vessel goes through an adsorbing-purging cycle and cannot continuously adsorb CO₂. PSA separation yields high purity CO₂, but it loses some CO₂ during regeneration and is relatively expensive.



Figure 1.1. Schematic illustration of one separation cycle in a PSA vessel.

Fractional/cryogenic distillation relies on the significant boiling point difference between CO₂ (194.75 K) and H₂ (20.28 K).¹ The process includes cooling and pressurizing the gas mixture to below the boiling point of both CO₂ but above that of H₂. Then CO₂ in the liquid phase can then be separated from H₂ in the gas phase. This method is in commercial operation by itself or in combination with PSA. Unfortunately, cooling the gases to such low temperatures and high pressures is energy intensive. In membrane separations (Figure 1.2), mass transport takes place through a barrier between two phases. The separation can arise from differences in the size, charge density, or solubility of the permeating species, as well as combinations of these factors. Over the past 50 years, membrane separation has emerged as an attractive industrial alternative to traditional separation approaches such as distillation, because membrane separation usually requires much less energy.⁵



Figure 1.2. Conceptual drawing of membrane separation, which involves selective transport through a membrane between two phases.

Nevertheless, membrane separation is not in commercial operation for H_2/CO_2 separations. Compared to PSA and fractional/cryogenic separations, membrane separation is promising because of low energy consumption, the possibility of continuous operation, low capital costs, and ease of operation.⁴ The major challenge to using

membrane for gas separation at industrial plants is that the performance of membranes declines at high pressures and in high-humidity environments.⁶ If the hydrogen economy develops to a larger scale in the future, research and development on membrane-based H_2 purification will become even more important.

1.3 Membrane Separations

A membrane is a thin film that separates two phases and acts as a selective barrier to the transport of the matter. Studies of membranes began as early as the eighteenth century, but it was not until the twentieth century that research on synthetic membranes started to spawn a multi-billion dollar per year industry.⁷ In 1907, Bechhold developed the earliest device to control solvent evaporation rates and created nitrocellulose membranes with graded pore sizes. With the advent of reproducible membrane separations, more research appeared. By the 1930s, microporous collodion (nitrocellulose) membranes were commercially available.⁷

Perhaps the most notable breakthrough in membrane research was the introduction of asymmetric membranes. In the early 1960's Loeb and Sourirajan developed defect-free, anisotropic cellulose acetate reverse osmosis (RO) membranes.⁸ These materials consisted of a dense, selective layer on the surface of a relatively permeable material. The small thickness of the dense layer allowed for a reasonable flux along with high salt rejection. Not long after this breakthrough, asymmetric microfiltration and ultrafiltration membranes became commercially available. Research on RO membranes for water desalination has been an ongoing effort since that time. By

2009, there were 14,451 desalination plants in operation worldwide, producing 59.9 million cubic meters of water per day (15.8 billion gallons a day), with an annual increase in capacity of 12.3%.⁹

Rapid advances in polymerization also occurred in the 1950s and 1960s, and this promoted subsequent research in membrane technology. In addition to desalination, a second branch of membrane technology focused on biological applications, such as artificial kidneys. In biological and medical areas, membranes were also used in artificial organs and controlled drug delivery systems. The market of membranes sales in the biological area now exceeds that for traditional separation membranes.⁷

Because gas molecules are much smaller than typical solvated molecules and ions, gas-separation membranes appeared after membranes for solution-based applications. In 1980, DuPont introduced the Prism[®] hollow fiber membrane for H₂ separations.¹⁰ The isolation of H₂ was based mainly on its small size relative to nitrogen, ammonia, and other gases. By 1982, Generon produced a membrane to purify N₂ from air. Multiple companies including Ube, Medal, and Generon launched advanced membrane materials for O_2/N_2 , H₂/N₂, and H₂/CH₄ separations by 1987.¹¹ Starting in 1988, multiple companies installed membrane gas separation plants. Recently, the market for gas separation membranes has grown to a \$500 million per year business, totaling 24% of the entire membrane market.¹²

1.4 H₂ Separation Membranes and the Solution-diffusion Model.

The mechanisms of membrane-based separation of H_2 from CO_2 fall into size-based and solubility-based (Reverse-selective) categories (Figure 1.3). Table 1.1 presents some physical properties of CO_2 and H_2 . Importantly, H_2 is lighter, smaller and less condensable than CO_2 . Thus in general, H_2 will interact less strongly with membranes than CO_2 . The transport rates in size-sieving membranes depend on either the rate of gas diffusion or entry into a pore. Because gas-diffusion rates decrease with molecular mass, H_2 permeates through the membrane faster than CO_2 in both cases. Although this may provide selectivity and useful membranes, one disadvantage of these mechanisms is that the purified H_2 on the permeate side of the membrane is at low pressure so compression may be necessary.



Figure 1.3. Two representative categories of membrane-based separation of CO_2 and H_2 . The reverse-selective membrane relies on solubility differences between the gases.

	Size		Condensability	
	Critical Volume (cm ³ /mol)	Kinetic Diameter (nm)	b.p. (K)	Critical Temp (K)
Н2	65.1	0.289	20.4	33.2
CO ₂	93.9	0.330	195	304.2

Table 1.1. Physical properties of H_2 and CO_2 .¹³

Reverse-selective membranes (Figure 1.3, right) allow selective passage of the larger of two gases. Instead of taking advantage of size differences, the separation mechanism in reverse-selective membranes relies on selective dissolution of a gas at the

membrane-feed interface prior to diffusion across the membrane, and desorption at the low-pressure permeate side (Figure 1.4). According to Fick's law of diffusion, with a linear concentration gradient the flux of gas A through a membrane with thickness l is:

$$J_{A} = -D_{A} \frac{C_{m,2,A} - C_{m,1,A}}{l}$$
(2)

where $C_{m,1,A}$ and $C_{m,2,A}$ are the concentrations of gas A in the membrane at the feed side surface and permeate side surface, respectively. We define the solubility, S_A , of gas A in the membrane, as shown in equation (3)

$$C_{m,1,A} = S_A p_{A,1}$$

$$C_{m,2,A} = S_A p_{A,2}$$
⁽³⁾

where $p_{A,1}$ and $p_{A,2}$ are partial pressures of gas A at the feed side and permeate side of the membrane, respectively. Under most circumstances, the feed side has a higher pressure than the permeate side, and Δp_A as defined in equation (4) is positive.

$$p_{A,1} - p_{A,2} = \Delta p_A \tag{4}$$

Substitution of (3) and (4) into (2) gives (5).

$$J_A = D_A S_A \frac{\Delta p_A}{l} \tag{5}$$



Figure 1.4 Illustration of the solution-diffusion model for gas transport across a membrane. The dashed line represents the concentration profile of a gas transporting through the membrane. $C_{m,1,A}$ and $C_{m,2,A}$ are the concentrations of a gas in the membrane at the feed side surface and permeate side surface, respectively.

Defining the permeability, P_A , of a membrane for gas A using equation (6),

$$P_A = D_A S_A \tag{6}$$

we finally get equation (7), which is the usual expression for flux through a membrane in the solution-diffusion model.

$$J_A = D_A S_A \frac{\Delta p_A}{l} \tag{7}$$

For a polymer membrane that separates two gases (**A** and **B**), the ideal permeability selectivity, α_{AB} , in equation (8) frequently characterizes the separation.

$$\alpha_{AB} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B}$$
(8)

Component A is the more permeable species in the above equation, and D_A/D_B is the diffusivity selectivity whereas S_A/S_B is the solubility selectivity between the two components. Because permeability depends on the product of solubility and diffusivity, gas **A** may be more permeable than gas **B** in a particular polymer film because: (i) **A** is more soluble in this polymer than **B**, (ii) **A** has a larger diffusion coefficient than **B**, or (iii) both. Thus, gas separation membranes typically separate gases based on differences in gas molecule diffusivity in a polymer (so-called strongly size-sieving or high diffusivity-selective materials) or on differences in gas solubility in polymers (so-called solubility-selective or weakly size-sieving materials).⁵

In reverse-selective membranes, larger gases selectively permeate through the membrane.¹⁴ Although diffusivity decreases with molecule size, equation (8) shows that

reverse selectivity is possible by taking advantage of solubility selectivity. Generally, penetrant solubility increases with increasing condensability (i.e. higher critical temperature or higher normal boiling point) and more favorable interactions with the polymer, whereas gas diffusivity increases with decreasing penetrant size, increasing polymer fractional free volume, increasing polymer chain flexibility, and decreasing polymer–penetrant interactions.¹⁵ CO₂ should have a higher solubility in most polymers and liquids compared to H₂ because of higher condensability, but H₂ has a higher diffusivity than CO₂ because of its smaller physical size.

Separation of H_2 from CO₂ with reverse-selective membranes affords purified H_2 at the high-pressure feed side of the membrane and would save significant energy by avoiding H_2 re-compression. Thus reverse-selective membranes may be more economical than size-sieving membranes for purifying H_2 . Additionally, Reverse-selective membranes could remove higher hydrocarbons from methane in the purification of natural gas, separate organic monomers from nitrogen in the production of polyolefins, and remove hydrocarbons from H_2 in refinery applications.¹⁴

1.5 Solubility of Gases in Polymers and PEO-based Materials as Reverse-selective Membranes.

In the solution-diffusion model, the CO_2 solubility in a polymer film directly affects the CO_2/H_2 selectivity. The Flory-Huggins model describes penetrant solubility in rubbery polymers¹⁶⁻²⁰ based on three assumptions for polymer-solution interactions: (i) the process of dissolving polymer in solvent has no volume change, i.e. the total solution volume equals the volume of polymer plus volume of solvent, (ii) the mixing process is athermal (i.e. ΔH_{mix} =0), and (iii) the solvent molecules and polymer segments, which have the same size as solvent molecules, are considered as a lattice after the formation of the solution.¹⁶ Figure 1.5 illustrates this lattice. Based on the three assumptions above, we can analyze statistically how many ways one can place the polymer into this lattice, and the total possibility that this lattice could be arranged without breaking polymer chain is defined as this lattice's thermodynamic probability Ω .



Figure 1.5. Illustration of the lattice positions of a polymer segment and solvent. Black dots shows polymer segments that have same size as solvent molecules (hollow dots).¹⁸
Based on the Boltzman Equation, (9), the entropy of mixing polymer and solvent, ΔS_m , is given by equation (10)

$$\Delta S = k \ln \Omega \tag{9}$$

$$\Delta S_m = -R\left(x_1 \ln \phi_1 + x_2 \ln \phi_2\right) \tag{10}$$

where *R* is the gas constant, x_i is the molar fraction of solvent or polymer, and ϕ_i is the corresponding volume fraction. Subscript 1 refers to the solvent and subscript 2 to the polymer. Based on assumption (ii) that the enthalpy of mixing is zero, the Gibbs free energy of this mixing process is:

$$\Delta G_m = -T\Delta S_m = RT\left(x_1 \ln \phi_1 + x_2 \ln \phi_2\right) \tag{11}$$

where *T* is temperature. Because ϕ_i is always less than one, ΔG_m is negative. Physically, this means that the mixing process is thermodynamically favorable when $\Delta H_m=0$. However, under most circumstances ΔH_m is not close to zero, and equation (12) describes the enthalpy of mixing.

$$\Delta H_m = N_1 x_2 \chi R T \tag{12}$$

In this equation, N_I is the number of solvent molecules in the system and χ is the Flory-Huggins interaction parameter. This parameter describes the relative energy change difference between mixing solvent molecules and the polymer-solvent molecules. Using equation (12), the Gibbs free energy can be written as equation (13), which is also called the *Flory-Huggins equation*.²¹

$$\Delta G_m = \Delta H_m - T\Delta S_m = RT \left(N_1 x_2 \chi + x_1 \ln \phi_1 + x_2 \ln \phi_2 \right)$$
(13)

In the system of gas penetrating through a polymer film, the Flory-Huggins interaction parameter χ depends on the penetrant and polymer solubility parameters, as shown in equation (14),²²

$$\chi = \beta + \frac{\overline{V}(\delta_1 - \delta_2)^2}{RT}$$
(14)

where β is a constant, \overline{V} (cm³/mol) is the partial molar volume of the gas penetrant in the polymer, δ_1 is the solubility parameter of the polymer, and δ_2 is the solubility parameter of penetrant gas. Based on this model, maximum values of gas solubility (minimum of G_m) occur when the solubility parameters of the gas and polymer are the same. Equation (15) describes the solubility parameters of liquids where

$$\delta \equiv \sqrt{\left(\Delta H_{vap} - RT\right)/V} \tag{15}$$

 ΔH_{vap} is the enthalpy of vaporization, and V is the molar volume of this liquid at 25 °C. Thus, the solubility parameter is the square root of the cohesive energy density. However, the determination of solubility parameters of polymers is much more complicated than determination of the solubility parameters of liquids because the polymers are not volatile. Thus accurate enthalpy of vaporization data is hard to obtain. Freeman and co-workers summarized the experimental data for CO_2 solubility in various solvents. The maximum solubility occurred when the solvent solubility parameter is close to that of CO_2 , around 22 MPa^{0.5}.¹⁵ This suggests that the theoretical approach by Flory and Huggins is applicable in studying the system of gas molecules dissolving in liquids.

Polymers containing ether oxygens exhibit high CO₂ solubility presumably due to the quadrupole-quadrupole interactions.¹⁵ The solubility parameter for poly(ethylene oxide) is 19.8 MPa^{0.5,22} Currently, polymer films containing poly(ethylene glycol) (PEG), chains show great potential for removing CO₂ from H₂.^{5,6,15,23-27} However, most studies employed relatively thick (100-300 µm) membranes,²³ and the high thickness limits flux. Thus, the main subject of my research is to facilitate formation of thin, PEG-based polymer films on porous supports to increase flux in CO₂/H₂ separations.

1.6 Growth of Polymer Brushes by SI-ATRP

1.6.1 Overview of Strategies for Brush Growth

The most common ways to prepare composite membranes with a thin skin on a permeable support include solution casting,²⁸ solution coating,²⁹ interfacial polymerization,³⁰ plasma polymerization^{31,32} and UV-induced grafting.^{33,34} The

principle challenge in these methods is the difficulty of controlling film thickness.³⁵ Surface-initiated ATRP allows controlled growth of polymer brushes, and it should provide access to membranes with well-defined polymer skins.



Figure 1.6. "grafting from" (left) and "grafting to" (right) methods for the generation of polymer brushes from surface. "i" represents initiator molecules.

A polymer brush is an assembly of polymer chains linked by one end to an interface. Typically, there are two strategies of creating polymer brushes covalently linked to surfaces, namely "grafting to" and "grafting from" methods.³⁶ Figure 1.6 illustrates these two approaches. The "grafting from" method employs polymerization from immobilized initiators.³⁷ In controlled, surface-initiated polymerization, the brush thickness varies approximately linearly with time, and the polymer film has low polydispersity index (PDI= M_w/M_n). At the same time, when initiation occurs only at the surface there is minimal solution polymerization.

In contrast, the "grafting to" method employs solution polymerization to form polymer chains prior to covalent linking of these chains to a surface. One drawback of this strategy is that steric hindrance prevents incoming polymer chains from diffusing through the film and leads to a low polymer density on the surface.³⁸ Nevertheless the "grafting to" method affords more control of polymer chain length and PDI. Thus allows better characterization of these chains.

Surface-initiated polymerization can occur on a wide range of substrates including Si, gold-coated surfaces, nanoparticles, and carbon nanotubes.³⁹ One of the most common methods of initiator attachment involves adsorption of thiol-terminated initiators on gold.³⁸ Over the past two decades, numerous reports examined surface-initiated polymerization mechanisms including cationic,^{40,41} Anionic,⁴²⁻⁴⁴ ring opening,⁴⁵ ring opening methathesis,⁴⁶⁻⁴⁸ radical,⁴⁹⁻⁵¹ and ATRP.^{37,52-56} This dissertation primarily employs ATRP, which I discuss in more detail below.

1.6.2 ATRP Mechanism

ATRP is perhaps the most versatile process for creating well-defined polymers. ⁵⁷ As Figure 1.8 shows, a transition metal complex extracts a terminal halogen atom from the initiator or polymer chain, R-X, to create a radical. The equilibrium for this step favors radical deactivation because the rate constant for recovering a halogen atom, k_{deact} , is much greater than the constant for atom extraction, k_{act} . Thus the concentration of radicals is much smaller than the concentration of dormant species. Because termination by radical recombination or disproportionation is proportional to the square of radical

concentration, low termination rates in ATRP lead to high molecular weight polymers, as well as a low PDI.



Figure 1.7. The mechanism of ATRP.

Copper complexes are the most common and versatile ATRP catalysts. When using such catalysts, equation (16) describes the ATRP rate for the ideal case of no polymerization termination and 100% initiation efficiency.

$$R_{\text{ATRP}} = k_p \, \frac{k_{act}}{k_{deact}} [\text{M}] [\text{I}]_0 \, \frac{[\text{Cu}^{\text{I}}]}{[\text{XCu}^{\text{II}}]} \tag{16}$$

The rate of ATRP is proportional to the monomer concentration in the solution [M], as well as the ratio of activation and deactivation rate constants (k_{act}/k_{deact}). Importantly, (k_{act}/k_{deact}) is a function of the Cu-binding ligand, the reaction solvent, and temperature. Increasing the concentration of the Cu^I complex will increase the polymerization rate, wherease incrasing the concentration of the Cu^{II} complex should slow down ATRP. Overall the catalyst system and monomer reactivity define the control and rate of ATRP.

1.6.3 ATRP Catalysts

Effective ATRP catalysts include a transition metal ion with accessible oxidation states separated by one electron to facilitate halogen removal from the ATRP initiator. Also, the coordination sphere around the metal should expand upon oxidation to selectively accommodate a halogen.⁵⁸ A wide range of transition metals including Cu, ^{57,59-62} Pd, ⁶³ Ni, ⁶⁴⁻⁶⁷ Rh, ⁶⁸ Fe, ^{69,70} Ru, ⁷¹⁻⁷³ Re, ⁷⁴ Co⁷⁵ and Mo⁷⁶ have served as ATRP catalysts. Nevertheless, Cu complexes are perhaps the most economical and versatile catalysts for polymerization of different types of monomers. This versatility stems in large part from the large number of ligands that bind Cu^{II} and Cu^{II}.

1.6.4 Ligands for ATRP Catalysts

Ligands solubilize and stabilize the transition metal ions to form an ATRP catalyst system. Selection of ligands depends mostly on the metal ion. For example, Cu^I complexes tend to form square planar or tetrahedral geometries, so the most common ligands for Cu catalysts provide tetradentate or bidentate coordination. Moreover, the ligand should allow fast initiation, minimum side reactions, and an equilibrium that favors the lower oxidation state, such as Cu^I. As mentioned above, Cu^I / Cu^{II} is the most common ATRP catalyst system, and nitrogen-containing ligands bind strongly to Cu and stabilize the Cu^I complex. Sulfur, oxygen, or phosphorus ligands are less effective due to inappropriate electronic effects or unfavorable binding constants.⁵⁸ Scheme 1.1 shows some examples of ligands used for ATRP with Cu catalyst systems.

Scheme 1.1. Selected ligands for copper-mediated ATRP.^{58,35}



1.6.5 ATRP Initiators

The initiator has two main functions in ATRP. Firstly, the amount of initiator defines the maximum number of polymer chains if chain transfer is negligible. Secondly, the structure of the initiator plays a role in ATRP mechanism. The leaving halogen group should have affinity to the carbon of the polymerizing chain to promote deactivation. Additionally, the R-X bond should always give homolytic rather than heterolytic cleavage in the presence of catalyst. Last but not least, the initiation step should be relatively faster than the propagation to insure low PDI. When selecting an initiator in ATRP, several issues are worth consideration. (a) In the order of the stabilizing ability, CN > COR > COOR > Ph > Cl > Me are the common groups that stabilize radicals when halogen is removed.⁷⁷ (b) The C-halogen bond strength decreases in the order of R-Cl > R-Br > R-I. Thus R-I initiators offer the most rapid initiation rates, but iodine-containing compounds are sensitive to light and temperature.⁷⁸ Bromine and chlorine-terminated molecules are the typical initiators. In most studies, the halogen in the initiator is also the anion that couples with the metal cation when preparing the catalyst system. However, some studies indicate that halogen exchange can offer better control over the polymerization.^{79,80} For polymer growth from surfaces, ATRP initiators need a functional group for anchoring to a surface in addition to a group that initiates the polymerization. As the anchoring group differs for various substrates, the section introduces specific initiators for polymerization from a surface.

Scheme 1.2. Common ATRP initiators.^{58,35}

Halogenated Alkanes and Benzylic Halides



Bromoesters



1.6.6 ATRP Monomers

A wide range of monomers can polymerize via ATRP. Scheme 1.3 provides some examples from styrenes, methacrylates, and acrylates. The common features of ATRP monomers is that they contain functional groups that help stabilize the radical.⁵⁸ This

dissertation focuses on ATRP of PEGMEMA and poly(ethylene glycol diacrylate) (PEGDA) because the PEO side chains favor solubility selectivity for CO_2 over H_2 . For a given monomer, the rate of polymerization depends on the catalyst system, and the reaction media.⁸¹ The solubility of the ligand, the procedure of preparing the catalyst, the solvent, the solubility of the initiator, and the temperature all play a role in ATRP, mainly because each component impacts the equilibrium illustrated in Figure 1.7, and temperature increases the polymerization rate constant.

Scheme 1.3. Representative monomers amenable to ATRP.⁵⁸



Scheme 1.3 (cont'd)



PEGDA PEGMA PEGMEMA MES

1.6.7 Substrates for SI-ATRP

Huang and Wirth initially reported SI-ATRP when they successfully grafted poly(acrylamide) (PAM) brushes from benzyl chloride-derivatized silica particles.⁸² Shortly after this discovery, a number of studies described SI-ATRP on various substrates. Growth of polymer brushes from a surface requires initiator immobilization, and the discussion below describes initiator anchoring and polymerization from different substrates.

1.6.7.1 SI-ATRP from Silicon Oxide

Silicon oxide surface is the most extensively studied substrate for SI-ATRP. Physically, such substrates include lightly oxidized silicon wafers, glass, quartz sides, nanoparticles, capillaries, membranes or silicon oxide coatings on other substrates. Formation of organosilane monolayers or multilayers is the most common method for anchoring initiators on SiO₂. After treatment with oxygen plasma or piranha solution (a mixture of sulfuric acid and H_2O_2), the SiO₂ surface contains a high density of silanol groups (Si-OH) that can react with organosilane molecules such as R'SiR_xX₃-X (X=Cl, OR, or NMe₂) to form a Si-O-Si bond.⁸³ The silanes may also react with H₂O and neigboring organosilane molecules to form organosilane clusters instead of monolayers. Practically, organosilane molecules with one hydrolyzable group tend to form better defined monolayers than those with more than one hydrolyzable group. Table 1.2 illustrates common initiator examples for ATRP from silicon oxide.

Initiator	Substrate	Reference
CI CI-Si- CI'-Si-CI O	Oxidized silicon wafer; glass slide; SiO ₂ deposited Au wafer	84-86
$CI \\ CI-Si-(CH_2)_{11}-O \\ CI' Br$	Oxidized silicon wafer; glass slide; silicon ATR crystal; quartz; fused silica capillary column; porous silica; silica nanoparticles	56, 87-101
$\begin{array}{c} CI \\ CI-Si-(CH_2)_6 - O \\ CI \\ \end{array} \\ Br \\ Br \\ \end{array}$	Oxidized silicon wafer, silica nanoparticles	37, 102, 103

Table 1.2. Initiators employed for growing polymer brushes from silicon oxide.

Table 1.2 (cont'd)

$ \begin{array}{c} Cl \\ Cl-Si-(CH_2)_3-O \\ Cl' \\ Br \end{array} $	Oxidized silicon wafer	104, 105
$ \begin{array}{c} CI \\ CI-Si-(CH_2)_3-O \\ CI \\ \end{array} Br $	Silica nanoparticles	106
	Silica nanoparticles	107, 108
EtO EtO-Si EtO	Porous silica microparticles	109
EtO EtO-Si-(CH ₂) ₆ -O EtO	Oxidized silicon wafer; quartz; silica nanoparticles	110-114
EtO EtO-Si-(CH ₂) ₁₁ -0 EtO Br	Si/SiO ₂ core-shell nanowire	124
$ \begin{array}{c} EtO \\ EtO - Si - (CH_2)_3 - N \\ EtO \\ H \\ H \\ $	Si/SiO ₂ core-shell nanowires	115
MeO MeO-Si MeO MeO	Oxidized silicon wafer	52, 116-118

Table 1.2 (cont'd)

MeQ MeO-Si-(CH ₂) ₃ -O MeO Br	Oxidized silicon wafer; glass side; silica nanoparticles; Si/SiO ₂ core-shell nanowires	75, 115, 120-126, 119
EtO-Si-(CH ₂) ₃ -O Br	Oxidized silicon wafer; silica nanoparticles; CdS/SiO ₂ core-shell nanoparticles	127-133
EtO-Si-CI	Silica nanoparticles	134
$CI \rightarrow Si - (CH_2)_3 - O \rightarrow Br$	Oxidized silicon wafer	135
$CI - Si - (CH_2)_{11} - O $ Br	Oxidized silicon wafer	136-138
CI-Si-(CH ₂) ₆ -O Br	Silica nanoparticles; porous silica microparticles	139-142

Table 1.2 (cont'd)

$CI \rightarrow Si - (CH_2)_3 - O \qquad Br$	Oxidized silicon wafer; silica nanoparticles; silsesquioxane microgel nanoparticles; silicone nanofilaments	143-153
$CI \rightarrow Si - (CH_2)_6 - O \rightarrow Br$	Porous silica microparticles	142
CI-Si	Silica nanoparticles	154
Cl-Si-(CH ₂) ₃ -O Br	Oxidized silicon wafer	155
	Silica nanoparticle	156

Table 1.2 (cont'd)



Table 1.2 (cont'd)



Organosilane-based ATRP initiators also offer an opportunity to control the polymer brush density and pattern polymer brushes. Bao et al¹³⁶ studied the effect of initiator density on polymer brush thickness by simultaneously depositing a monochlorosilane initiator and a similar monochlorosilane molecule with no halogen. Jonas successfully printed polymer brush patterns via UV-light removal of initiator areas followed by ATRP.¹⁴⁴

Armes and coworkers developed macroinitiators for ATRP from silicon.¹⁵⁷⁻¹⁵⁹ Positively charged polyelectrolytes attach to the negatively charged silicon dioxide surface through electrostatic forces, and macroinitiator adsorption can occur from water. The initiators appear at the bottom of Table 1.2.

1.6.7.2 SI-ATRP from Gold

Similar to the monolayers on cleaned silicon oxide, the most common method of attaching initiators on Au is adsorption of functionalized thiols or disulfides. $BrC(CH_3)_2COO-(CH_2)_{11}SH^{81}$ and $(BrC(CH_3)_2COO(CH_2)_{11}S)_2^{55}$ are two extensively used initiators in ATRP from gold. Physically, typical gold surfaces are silicon wafers coated with gold or gold nanoparticles.

For the same monomer and catalyst system, the surface and method of initiator attachment may affect the polymer brush thickness. Saha and coworkers studied the growth of poly(methyl methacrylate) (PMMA) from gold surfaces and gold surfaces coated with a cross-linked silane. Their study implicates thiols in terminating growing polymer brushes to give polymer chains with low molecular weights and low film thicknesses.¹⁶⁰

1.6.7.3 SI-ATRP from Polymeric Substrates

ATRP from polymeric substrates is not as common as from SiO_2 or Au because some polymers do not tolerate organic solvents or high temperature. However, studies of ATRP from polymers are increasing and there are successful examples. Polymeric substrates fall roughly into two categories: functional and inert surfaces. Functional polymeric surfaces have exposed groups that are either nucleophilic or electrophilic, while inert polymeric surfaces are unreactive.

Cellulose offers pendant -OH groups, and Carlmark and Malmstrom immobilized initiators by allowing these group to react with 2-bromoisobutyryl bromide in the presence of triethylamine. They successfully polymerized poly(methyl acrylate) (PMA)*block*-poly(2-hydroxyethyl methacrylate) (poly(HEMA)) copolymers from filter paper.¹⁶¹ Later, Lindqvist and Malmstrom successfully polymerized polystyrene from filter paper and regenerated cellulose. Based on FTIR spectra, the regenerated cellulose surface offers lower polymer grafting density than natural cellulose.¹⁶² Singh and Husson performed ATRP of poly(poly(ethylene glycol) methacrylate) (PEGMA) and poly(acrylic acid) (PAA) on regenerated cellulose membranes using similar initiator attachment.^{163,164} Poly(ethylene terephthalate) (PET) membranes also offer pendant and Demoustier-Champagne and co-workers OH groups. polymerized Nisopropylacrylamide (NIPAM) from the walls of track-etched, initiator-modified PET membranes.¹⁶⁵ Polyvinylidene fluoride (PVDF) films expose C-F bond that could initiate ATRP, and Chen successfully polymerized poly[poly(ethylene glycol methyl ether methacrylate)] (PPEGMEMA) and PPEGMEMA-b-PS block copolymer brushes from PVDF.¹⁶⁶

Inert polymeric substrates that require activation through oxidization likely produces some -OH or -COOH groups on the surface. Subsequent reaction with 2-

bromoisobutyryl bromide in the presence of a base provides immobilized initiators for ATRP. This strategy successfully anchored ATRP initiating groups onto ozone-treated polypropylene hollow fiber membranes.¹⁶⁷

Some inert polymeric substrates do not survive exposure to organic solvents, and extensive oxidation may alter their pore size. Jain reported layer by layer deposition of macroinitiators on polyethersulfone (PES) films. This initiator attachment technique and polymerization of PHEMA both occur in aqueous conditions.¹⁶⁸ The method offers an opportunity to attach ATRP initiators on other inert polymeric substrates.

1.7 Outline of This Dissertation.

This work focuses on development of polymeric films for CO_2/H_2 separation. Chapter 2 describes collaborative work on the synthesis and characterization of poly(PEGMEMA-1100-*co*-PEGMEMA-475) copolymer films. The presence of both long and short side PEO chains in the copolymer successfully prevented crystallization of the long chains (23-24 PEO units) from PEGMEMA-1100. FTIR studies indicated that the molar ratio of both monomers in the polymer film is comparable to the molar ratio of the monomers in the polymerization solution. The CO_2/H_2 selectivity of the copolymer film (~13) is comparable to an amorphous poly(PEGMEMA-1100) film, but the copolymer film shows no sign of crystallization in over a year. This selectivity is among the highest values for reverse-selective membranes. Chapter 3 discusses ATRP of PEGMEMA-1100, PEGMEMA-475, and PEGDA from regenerated cellulose. FTIR spectra is used to study the extent of cross-linking by PEGDA, and the gas separation tests suggest that cross-linking due to a 25% mole fraction of PEGDA causes a slight decline in CO₂/H₂ selectivities ranging from 6.5 to 19.9, but the CO₂ permeability decreased to only 5-15 Barrer.

Chapter 4 focuses on nanocomposite membrane coatings prepared by SI-ATRP of PEGMEMA and PEGDA in the presence of initiator-modified SiO₂ nanoparticles. Electron microscopy provides evidence for nanoparticle incorporation in the membrane coating. Unfortunately, inclusion of nanoparticles did not significantly increase selectivity. The rubbery nature of the polymer many limit the formation of free volume around the nanoparticles and minimize their effect on permeation.

Chapter 5 investigates why aqueous SI-ATRP of PEGMEMA results in films with extraordinarily high thicknesses. SI-ATRP yields $\sim 100 \ \mu m$ thick films in only 30 min. Preliminary studies suggest that the most likely hypothesis is that high concentrations of PEGMEMA-1100 change the polarity of the solvent and the activity of the catalyst.

Finally, Chapter 6 discusses future work and what impact these studies may have on forming coatings for membranes or other potential applications. REFERENCES

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Chapter 2 Incorporation of Long and Short PEO side chains in polymer brushes to prevent crystallization and provide CO_2/H_2 selectivity

This work was performed in collaboration with Dr. Sebastian T. Grajales and recently published in Chemistry of Materials.¹ Dr. Grajales and I are equal coauthors of this work.

2.1 Introduction

Selective removal of CO₂ from gas streams is becoming increasingly important for applications such as CO₂ sequestration,² fuel cell operation,³ and H₂ synthesis.⁴ In the case of H₂ production, steam reforming of methane produces 9 million tons of H₂ per year in the U.S. alone.⁵ However, the product stream from steam reforming theoretically contains 20 mole% CO₂, so purification of the H₂ is an important and expensive part of the production process.⁶ A number of studies examined membrane-based gas separation as a possible alternative, or as a pre-purification step, to the pressure swing adsorption process currently used in H₂ purification.^{7,8} The viability of membrane processes for purifying H₂ streams depends critically on achieving both high flux and high selectivity, and a recent review summarizes the types of membranes employed for H₂ purification.⁹ Processes such as H_2 recycle in ammonia synthesis have employed H_2 -selective membranes for several decades.¹⁰ In the case of CO₂ removal from H_2 streams, however, CO₂-selective membranes are attractive because purified H_2 remains on the high pressure side of the membrane and does not need to be recompressed.

The solution diffusion model for transport through membranes (equation 2.1) illustrates how the flux, J, of a gas through a membrane depends on the pressure drop across the membrane, Δp , the membrane thickness, l, and the gas permeability, P, which is the product of the solubility coefficient, S, and diffusivity, D, for the gas of interest.¹¹ Equation 2.2 shows that the ideal selectivity of gas A over gas B, $\alpha_{A/B}$, depends on the solubility coefficients and diffusivities of the two gases. Because of its small size, H₂ has a greater diffusivity than CO₂, so CO₂/H₂ selectivity requires high solubility selectivity for CO₂ over H₂. Fortunately, CO₂ is the more condensable of the two gases, and solubility selectivity typically favors CO₂ transport.¹¹

$$J = \frac{P\Delta p}{l} \quad P = SD \tag{2.1}$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A \times D_A}{S_B \times D_B}$$
(2.2)

Membrane materials employed for selective passage of CO_2 over H_2 should thus have a higher affinity for CO_2 than H_2 along with a relatively high free volume that

minimizes the difference between CO2 and H2 diffusivities. One method of increasing $\rm CO_2$ solubility is the incorporation of protonated amines within the membrane.^{12, 13} In this case, facilitated transport can lead to CO2/H2 selectivities over 100, but carrier saturation limits the application of these systems to low feed pressures (less than 0.05 bar).¹⁴⁻¹⁶ At room temperature, amorphous poly(ethylene glycol) (PEG)-containing membranes exhibit CO₂/H₂ selectivities ranging from 5 to 12, presumably because of quadrupole-dipole interactions between CO_2 and the ether functional groups of PEG.¹⁷⁻ 20 Unfortunately, however, crystallization of PEG chains decreases both the permeability and selectivity of such membranes. To overcome this challenge, several studies employed cross-linked, solution-cast, PEG-containing membranes to maintain a high free volume, decrease crystallinity, and increase chemical stability.^{8, 21-23} In the best case. the cross-linked membranes show CO₂ permeabilities of up to 600 Barrers [1 Barrer = 10^{-10} cm³ (STP) •cm / (cm²•s•cmHg) = 7.5×10^{-18} m³ (STP) •m/(m²•s•Pa)] and CO_2/H_2 selectivities of approximately 12 at room temperature.²⁴

Nevertheless, the high thickness (>100 μ m) of solution-cast membranes yields a permeance (permeance is defined as flux/ Δ p) too low for practical separations. This work examines the use of atom transfer radical polymerization (ATRP) from porous substrates to create composite membranes with thin (50-500 nm) skins of PEGcontaining films that allow selective removal of CO₂ from H₂ streams. ATRP is attractive for synthesizing these membrane skins because it often affords control over film thickness along with polymer chains with relatively low polydispersity.^{25,26} Scheme 2.1 shows two permutations of the ATRP process for forming membranes on porous alumina substrates, and similar processes on porous polymer supports are also possible. Initiator attachment occurs either via adsorption of a disulfide initiator to goldcoated alumina to generate **A** (scheme 2.1), or attachment of a silane directly to the alumina to generate **B**. Subsequent atom transfer radical polymerization with a $Cu^+/1,1,4,7,10,10$ -hexamethyltriethylenetetramine (HMTETA) catalyst yields the membrane skin. The permeance of the modified alumina membranes is several orders of magnitude greater than that of solution-cast membranes.⁹

Additionally, this work examines the use of copolymers prepared from poly(ethylene glycol methyl ether methacrylate) (PEGMEMA) monomers with different PEG chain lengths (Scheme 2.2) to inhibit the crystallization of the PEG side chains. The combination of monomers with 8-9 and 23-24 ethylene oxide repeat units yields films that do not crystallize over many months and membrane skins with a room temperature CO_2/H_2 selectivity of around 13.

Scheme 2.1. Methods for growth of a poly(PEGMEMA) membrane from porous alumina. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.



Scheme 2.2. Copolymerization of PEGMEMA-475 and PEGMEMA-1100 to provide a membrane skin.



2.2 Experimental

2.2.1 Chemicals and Materials

PEGMEMA monomers with $M_n = 300$ Da (PEGMEMA-300), $M_n = 475$ Da (PEGMEMA-475), and $M_n = 1,100$ Da (PEGMEMA-1100) were obtained from Aldrich. These monomers contain both 100 ppm 4-methoxyphenol and 300 ppm 2,6-di-tert-butyl-4-methylphenol as inhibitors. Proton NMR spectra (Figure 2.1) show that the average numbers of ethylene oxide units in PEGMEMA-300, PEGMEMA-475, and PEGMEMA-1100 are 4.4, 8.8, and 23.1, respectively. In some cases, the inhibitors were removed from the monomers using flash column chromatography with basic alumina, but this did not have a significant effect on polymerizations, so in most reactions the monomers were used received. CuCl₂, CuCl, CuBr, CuBr₂, and 1,1,4,7,10,10as hexamethyltriethylenetetramine (HMTETA) were purchased from Aldrich, and deionized water was obtained from Millipore system (Milli-Q, 18.2 MΩ•cm). THF was distilled over sodium metal with benzophenone, and DMF was distilled over 4 Å molecular sieves. Silicon (100) wafers were obtained from NOVA Electronic Materials and sputter-coated with 20 nm of chromium followed by 200 nm of gold by LGA Thin Films (Santa Clara, CA). The porous alumina substrates were Anodisc membrane filters (25 mm disks with 0.02 μ m surface pores) purchased from Whatman, and the disulfide, [Br-C(CH₃)₂-COO(CH₂)₁₁S]₂, and silane, SiCl(CH₃)₂(CH₂)₁₁OCOC(CH₃)₂Br, initiators were synthesized as described previously.²⁷⁻³⁰



Figure 2.1. Proton NMR spectra of (A) PEGMEMA-300, (B) PEGMEMA-475, and (C) PEGMEMA-1100. The integrals of the peaks with a chemical shift between 3.4 ppm and 4.5 ppm (arising from the four hydrogen atoms on the ethylene oxide repeat units) were summed and divided by 4 to give the average number of EO units per monomer. (The intensity of the alkene protons was set to 1 for normalization.) Peak areas in these spectra were averaged with areas from two additional replicate spectra to generate values for the number of average ethylene oxide units per molecule.

Figure 2.1 (cont'd)



2.2.2 Polymerization

Porous alumina substrates were initially rinsed with ethanol, dried with N₂, cleaned with UV/O₃ (Boekel UV-Clean Model 135500) for 15 min, and sputter coated with 5 nm of gold in a Pelco SC-7 sputter coater. The thickness of the gold coating was monitored with a Pelco FTM-2 quartz crystal microbalance. Attachment of a monolayer of the disulfide initiator to gold-coated Si wafers or porous alumina occurred during an overnight immersion of the substrate in an ethanolic solution containing 1 mM disulfide initiator. The resulting sample was rinsed with 5 mL of ethanol and dried in a N₂ stream. Attachment of the silane initiator occurred during overnight immersion of an uncoated, UV/ozone-cleaned porous alumina substrate in a solution containing 8 mM silane in THF. The resulting sample was rinsed with 5 mL THF and dried in a N₂ stream. The two different types of initiator-modified membranes were handled identically in the ensuing polymerization steps.

Following a previous procedure, the catalyst stock solution was prepared by first dissolving 0.06 g (0.6 mmol) of CuCl and 0.04 g (0.2 mmol) of CuBr₂ in 30.0 mL of distilled, degassed DMF.^{31, 32} This solution was further degassed via three freeze, pump, thaw cycles. In a N₂-filled glove bag, 490 μ L (1.8 mmol) of degassed 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) ligand was added to this solution, which subsequently turned a dark green color during several hours of stirring. During this initial stirring, a small amount of precipitation occurred, but the resulting catalytic

activity of the solution remained constant for at least several weeks. The nominal mole ratio of $Cu^+:Cu^{2+}:HMTETA$ was 3:1:9.

The monomer solution, which contained 0.75 M PEGMEMA in water, was initially degassed via three freeze, pump, thaw cycles. (When different molecular weight monomers were used, the total monomer concentration was maintained at 0.75 M). The polymerization solution was prepared in a N₂-filled glove bag by combining degassed monomer and catalyst solutions in a 9:1 volume ratio to produce a blue-green solution containing 0.67 M monomer, 2.0 mM CuCl, 0.60 mM CuBr₂, and 6.0 mM HMTETA. The initiator-modified membranes or wafers were immersed in the polymerization solution for designated periods of time, and the resulting polymer films were rinsed with 5 mL water and soaked in water for at least two hours before rinsing with 5 mL of ethanol and drying under a N₂ stream.

2.2.3 Characterization methods

Reflectance FT-IR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer with a Pike grazing angle (80°) attachment. A UV/ozone-cleaned, gold-coated Si wafer was used to obtain the background spectrum. Thicknesses of films formed on gold-coated silicon were determined with a rotating analyzer ellipsometer (J.A. Woollam model M44) at an incident angle of 75°. A two-term Cauchy equation was employed to simultaneously fit film thickness and the Cauchy constants needed to model the wavelength-dependence of the film refractive index. Thicknesses were determined at a minimum of three locations on each substrate. Scanning electron microscopy was

performed with the JEOL semi-in-lens cold cathode field-emission scanning electron microscope, model JSM-7500F, operating with a r-filter in signal maximum mode. Samples were sputter coated with 5 nm of gold prior to imaging.

2.2.4 Gas Permeation

Single-gas permeation experiments were performed by exposing the membrane to individual gases at varying pressures in an Advantec/MFS UHP-25 cell with a pressure relief valve. The gas flow rate through the membrane was measured with either an Optiflow 420 electronic soap bubble meter or a manual soap bubble meter. Mixed-gas experiments were performed by loading the membrane into a custom membrane holder (all connections utilized Swagelok fittings and were tested to ensure that they maintained pressure over a time-scale longer than the experiment) that allowed cross-flow of the feed gas as well as a sweep gas on the permeant side. A backpressure valve was employed to sustain the feed gas pressure, and the feed flow rate was high enough to maintain constant composition at the face of the membrane (the stage-cut, or ratio of permeant flow to feed flow, was <1%). The N₂ sweep gas/permeant stream was connected to an automated sixport injector valve on a Hewlett-Packard 6890 GC equipped with a thermal conductivity detector (TCD) and an Agilent GS-CarbonPLOT capillary column (i.d. = 0.53 mm, length = 30 m, 3 μ m coating). The mixed gas permeances as well as pure gas permeances were calculated from GC results using equation 2.3,

Permeance =
$$\frac{\chi_{\rm B} \times \Phi_{\rm N_2}}{\chi_{\rm N_2} \times {\rm A} \times \Delta p}$$
 (2.3)

where χ_B is the mole fraction of a particular permeate gas, B, in the gas mixture injected into the GC column, Φ_{N2} is the sweep gas flow rate, χ_{N2} is the mole fraction of N₂ in the gas injected into the GC column, Δp is the transmembrane partial pressure difference for the gas of interest, and A is the membrane area. (Φ_{N2}/χ_{N2} is the sum of the permeate and sweep gas flow rate, and χ_{N2} was determined by subtracting the mole fractions of the permeates from unity. This assumes that the amount of N₂ passing from permeate to feed was negligible.) The sweep gas flow rate was programmed into a mass flow controller, pressure and area were measured, and the mole fractions were determined from the integrated GC spectra and a calibration curve.

2.3 Results and Discussion

2.3.1 Polymerization Rates as a Function of Monomer Composition

The first step in developing surface-initiated ATRP for creating membrane skins, especially for forming copolymer skins, is examination of polymerization from model flat substrates such as gold-coated Si wafers.³³ Such substrates facilitate ellipsometric and spectroscopic characterization of polymer growth and composition. We are particularly interested in the relative growth rates of PEGMEMA-475 and PEGMEMA-1100 because the short side chains of PEGMEMA-475 do not crystallize, whereas the long chains of PEGMEMA-1100 should promote CO_2/H_2 selectivity.³⁴ As Figure 2.2 shows, polymerization of PEGMEMA-475 by itself gives the most rapid initial growth in film

thickness, but the growth rate decreases dramatically after 15 min of polymerization. In contrast, polymerization of PEGMEMA-1100 is slower, but the growth rate is essentially constant for 120 min. Interestingly, polymerizations of mixtures in which PEGMEMA-475 constitutes either 25 or 75 mole% of the total monomer show relatively high and steady growth rates.



Figure 2.2. Evolution of film thickness with polymerization time for pure and mixed monomer solutions. For copolymers, the legend shows the solution PEGMEMA-475 mole percentage with respect to the total monomer (PEGMEMA-475 plus PEGMEMA-

1100). The overall monomer concentration was 0.67 M, and the catalyst system was 2.0 mM CuCl, 0.60 mM CuBr₂, and 6.0 mM HMTETA. The error bars, which in many cases are obscured by the symbols, represent one standard deviation.

Decreases in growth rates with polymerization time, particularly for poly(PEGMEMA-475), suggest that the HMTETA-Cu^{+/2+} catalyst system gives a high concentration of radicals that results in significant termination by radical-radical coupling. The large side chains of PEGMEMA-1100 may provide steric hindrance to both polymerization and termination. In solution polymerization studies, Haddleton et al. attributed the high ATRP activity of PEGMEMA-475 relative to PEGMEMA-1100 to ethylene oxide coordination with the Cu catalyst in close proximity to the double bond.³⁵ However, steric issues seem equally likely to affect polymerization.³⁴ In the case of homopolymerization, the PEGMEMA-1100 solutions are also more viscous and contain less water than PEGMEMA-475 solutions, and both of these factors should also lead to lower polymerization rates for the PEGMEMA-1100. Mixtures of PEGMEMA-475 and PEGMEMA-1100 have intermediate polymerization rates, and the side chains are apparently still sufficiently large to reduce termination relative to pure PEGMEMA-475. For PEGMEMA-475, PEGMEMA-1100, and their mixtures, film growth is rapid compared to polymerization of most other monomers and non-aqueous polymerizations.³⁶⁻³⁸ A number of studies demonstrated that the presence of water frequently enhances the rate of ATRP.^{39, 40}

2.3.2 Determining the Composition of Copolymer Films

The molar ratio of PEGMEMA-475 to PEGMEMA-1100 in a film may not correspond to the monomer ratio in the polymerization solution. In particular, the smaller monomer may be more reactive because of faster diffusion to the surface or less steric hindrance to polymerization. In an attempt to determine the relative amounts of each monomer incorporated in poly(PEGMEMA-475-*co*-PEGMEMA-1100) films, we compared the intensities of carbonyl (1731 cm⁻¹) and C-O-C (1149 cm⁻¹) stretches in both homopolymer and copolymer films. The reflectance FTIR spectra in Figure 2.3 show that for amorphous homopolymers, the intensity of the C-O-C stretch relative to the C=O stretch is much higher for poly(PEGMEMA-1100) than poly(PEGEMEMA-475), as we expected because of the longer PEG chain in the higher molecular weight monomer.



Figure 2.3. FTIR spectra of 152 nm-thick poly(PEGMEMA-475) (black line) and 118 nm-thick poly(PEGMEMA-1100) (dashed red line) films on gold-coated substrates. Spectra were taken immediately after polymerization before the PEG side chains in poly(PEGMEMA-1100) crystallized. The spectra are offset for clarity.

We initially planned to estimate the mole ratios of monomers incorporated into a copolymer film using equation 2.4, where χ_{475} is the mole fraction of PEGMEMA-475 in a copolymer film and R_{co}, R₁₁₀₀, and R₄₇₅ are the ratios of the C-O-C peak height (1149 cm⁻¹) to the C=O peak height (1731 cm⁻¹) for copolymer, poly(PEGMEMA-1100), and poly(PEGMEMA-475) films, respectively.

$$R_{co} = x_{475} R_{475} + (1 - x_{475}) R_{1100}$$
(2.4)

However, Figure 2.4 suggests that in some cases peak height and peak area ratios for the C-O-C to C=O absorbance increase with thickness for homopolymer and copolymer



Figure 2.4. Ratios of C-O-C to C=O peak heights (A) and peak areas (B) in reflectance FTIR spectra of poly(PEGMEMA-1100), poly(PEGMEMA-475), poly(PEGMEMA-300) and poly(PEGMEMA-475-*co*-PEGMEMA-1100) films on gold-coated substrates. The ratios are plotted as a function of the ellipsometric thickness of the film, and for the copolymers, the legend shows the mole fraction of PEGMEMA-475 (relative to total monomer) in the polymerization solution. All polymerizations employed a total monomer concentration of 0.67 M, and the experimental section describes the polymerization conditions.

films. This increasing ratio of C-O-C to C=O absorbance likely occurs because reflectance measurements plot $\log(R_0/R)$, where R_0 and R are the reflectivities of bare and film-covered substrates, respectively. These reflectivities are complicated functions of the film thickness and the complex refractive indices, $\tilde{n} = n - ik$, of the substrate and the film. To account for these complications in reflectance FTIR spectroscopy, it is necessary to use Fresnel calculations to determine the absorption coefficient, *k*, for different films at the wavelengths of interest. We plot reflectance IR spectra as $log(R_0/R)$, where R_0 is the fraction of the incident light intensity reflected by a bare gold substrate (Figure 2.5A) and R is the fraction of incident light intensity reflected by a film-coated substrate (Figure 2.5B). The value of R_0 is simply the Fresnel reflection coefficient, r_{13} , multiplied by its complex conjugate (equation 2.5), where the Fresnel coefficient is given by equation 2.6. In equation 2.6, \tilde{n}_3 is the complex refractive index of gold, *n-ik*, (assumed to be 3-30*i*), θ_1 is the angle of incidence (80°), n_1 is the refractive index of air (assumed to be 1.000), and $\tilde{\theta}_{au}$ is the complex angle of refraction in the gold film. The value of $\tilde{\theta}_{au}$ was calculated using Snell's law, equation 2.7. (Tilda superscripts indicate a complex number, and the IR beam was polarized with the electric field parallel to the substrate.)

$$R_o = \tilde{r}_{13}\tilde{r}_{13}^* \tag{2.5}$$

$$r_{13} = \frac{\tilde{n}_3 \cos \theta_1 - n_1 \cos \tilde{\theta}_{Au}}{\tilde{n}_3 \cos \theta_1 + n_1 \cos \tilde{\theta}_{Au}}$$
(2.6)

$$n_1 \sin \theta_1 = \tilde{n}_3 \sin \tilde{\theta}_{Au} \tag{2.7}$$



Figure 2.5. Schematic drawing of the reflection of light from (A) a bare gold surface and (B) a film-covered gold surface

Equation 2.8 allows calculation of the reflectance, R, of the film-covered substrate, where the * represents the complex conjugate. In this equation, \tilde{t}_{12} is the Fresnel reflection coefficient for the air-film interface (equation 2.9), \tilde{t}_{23} is the Fresnel reflection coefficient for the film-gold interface (equation 2.10), λ is the wavelength of the incident light in air, \tilde{n}_2 is the complex refractive index of the film, *l* is the film thickness, and cos $\tilde{\theta}_2$ and $\cos \tilde{\theta}_3$ can be calculated using Snell's law for the appropriate interfaces.

$$R = \left(\frac{\tilde{r}_{12} + \tilde{r}_{23}e^{-2i\delta}}{1 + \tilde{r}_{12}\tilde{r}_{23}e^{-2i\delta}}\right) \left(\frac{\tilde{r}_{12} + \tilde{r}_{23}e^{-2i\delta}}{1 + \tilde{r}_{12}\tilde{r}_{23}e^{-2i\delta}}\right)^{*}$$

$$\delta = \frac{2\pi\tilde{n}_{2}}{n_{1}\lambda} l\cos\tilde{\theta}_{2}$$
(2.8)

$$r_{12} = \frac{\tilde{n}_2 \cos \theta_1 - n_1 \cos \theta_2}{\tilde{n}_2 \cos \theta_1 + n_1 \cos \tilde{\theta}_2}$$
(2.9)

$$r_{23} = \frac{\tilde{n}_3 \cos \tilde{\theta}_2 - n_2 \cos \tilde{\theta}_3}{\tilde{n}_3 \cos \tilde{\theta}_2 + n_2 \cos \tilde{\theta}_3}$$
(2.10)

To calculate the absorption coefficient, k, for a specific polymer film, we determined the absorbance peak heights at 1731 cm⁻¹ (C=O stretch) and at 1149 cm⁻¹ (C-O-C stretch) from reflectance IR spectra. It is important to note that the presence of a film on the gold substrate changes the reflectivity of the surface even in the absence of absorption (when k=0), meaning that the film-covered gold gives rise to a baseline shift that must be taken into consideration when calculating peak heights. Specifically, this correction was made by calculating the absorbance when k=0 and subtracting this from the calculated peak absorbance to generate a corrected, calculated peak height. This correction was used along with the above equations to iteratively calculate the absorption coefficient, k, that gives rise to the measured peak height value for a particular film. The ratios of calculated absorption coefficients, $k_{C-O-C}/k_{C=O}$, were reasonably independent of thickness for a given film composition, as Figure 2.6 shows.



Figure 2.6. Ratios of the C-O-C (1149 cm⁻¹) and C=O (1731 cm⁻¹) absorption coefficients in poly(PEGMEMA) homo and copolymer films as a function of film thickness. In the case of copolymer films, the legend shows the PEGMEMA-475 mole percentage of total monomer in the polymerization solution, and the rest of the monomer was PEGMEMA-1100. The polymerization was performed as described in the experimental section

Table 2.1. Absorption coefficients, k, of homopolymer films. The k values were calculated using equations 2.5-2.10 and the peak absorbances corresponding to C-O-C and C=O stretches. The uncertainty is one standard deviation of the values obtained from films with a range of thicknesses

	-1	Bond	Absorption
Homopolymer	Wavenumber, cm	Stretch	Coefficient, k
	11.40	<u> </u>	0.00.000
	1149	С-О-С	0.30 ± 0.08
PEGMEMA-300	1731	C=O	0.14 ± 0.03
	1149	С-О-С	0.42 ± 0.05
PEGMEMA-475	1731	C=O	0.11 ± 0.01
	1149	C-O-C	0.48 ± 0.08
PEGMEMA-1,100	1731	C=O	0.045 ± 0.006
,			

We used the absorption coefficients k values (see Table 2.1) for three homopolymer films, poly(PEGMEMA-300), poly(PEGMEMA-475), and poly(PEGMEMA-1100), to create a calibration curve (Figure 2.7) of the $k_{C-O-C} / k_{C=O}$ ratio versus the average number of ethylene oxide units per repeat unit, EO_{avg}, and then calculated EO_{avg} in copolymer films. For poly(PEGMEMA-475-*co*-PEGMEMA-1100), this EO_{avg} value is a direct function of the fraction of each monomer in the copolymer and the average number of ethylene oxide units in each monomer (equation 2.11).

$$EO_{avg} = 8.8x_{475} + 23.1(1 - x_{475})$$
(2.11)



Figure 2.7. Ratios of C-O-C (1149 cm⁻¹) and C=O (1731 cm⁻¹) absorption coefficients, k, as a function of the average number of ethylene oxide units per repeat unit, EO_{avg}, in poly(PEGMEMA-300), poly(PEGMEMA-475), and poly(PEGMEMA-1100) films. The ethylene oxide units per monomer were calculated from 1H-NMR spectra of monomers (Figure 2.1), and the standard deviations in the absorption coefficient ratios were determined using films with thicknesses ranging from 5 to 454 nm. The line is a fit to the data with a zero intercept.

The reflectance FTIR data and the Fresnel calculations show that the ratios of PEGMEMA-475 to PEGMEMA-1100 in poly(PEGMEMA-475-*co*-PEGMEMA-1100) films are approximately the same as those in the solutions from which they grow (Table 2.2). This is somewhat surprising considering the large differences in the initial growth rates as well as termination rates for surface-initiated homopolymerization of the two monomers (Figure 2.2). However, in the case of copolymers, solutions containing 25 mole% and 75 mole% PEGMEMA-475 give essentially the same initial growth rate (Figure 1), which is consistent with the similarity between solution and film compositions. This direct correlation between solution and film compositions affords straightforward control over the ratio of long and short side chains to minimize PEG crystallization and maximize CO_2/H_2 selectivity in membranes.

Monomer Solution, mole%	Polymer Composition, mole%	EO _{avg}
PEGMEMA-475	PEGMEMA-475	
0	0	23 ± 1
25	33 ± 2	18 ± 1
50	54 ± 3	15 ± 1
75	71 ± 7	13 ± 1
100	100	8.7 ± 0.6

Table 2.2. Composition of poly(PEGMEMA-475-*co*-PEGMEMA-1100) films^a as a function of the PEGMEMA-475 mole percentages in the monomer solution.^b

^aFilm compositions were determined from reflectance FTIR spectra and Fresnel calculations and are expressed as both mole percent and the average number of ethylene

oxide (EO_{avg}) groups per repeat unit. The uncertainties, which were calculated using propagation of error, represent one standard deviation.

^bThe mole percentage in the monomer solution is relative to the total amount of monomer in solution.

2.3.3 Crystallization of PEG Side Chains

PEG chains crystallize in helices that contain two turns per 7 EO units over a length of 19.3 Å,⁴¹⁻⁴³ and helix formation leads to splitting of the 1150 cm⁻¹ C-O-C IR band into peaks at 1120 and 1148 cm⁻¹ and a narrowing of the CH₂ wagging peak at 1360 cm⁻¹.^{41, 42} In PEGMEMA films, long PEG side chains crystallize similarly, and Figure 2.8A demonstrates the changes in reflectance FTIR spectra that occur upon crystallization of a poly(PEGMEMA-1100) film. Previous reports of PEG crystallization in related coatings suggest that the helical axis preferentially orients perpendicular to the surface in films less than 100 nm thick, and both perpendicular and parallel in thicker films.^{28, 44-47}



Figure 2.8. Reflectance FTIR spectra of (A) 60 nm-thick poly(PEGMEMA-1100) immediately after polymerization (solid line) and 24 hours later (dashed line) and (B) 97 nm-thick poly(PEGMEMA-475-*co*-PEGMEMA-1100) immediately after polymerization (solid line) and 404 days later (dashed line). The copolymer was prepared from a solution containing 25 mole% PEGMEMA-475 and 75 mole% PEGMEMA-1100.

However, the presence of crystallinity, rather than its orientation, is the primary concern for creating selective membranes with high permeabililties, and prior studies reveal that the PEG chain length, not film thickness, is the primary factor in determining whether crystallization occurs.^{48, 49} In contrast to poly(PEGMEMA-1100), poly(PEGMEMA-475) films do not show any evidence of crystallization in reflectance FTIR spectra, presumably because neighboring PEG side chains are too short to crystallize in this environment.⁵⁰

Importantly, copolymers prepared from PEGMEMA-1100 and PEGMEMA-475 show no sign of crystallization, even when the fraction of PEGMEMA-475 in the film is only ~25%. Figure 2.8B shows that the reflectance FTIR spectrum of a poly(PEGMEMA-475-*co*-PEGMEMA-1100) film remains essentially unchanged even after more than a year at room temperature. The presence of the short chains is apparently sufficient to inhibit crystallization of the longer side chains, and this effect occurs for films prepared from solutions containing PEGMEMA-475 as 25, 50, and 75 mole% of the total monomer.

2.3.4 Formation of Gas-Separation Membranes by ATRP

Composite membranes are attractive for gas separations because the minimal thickness of the thin, selective skin allows for high flux, and the underlying support provides mechanical strength. Hence, the goal in using ATRP to create a membrane skin is to completely cover a porous substrate with a thin film without filling the underlying pores. The first step in the formation of membranes by ATRP is attachment of an initiator to the surface. To be consistent with our work on gold wafers, we sputtered 5 nm of gold on porous alumina and subsequently adsorbed a monolayer of the disulfide initiator on the surface (Scheme 2.1A). In a separate procedure, to avoid the deposition of gold on the membrane surface, we also attached a silane initiator directly to the alumina (Scheme 2.1B).

Subsequent polymerization of PEGMEMA from initiators on alumina yields the desired composite membranes. Figure 2.9 shows a SEM image of a composite membrane

containing a poly(PEGMEMA-475-*co*-PEGMEMA-1100) skin on a porous alumina support. The film is thin (130 nm) and clearly covers the pores without filling them. However, selective gas permeation studies are needed to demonstrate that the films are defect-free and non-crystalline.



Figure 2.9. SEM image of the cross section of a gold-coated porous alumina membrane modified with a poly(PEGMEMA-475-*co*-PEGMEMA-1100) film. The alumina exhibits unfilled vertical pores covered by a 130 nm-thick film that was grown from an aqueous solution containing 25 mole% PEGMEMA-475 and 75 mole% PEGMEMA-1100.

2.3.5 Gas Permeation through Poly(PEGMEMA) Membranes

Figure 2.10 shows the CO_2 and H_2 fluxes through porous alumina membranes coated with either a poly(PEGMEMA-1100) film or a copolymer film grown from a solution containing a 1:1 mole ratio of PEGMEMA-475 and PEGMEMA-1100. For poly(PEGMEMA-1100), the initial CO₂/H₂ selectivity is 12 ± 1 . The highest roomtemperature CO₂/H₂ selectivity of PEG-containing membranes in the literature is also 12.^{8, 22-24} However, the CO₂/H₂ selectivity of the poly(PEGMEMA-1100) film drops to less than 1 within a day because the CO₂ flux decreases 12-fold. This drop in CO₂ flux is almost certainly due to crystallization of the PEG side chains, which as noted above occurs within one day of synthesis of poly(PEGMEMA-1100) films.



Figure 2.10. Single-gas fluxes through gold-coated porous alumina membranes capped with (A) poly(PEGMEMA-1100) or (B) poly(PEGMEMA-475-*co*-PEGMEMA-1100) grown from a solution containing 50 mole% PEGMEMA-475. (Fluxes are normalized by multiplying by the SEM thickness of the membrane skin.) The circles represent CO_2 data, and the triangles represent H₂ data; filled symbols represent measurements taken immediately after synthesis, and open symbols represent data obtained 24 h later. The inset in Figure A shows the data on an expanded ordinate for clarity.

Figure 2.10 (cont'd)



By comparison, poly(PEGMEMA-475) films exhibit an initial CO₂/H₂ selectivity of 9 \pm 2. On silvlated supports, poly(PEGMEMA-1100) and poly(PEGMEMA-475) films show selectivities of 13 \pm 1 and 5.8 \pm 0.5, respectively, demonstrating that there is a

significant difference between the gas selectivities of these two polymers. The poly(PEGMEMA-475) films contain a smaller overall fraction of PEG than poly(PEGMEMA-1100), which likely explains their lower selectivity. However, the selectivity of the poly(PEGMEMA-475) does not decrease with time because the shorter chains do not crystallize.

The goal of using copolymers as membranes is to achieve the initial selectivity of poly(PEGMEMA-1100) films while avoiding decreases in selectivity and flux due to film crystallization. Figure 2.10B shows that a poly(PEGMEMA-475-co-PEGMEMA-1100) film (prepared on gold-coated alumina using a solution containing 50 mole% PEGMEMA-475) has an initial CO₂/H₂ selectivity of 12-13, which is essentially the same as that of the pure poly(PEGMEMA-1100). Moreover, the selectivity of the copolymer membranes is constant over at least several weeks at room temperature, again presumably because the side chains of PEGMEMA-475 inhibit crystallization. Figure 2.11 shows the dependence of CO_2/H_2 selectivity on the mole fraction of PEGMEMA-475 in poly(PEGMEMA-475-co-PEGMEMA-1100) films. As long as there is 75 mole% or less PEGMEMA-475 in the polymerization solution, membranes formed on goldcoated alumina maintain average CO₂/H₂ selectivities of 12 at room temperature. The films grown from silvlated alumina show a maximum CO_2/H_2 selectivity of 17 ± 2 with copolymers generated from a 50 mole% PEGMEMA-475 polymerization solution, but a selectivity of only 7 when using 75 mole% PEGMEMA-475. Silanization is more likely to produce initiators within the pores of the alumina, which might somewhat alter film structure at the support surface and change selectivity relative to films on gold-coated

alumina. Moreover, the initiator packing densities might be different for the gold-coated and silylated surfaces.



Figure 2.11. Single-gas CO_2/H_2 selectivity vs. mole fraction of PEGMEMA-475 in the monomer solution used to create amorphous poly(PEGMEMA-475-*co*-PEGMEMA-1100) films on porous alumina membranes. The triangles represent films grown from silylated alumina, and the squares represent films grown from initiators on gold-coated alumina. For the poly(PEGMEMA-1100) homopolymer on silylated alumina, the open circle near the origin represents selectivity after crystallization. Error bars are one standard deviation.

Determination of the permeability, P, of the films on porous alumina is challenging because of the difficulty in obtaining accurate values for film thickness (see equation 2.1). Film thicknesses in multiple cross-sectional SEM images of a given membrane typically show a relative standard deviation (rsd) of 10-30%, although sometimes we see even larger variations. Based on SEM images of membranes with a rsd in thickness <25%, the H₂ permeability of poly(PEGMEMA-475-*co*-PEGMEMA-1100) films ranges from 2 to 6 Barrers, and the CO₂ permeability ranges from 20 to 60 Barrers. (Given the uncertainty in thickness, we could not differentiate among permeabilities of films with different compositions.) Typical CO₂ permeabilities of PEG-containing films range from 12 Barrers in pure PEG to 570 Barrers in cross-linked PEG-based acrylates.^{50, 52} This wide range of permeabilities in different PEGcontaining polymers stems from differences in fractional free volume and the presence of different polar groups that alter the solubility of gases in the membrane.^{24, 53, 54} Although the poly(PEGMEMA-475-*co*-PEGMEMA-1100) films do not exhibit as high a permeability as some cross-linked films, the ultrathin skin maximizes permeance for a given permeability.

Selectivities in gas mixtures can differ significantly from those with single gases, particularly when absorption of a gas such as CO_2 plasticizes the membranes.⁵⁵ In mixed-gas experiments, plasticization may increase the flux of H₂ and decrease CO_2/H_2 selectivity relative to single-gas measurements. With feed gas streams of 79.7 mole% H₂ and 20.3 mole% CO_2 , the CO_2/H_2 selectivity was only 13% lower on average than the pure gas CO_2/H_2 selectivities.

2.4 Summary

In their amorphous state, poly(PEGMEMA-1100) membranes provide high CO₂ permeabilities and CO₂/H₂ selectivities, but crystallization can decrease flux by an order of magnitude and reduce CO₂/H₂ selectivity to below 1. Copolymerization of two PEGMEMA monomers, one containing 8-9 and the other 23-24 ethylene oxide units per side chain, avoids the problem of crystallization and yields films that maintain an amorphous state for more than a year. Reflectance FTIR spectra indicate that the ratio of the PEGMEMA-475 and PEGMEMA-1100 incorporated into copolymer films is within 8% of the ratio of the monomers in the polymerization solution. Membranes consisting of porous alumina supports coated with copolymer films exhibit stable single-gas CO₂/H₂ selectivities around 12 at room temperature, which is attractive for CO₂ removal from H₂ streams.

2.5 Acknowledgements & Copyright

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Chapter 3 Coating of Regenerated Cellulose Membranes for CO₂/H₂ Separations

3.1 Introduction

Over 90% of US hydrogen production employs steam reforming of natural gas followed by a water gas shift reaction. The raw product of this process contains over 20% CO_2 , which is removed from the H₂ stream by pressure swing adsorption (PSA).¹ Compared to PSA, membrane separations of CO_2 and H_2 offer the potential for low capital investment, a small footprint, simple scale-up, and low energy consumption.² Reverse-selective separations that remove CO2 and retain H2 at the high pressure feed side of the membrane are especially attractive to avoid re-pressurizing the H2. The challenges in applying reverse selective CO2/H2 separation membranes at a large scale include (1) development of thin polymer films on porous substrates to maximize flux and separation efficiency; and (2) selection of substrates that can pack into spiral-wound modules for industrial scale applications.³ W.R. Grace developed a spiral-wound module for CO2/CH4 separations,⁴ but spiral-wound modules and flat-sheet membranes for CO2/H2 separation remain in research labs or small scales. The alumina substrates described in chapter 2, while interesting for fundamental studies, are simply too expensive and fragile for practical separations. Polymeric membranes are more robust and less inexpensive than flat-sheet ceramic membranes, and thus are the most likely substrates for composite, reverse-selective membranes.

Among the materials used to form polymeric membranes, cellulose is natural, abundant and inexhaustible.⁵ Cotton, for example, is over 90% cellulose. Regenerated cellulose (RC, also termed cellulose II, rayon or cellophane) results from chemical or mechanical treatment of native cellulose (or cellulose I), which was traditionally one of the materials in membranes for dialysis/hemodialysis processes.⁶ Mechanical treatment of cellulose is usually performed through compression under high pressure.⁷ Scheme 3.1 illustrates the chemical treatment that creates RC. Regenerated cellulose often has less exposed –OH groups but a better defined structure than cellulose.⁸

Scheme 3.1. Production of regenerated cellulose from through chemical treatment of cellulose.



RC membranes are commonly used for ultrafiltration and microfiltration and are available in a wide range of molecular weight cut-offs (MWCOs). Liu *et al.* used RC

membranes (MWCO=100 kDa) to separate immunoglobulin (MWCO=180 kDa) from chicken egg yolk based on the size difference of the proteins, and the immunoglobulin purity was 85% after a single-stage separation and 91% after two consecutive separations.⁹

Surface-initiated grafting of polymer brushes to RC membranes should be relatively straightforward using literature procedures for modifying cellulose.¹⁰ In the presence of triethylamine (TEA), exposed –OH groups will react with 2-bromoisobutyryl bromide to immobilize an ATRP initiator from which polymerization can occur. Several groups examined modified RC membranes because synthetic polymer coatings on the membranes offer control over wettability, pore size, roughness, and propensity for fouling. Chen and coworkers grafted poly(glydicyl methacrylate) (PGMA) on a RC membrane via ATRP and opened the expoxide ring by reaction with N-methylglucamine. The ring opening leads to a high density of hydroxyl groups, and the resulting membrane exhibited high affinity for boron and arsenic, which might be useful for removal of boron from water.¹¹ Husson and co-workers grew poly(acrylic acid) (PAA) brushes in the 1 µm pores of RC, and the resulting membranes exhibited a high binding capability for lysozyme.¹² Bhut *et al.* also grew poly(2-dimethylaminoethyl methacrylate) (poly(DMAEMA)) brushes from RC membranes. The polymer brush thickness increased linearly with polymerization times of 0-15 hr. BSA binding to the brushes increases linearly with brush thickness before reaching a plateau of 66.3 mg BSA/mL of membrane.¹³ Lin and coworkers grafted zwitterionic sulfobetaine from cellulose

membranes via surface-initiated ATRP. Decreased nonspecific protein adsorption and platelet adhesion to these membranes may increase their biocompatibility.¹⁴

To the best of my knowledge, no reverse-selective gas separation membranes were developed from cellulose based substrates. Eckelt and coworkers prepared cellulose membranes that were size selective with a H₂/CO₂ selectivity of 6.2±1.1, and the selectivity dropped to 1.4 after regeneration.¹⁵ This chapter describes my work in poly(PEGMEMA-1100-co-PEGMEMA-475) brushes growing from regenerated cellulose to create composite membranes for CO₂/H₂ separations. The results in chapter 2 show that similar films on porous alumina exhibit a CO_2/H_2 selectivity of 12, and the copolymer film shows no sign of crystallization after over a year of preparation. The H₂ permeability of poly(PEGMEMA-475-co-PEGMEMA-1100) films ranges from 2 to 6 Barrers, and the CO₂ permeability ranges from 20 to 60 Barrers.³ Freeman and coworkers prepared a cross-linked copolymer from PEGMEMA and poly(ethylene glycol diacrylate) PEGDA in 2005, and the CO₂ permeability decreased dramatically from 580 Barrers to 100 Barrers when the PEGDA weight percentage increased from 0 to 100 %. The maximum reported CO₂/H₂ selectivity of 13 for this system occurs for minimally cross-linked networks containing 99 wt % PEGMEMA. Increasing the fraction of PEGDA brings the selectivity down, presumably because crosslinking minimizes the fraction of free volume in the polymer.¹⁶ A later report with 30 wt% PEGDA in the poly(PEGDA-co-PEGMEMA-475) showed a CO₂ permeability of 160 Barrers and a

 CO_2/H_2 selectivity of 14 at 1 atm CO_2 partial pressure and 10 °C.¹⁷ In 2007, Freeman and coworkers reported another study of poly(PEGDA-*co*-PEGMEMA-475), also indicating that increasing the percentage of cross-linker has a negative effect on both permeability and selectivity.¹⁸

In my studies of CO_2/H_2 separations by polymer films on RC substrates, I examined the effect of cross-linking on poly(PEGMEMA-475-*co*-PEGMEMA-1100) films by introducing a 25% molar fraction of PEGDA during polymerization. The study aims to (1) grow polymer membranes on RC substrate and (2) observe the effect of cross-linking on the transport properties of poly(PEGMEMA-475-*co*-PEGMEMA-1100-*co*-PEGDA) films. In mixed-gas separations the cross-linked films on RC substrates show CO_2/H_2 selectivities ranging from 6.5 to 19.9, but the CO_2 permeability is only 5-15 Barrers.

3.2 Experimental

3.2.1 Chemicals and Materials

PEGMEMA monomers with $M_n = 475$ Da (PEGMEMA-475) and $M_n = 1,100$ Da (PEGMEMA-1100) were obtained from Aldrich. The cross-linker, PEGDA $M_n = 700$ Da, was purchased from Aldrich as well. All monomers contain both 100 ppm 4-methoxyphenol and 300 ppm 2,6-di-*tert*-butyl-4-methylphenol as inhibitors. The monomers were used as received without removal of the inhibitors. Proton NMR spectra show that the average numbers of ethylene oxide units in PEGMEMA-475 and

PEGMEMA-1100 are 8.8 and 23.1, respectively (see Figure 2.1).³ The 2bromoisobutyryl bromide (BiBB) (98%), CuCl (99.995%), CuBr₂ (99.999%), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%) were purchased from Aldrich, and deionized water was obtained using a Millipore system (Milli-Q, 18.2 $M\Omega$ •cm). Triethylamine (TEA) and dimethylformamide DMF (99.8%) were purchased from Jade Scientific and used as received. THF was distilled over sodium metal with benzophenone. The ultrafiltration regenerated cellulose membranes (PLGC02510, 25 mm disks with 10 kDa MWCO) were purchased from Milliopore, and the RC layer was supported by ultra-high molecular weight polyethylene. Silicon(100) wafers were obtained from NOVA Electronic Materials and sputter-coated with 20 nm of chromium followed by 200 nm of gold by LGA Thin Films (Santa Clara, CA). The [Br-C(CH₃)₂-COO(CH₂)₁₁S]₂ initiator was synthesized as described previously.¹⁹ A cylinder containing 20.3% CO₂ and 79.7% H₂ was purchased from Airgas.

3.2.2 Polymerization

3.2.2.1 Initiator Attachment

Scheme 3.2 illustrates the initiator attachment and ATRP procedures. The RC membrane was immersed in 20 mL deionized water for 1 h with the support side up. To ensure complete glycerin removal, the water was replaced every 20 minutes. After soaking in water, the RC membrane was rinsed with 5 mL deionized water twice and dried under flowing N_2 . The dried membrane was then placed in a Teflon membrane holder that exposed the RC surface and transferred into a glove bag. Under a N_2 blanket,

the RC membranes were rinsed with 2 mL anhydrous THF twice to remove any residual water. An initiator solution with 10 mM TEA and 10 mM of BiBB was made by adding 28 μ L of TEA and 25 μ L of BiBB to 20 mL anhydrous THF. The membrane was then coated with 2 mL of this solution for 2 min and rinsed with 2 mL anhydrous THF three times and 2 mL deionized water once. Finally, the RC membrane was transferred outside of the glove bag, and dried with flowing N₂. Both rinsing and drying occurred with the membrane remain in the holder. The initiator-modified RC membrane was stored in a N₂ filled glove bag and used for polymerization within 48 hr.

For Au-coated silicon wafers, the initiator attachment occurred by soaking UVozone-cleaned (10 min) wafers in 1 mM ethanolic $[Br-C(CH_3)_2-COO(CH_2)_{11}S]_2$ overnight. The wafers were then rinsed with ethanol and dried with a N₂ stream.



Scheme 3.2. Growth of a cross-linked copolymer brush from a RC membrane.

3.2.2.2 Catalyst Solution

A catalyst stock solution was prepared by first degassing 30.0 mL deionized H_2O via three freeze, pump, thaw cycles in a round bottom flask. At the third freezing period,

0.0596 g (0.6 mmol) of CuCl and 0.0450 g (0.2 mmol) of CuBr₂ were added to the round bottom flask prior to finishing the pump thaw cycle. No CuCl or CuBr₂ is lost during this pumping step. Two more freeze, pump, thaw cycles were performed to enhance oxygen removal. In a N₂-filled glove bag, 490 μ L (1.8 mmol) of HMTETA was added to this solution. The solution turned dark blue upon HMTETA addition. The catalyst solution was stored in a glove bag with constant stirring for future use. In some rare cases, precipitation is visible in the catalyst solution after over two weeks of preparation. With constant stirring, the precipitation does not appear, and the catalyst solution remains uniform and clear. The mole ratio of Cu⁺:Cu²⁺:HMTETA was 3:1:9.

3.2.2.3 ATRP

The monomer solution, which contained a total of 0.75 M monomer in water, was degassed via four freeze, pump, thaw cycles. Unless specifically stated, the molar ratio of PEGMEMA-1100:PEGMEMA-475:PEGDA is 3:3:2. Monomer solution and initiator-modified RC membranes were transferred into the glove bag with the catalyst solution. The polymerization mixture was prepared by combining degassed monomer and pre-made catalyst solutions in a 9:1 volume ratio to produce a light blue solution containing 0.67 M monomer, 2.0 mM CuCl, 0.60 mM CuBr₂, and 6.0 mM HMTETA. The initiator-modified membranes or gold coated wafers were immersed in the polymerization solution for designated periods of time, and the resulting polymer films were removed from the glove bag, and rinsed with 5 mL DMF three times followed by rinsing with 5 mL of ethanol three times and drying under a N₂ stream.

3.2.3 Characterization methods

Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer with a Pike grazing angle (80°) attachment. A UV-Ozone-cleaned, gold-coated Si wafer was used to obtain the background spectrum. An air background was obtained immediately prior to measurement of the RC samples. Attenuated Total Reflectance (ATR) FTIR spectra were obtained with a Perkin Elmer Spectrum one FTIR spectrometer using an air background. This spectrophotometer contains a diamond, single-reflection ATR crystal.

Scanning electron microscopy (SEM) was performed mainly with a JEOL semiin-lens cold cathode field-emission scanning electron microscope, model JSM-7500F, operating with an r-filter in signal maximum mode. Samples were sputter coated with 10 nm of osmium prior to imaging. A few SEM images were obtained with a JEOL 6400V microscopy with a LaB6 emitter (Noran EDS). The samples for JEOL 6400V were coated with 8 nm of gold before of imaging.

3.2.4 Gas Permeation

Mixed-gas experiments were performed by loading the membrane into a custommade membrane holder (all connections utilized Swagelok fittings and were tested to ensure that they maintained pressure over a time scale longer than the experiment) that allowed cross-flow of the feed gas as well as a sweep gas on the permeant side. A backpressure valve was employed to sustain the feed gas pressure, and the feed flow rate was high enough to maintain constant composition at the face of the membrane (the stage-cut, or ratio of permeant flow to feed flow, was <1%). The N₂ sweep gas/permeant stream was connected to an automated six-port injector valve on a Hewlett-Packard 6890 GC equipped with a thermal conductivity detector (TCD) and an Agilent GS-CarbonPLOT capillary column (i.d. = 0.53 mm, length = 30 m, 3 μ m coating). Figure 3.1 illustrates the entire apparatus.



Figure 3.2. Apparatus for testing mixed gas permeabilities.

The mixed-gas and pure-gas permeances were calculated from GC results using equation 2.3,

Permeance =
$$\frac{\chi_{\rm B} \times \Phi_{\rm N_2}}{\chi_{\rm N_2} \times {\rm A} \times \Delta p}$$
 (2.3)

where χ_B is the mole fraction of a particular permeate gas, B, in the gas mixture injected into the GC column, Φ_{N2} is the sweep gas flow rate, χ_{N2} is the mole fraction of N₂ in the gas injected into the GC column, Δp is the transmembrane partial pressure difference for the gas of interest, and Λ is the membrane area. (Φ_{N2}/χ_{N2} is the sum of the permeate and sweep gas flow rate, and χ_{N2} was determined by subtracting the mole fractions of the permeates from unity. This assumes that the amount of N₂ passing from permeate to feed was negligible.) The sweep gas flow rate was programmed into a mass flow controller, pressure and area were measured, and the mole fractions were determined from the integrated gas chromatograms and a calibration curve.



Figure 3.2. Reflectance FTIR spectrum of a cross-linked co-polymer brush (top, 25 mole% crosslinker, 37.5 mole% PEGMEMA-1100, and 37.5 mole% PEGMEMA-475 in the polymerization solution that contained 0.67 M total monomer), and spectra of spin-coated films of the three monomers. The co-polymer film was grown by ATRP from initiators immobilized on Au-coated Si, and the monomers were spin coated on the surface of Au-coated wafers. Compare the cross-linked copolymer absorbance with poly(PEGMEMA-1100) and poly(PEGMEMA-475) (Chapter 2, Figure 2.3.) the position of C=O peak and O-C-O peak was in match.

3.3 Results and Discussion

3.3.1 FTIR Studies of Cross-linked Copolymer Films

3.3.1.1 Reflectance FTIR Spectra of Cross-linked Copolymer Brushes on a Aucoated Silicon Wafer

In an attempt to examine crosslinking in poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA) brushes, we obtained reflectance FTIR spectra of a poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA) film grown from initiators on a Au-coated Silicon wafer. Figure 3.2 shows the spectrum of the cross-linked co-polymer film as well as spectra of the three monomers involved in polymerization. In the spectrum of poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA), the absence of the C=C peak at 1635 cm⁻¹ suggests that the brush does not contain a significant amount of residual C=C bonds. Assuming that the brush has the same composition as the monomer solution, the films contain 25% cross-linking agent, and the absence of signal from C=C bond indicates a highly cross-linked film. Nevertheless, we have no direct evidence for incorporation of PEGDA.

3.3.1.2 ATR-FTIR Study of Cross-linked Copolymer Grafted from RC

Figure 3.4 compares the ATR-IR spectra of an RC membrane before (bottom) and after (top) growth of a 1.5 μ m-thick film of poly(PEGMEMA-1100-*co*-PEGMEMA-475*co*-PEGDA, 25 mole % PEGDA in the polymerization solution). The IR spectrum of the bare RC membrane contains signature peaks at 3331 and 2904 cm⁻¹ representing –OH stretching (from both cellulose and water) and –CH stretching, respectively.²⁰ The 1635 cm⁻¹ peak is likely due to absorbed H_2O , this means water also contributes for 3331 cm⁻¹ peak. The 1470 cm⁻¹ peak is due to –OH in plane bending. Absorbances at 1375 and 1416 cm⁻¹ stem from the CH and CH₂ bending modes respectively,²¹ and the peak at 1100 cm⁻¹ peak is due to C-O stretching.

Equation 2.4 gives the expression for the penetration depth, d, in ATR,

$$d = \frac{\lambda}{2\pi n_1 \sqrt{\sin^2 \theta - \frac{n_2}{n_1}}}$$
(2.4)

where λ is the wavelength, n_1 (2.417) is the refractive index of the diamond crystal, n_2 is the refractive index of the polymer film (~1.5), and θ is the angle of incidence of the IR beam. For this particular system, the angle of incidence is 45°.²² At 3331 cm⁻¹, the penetration depth is 0.6 µm. The thickness of the cross-linked copolymer film is 1.5 µm (estimated from SEM images), which is more than twice the penetration depth in this region, so the polymer brush should attenuate most of the signal from the RC substrate. The film may also adsorb less water than the bare RC membrane.

For the cross-linked copolymer film, the absorbance at 1721 cm⁻¹ due to the C=O bond confirms the presence of the copolymer on the surface. Husson and co-workers polymerized poly[poly(ethylene glycol methacrylate)] (PPEGMA) from RC, and their ATR-IR spectra indicated similar peaks for the polymer layer.²³ The absorbance at 1096 cm⁻¹ stems from O-C-O bond stretching, and the absence of peak splitting indicates that

there is no crystallization of PEO side chains in this copolymer (see chapter 2 page 70).^{3,24} However, the C=C peak at 1631 cm⁻¹ suggests a significant amount of monomer trapped in the cross-linked framework or possibly unreacted cross-linking agent. However, this signal may also contain some absorbance from the RC membrane. Although the IR spectrum shows the presence of the film, it is unfortunately not very useful for determining film composition.



Figure 3.3. ATR-FTIR of a bare RC membrane (before, bottom), and after (top) modification by growth of a poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA) film.

3.3.2. SEM Characterization of RC Membranes and Cross-linked Polymer Films

Figure 3.4 shows SEM images of bare RC membranes. The RC membrane has a 200 μ m-thick support layer made from dense polyethylene fibers. Based on the is estimated by molecular weight cut off (MWCO) of 10 kDa, the RC layer on top of the polyethylene has pores with diameters of 2-4 nm. This pore size is lower than the SEM resolution. The thickness of the RC layer is about 30 μ m.



Figure 3.4 SEM images of cross-sections of an RC membrane. The black lines indicate the RC layer, which resides on support of polyethylene fibers.

Figure 3.5 shows cross-sectional images of RC membranes after growth of crosslinked polymer brushes. For most membranes the boundary between the polymer brush and RC is evident, but for some samples the contrast between RC and cross-linked polymer brush is not easy to detect by eye. Both RC and polymer films contain C, H and O, so energy-dispersive X-ray spectroscopy (EDS) cannot define the boundary between RC and the cross-linked brush. In such cases, two methods were used to find he interface of RC and polymer brush layer. (1) Application of an electron beam on a small area of the sample for 20-60 seconds can differentiate between the two materials. The polymer brush layer melts and slightly moves during this time, while the more stable RC layer shows no change in shape. This slight movement of the sample is very obvious under SEM. The RC is probably more stable due to the regeneration treatment. (2) The thickness of the RC layer is 30 μ m (Figure 3.4). The total thickness of RC and polymer brush could be measured and the thickness of polymer brush is determined by total thickness minus the thickness of the RC layer. Using these methods or the two methods combined, polymer brush film thicknesses could be obtained from SEM images.



Figure 3.5. SEM images of cross-sections of cross-linked copolymer films grafted on RC membranes. The black lines indicate the polymer film on top of the RC membrane.

3.3.3. Gas Separations

Using the apparatus illustrated in Figure 3.1, I determined the gas permeability of RC membranes modified with cross-linked polymer films. The feed gas cylinder initially contained 20.3% CO₂ and 79.7% H₂. Over the time frame of years, the CO₂/H₂ ratio of the mixed gas cylinder may have changed slightly, so I monitored its composition with GC to ensure an accurate CO_2/H_2 ratio. Pure CO₂ and H₂ served as standards. Figure 3.6 shows a sample gas chromatogram of the feed gas. The H₂ peak (2.9 min) area is 8414, whereas the CO₂ peak (4.35 min) area is only 19.3. The huge difference between the CO₂ and H₂ signals is due in part to the higher concentration of H₂ in the feed mixture, but the main factor for the large differences in the peak areas is that the thermal conductivity of the N₂ carrier gas is much closer to CO₂ than H₂.



Figure 3.6. Gas chromatogram of the feed mixed gas. The molar ratio of CO_2 to H_2 is 79.7: 20.3.

During the permeability test, the feed gas flowing past the membrane was adjusted to a pressure of 45 psi (3.1 bar), and the flow rate was much larger than rates of CO_2 or H_2 permeation through the membrane to ensure a constant feed composition. The permeate side is swept with ultra-pure N_2 , at a flow rate of 0.5 mL/min or 0.75 mL/min, depending on the permeability of the sample.



Figure 3.7. Gas chromatogram of the permeate of a mixed-gas separation with a RC membrane modified with a poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA) film. (The splitting of the H₂ peak is probably due to a mechanical disturbance on sample injection, but this does not affect the integral of peak area)

Figure 3.7 shows a chromatogram of the gas permeating through a RC membrane modified with a poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA) film. The H₂ peak area is 216.9, the CO₂ peak area is 13.3, and the N₂ sweep gas flow rate is 0.75 mL/min. Remarkably, the CO₂/H₂ selectivity is 18.7. Based on SEM images, the thickness of this particular film is 700 nm, so the CO₂ permeability is 15 Barrers. However, after exposure to CO₂/H₂ for over 30 min, the selectivity of the film dropped

from 19 to 8. Nevertheless, after sitting in air overnight, the selectivity of the membrane returns to approximately its original value of 18.

More than 10 membranes prepared under the same conditions with 25 mole% cross-linker in poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA) showed CO₂/H₂ selectivities from 6.5 to 19.9, and the permeability of CO₂ ranged from 5 to 15 Barrers. Comparing this permeability result with that for the poly(PEGMEMA-1100-*co*-PEGMEMA-475) films on alumina ($P_{CO2} = 3-6$ Barrers, chapter 2),³ the permeability for these cross-linked film (5-15 Barrers) may be slightly higher than for the non-cross-linked polymer. Freeman and coworkers claimed that the crosslinking would dramatically decrease both selectivity and permeability.^{16,18} However, for this particular case, 25 percent cross-linker did not affect the selectivity and permeability dramatically.

3.4. Conclusion

ATRP from initiators on RC yields poly(PEGMEMA-1100-*co*-PEGMEMA-475*co*-PEGDA) films. The cross-linker mole percentage was 25% in solution and presumably the same on the surface. FTIR spectra and SEM images confirm the presence of the film.

In mixed-gas separation tests, the CO_2/H_2 selectivity of the modified RC membrane ranged from 6.5 to 19.9, and the permeability of CO_2 varied from 5 to 15 Barrers. This is comparable to the poly(PEGMEMA-1100-*co*-PEGMEMA-475) films described in Chapter 2, showing that polymerization for polymers is a feasible method for creating membranes.

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Chapter 4 Synthesis of Nanoparticle-containing Membranes and Investigation of their CO₂/H₂ Separations

This chapter focuses on surface-initiated polymerization of poly(ethylene glycol methyl ether methacrylate) (PEGMEMA) and poly(ethylene glycol) diacrylate (PEGDA) in the presences of SiO_2 nanoparticles modified with initiators. Mixed-gas permeation studies examine whether incorporation of nanoparticles alters CO_2/H_2 separations with these films.

4.1 Introduction

4.1.1 Impact of Fractional Free Volume on Selectivity and Permeability

For non-porous polymer membranes, gas permeability (*P*) depends on both solubility (*S*) and diffusivity (*D*) according to equation (4.1). The solution diffusion model suggests that the ideal selectivity of gas **A** over gas **B**, $\alpha_{A/B}$, depends on the solubility coefficients and diffusivities of the two gases, equation (4.2).¹

$$P \equiv S \times D \tag{4.1}$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{S_A \times D_A}{S_B \times D_B}$$
(4.2)

The solubility of a certain gas in a polymeric membrane depends not only on the physical properties of the gas, but also on the similarity between the solubility parameters of the

polymer and the gas.² As discussed in Chapter 1, CO_2/H_2 diffusivity selectivity is always less than one because H_2 is smaller and lighter than CO_2 .

Equation 4.3 often describes the diffusivity of a gas in a polymer, where A is a constant that reflects the mean free path of the permeate. B is proportional to the diameter of the permeate, ^{3,4} and FFV is the fractional free volume in the polymer. Importantly, an increase in FFV will give higher permeability.

$$D = A\exp(-\frac{B}{FFV}) \tag{4.3}$$

To increase FFV, Freeman and coworkers blended fumed SiO₂ nanoparticles in poly(4-methyl-2-pentyne) (PMP), and the permeability of both N₂ and CH₄ increased with the amount of nanoparticles added. PMP containing 40% fumed SiO₂ nanoparticles showed a >2-fold increase in CH₄ permeability. Positron anihilation lifetime spectroscopy (PALS) indicated that FFV correlates with the wt% of nanoparticles in the polymer. This work also indicated that the diffusion coefficient increases more for large gases than for smaller ones.⁵ For reverse-selective CO₂/H₂ separations, an increase of FFV will positively impact both CO₂ permeability and CO₂/H₂ selectivity, because diffusivity selectivity, which favors H₂, will decrease.

4.1.2 Mixed Matrix Membranes for Gas Separation

Robeson summarized the selectivity and permeability data for a number of light gas combinations to determine upper bound in the performance of polymeric membranes for gas separations. For a given permeability selectivity is limited.⁶ Simply put, with size-sieving membranes more permeable materials show less selectivity. Freeman similarly summarized data for reverse selective polymers in CO₂/H₂ separations and also found an upper bound effect, but in this case selectivity may increase with permeability.⁵

With the acknowledgement of an upper bound of selectivity and permeability in polymeric gas separation materials, researchers focused on developing new materials with higher selectivity and/or permeability. Forming films containing nanoparticles or porous zeolites could break this upper bound. Mixed Matrix Membranes (MMMs) contain micro to nanometer sized inorganic particles blended with polymers. By combining two materials with different selectivity and permeability merits, MMMs may overcome the upper bound between selectivity and permeability. Inorganic materials applied in synthesizing MMMs include: zeolites,⁷⁻¹¹ metal-organic frameworks (MOFs)⁹ and nanoparticles.^{5,12} After physically mixing fumed SiO₂ nanoparticles with diameters smaller than 10 nm into poly(4-methyl-2-pentyne), Freeman and coworkers observed a surprisingly 3 fold increase in CO₂ permeability when 30 vol% nanoparticles are blended in. The size of voids between nanoparticles and the polymers enhanced the gas permeability.⁵ Polysulfone/ SiO₂ nanoparticle MMMs exhibit a similar permeability

enhancement compared to the pure polymer.¹² This work attempts to create similar improvements through incorporation of nanoparticles into membranes containing poly(PEGMEMA).

While more nanoparticles are blend in the polymer film, it is hard to obtain defect free film for gas separations. Introducing cross-links into polymers could help stabilize membrane under aggressive conditions.¹³ Freeman and co-workers focused on crosslinking poly(ethylene glycol) methyl ether acrylate (PEGMEA) films for CO₂/H₂ separations. On slowly increasing from 0% to 100% cross-linking monomer, poly(ethylene glycol) diacrylate (PEGDA), in polymerization of [methyl bis(trimethylsiloxy) silyl] propyl glycerol methacrylate, however, the resulting polymer shows a linear decrease in CO₂ peremeability.^{14,15} Poly(ethylene glycol) methyl ether acrylate (PEGMEA) with 10 wt% of PEGDA is very robust in separation of H₂S at humid and high pressure condition. The permeability of both CO_2 and H_2 in 30 wt% cross-linking increased with the respect of CO₂ pressure, especially at low temperature (-20 °C). At low temperature, CO_2/H_2 selectivity increased with CO_2 partial pressure as well.¹⁶

4.2 Experimental

4.2.1 Chemicals and Materials

PEGMEMA monomers with $M_n = 475$ Da (PEGMEMA-475) and $M_n = 1,100$ Da (PEGMEMA-1100) and a crosslinkable monomer, PEGDA $M_n=700$ Da, were purchased from Aldrich. All monomers contain both 100 ppm 4-methoxyphenol and 300 ppm 2,6-ditert-butyl-4-methylphenol as inhibitors and were used as received without removal of the inhibitors. Proton NMR spectra show that the average numbers of ethylene oxide units in PEGMEMA-475 and PEGMEMA-1100 are 8.8 and 23.1, respectively (see Figure 2.1).¹⁷ SiO₂ nanoparticles (12 nm diameter) were purchased from Aldrich, and the diameter of the nanoparticles measured in TEM images of 17 particles was 8.0 ± 3.5 nm (Figure 4.1).



Figure 4.1. TEM images of SiO₂ nanoparticles spotted on a carbon-coated Cu grid.

2-bromoisobutyryl bromide (BiBB) (98%), CuCl (99.995%), CuBr₂ (99.999%), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%) were purchased from Aldrich, and deionized water was obtained using a Millipore system (Milli-Q, 18.2 $M\Omega$ •cm). Triethylamine (TEA) and DMF (99.8%) were purchased from Jade Scientific, and used as received. THF was distilled over sodium metal with benzophenone. The porous alumina substrates were Anodisc membrane filters (25 mm disks with 0.02 µm surface pores) purchased from Whatman. Figure 4.2 shows the SEM images of the top and cross section of an alumina membrane. Silicon (100) wafers were obtained from NOVA Electronic Materials. A silane initiator, Cl(CH₃)₂Si(CH₂)₁₁OCOC(CH₃)₂Br, was synthesized as described previously.¹⁸ A mixed gas cylinder containing 20.3% CO₂ and 79.7% H₂ was purchased from Airgas, and a cylinder with 50% CO₂ and 50% H₂ was obtained from Praxair. A Sargent-Welch S-15700 (5000 rpm) centrifuge was used to separate nanoparticles from suspensions. The Sharpertek Stamina XP sonicator 40,000 Hz, 380 watt was used for dispersing the nanoparticles.



Figure 4.2. SEM images of the top (A) and cross-section (B) of porous alumina membranes with nominal 20 nm surface pores.

4.2.2 Polymerization

4.2.2.1 Initiator Attachement

Scheme 4.1 illustrates the initiator attachment to alumina membranes and SiO₂ nanoparticles. The SiO₂ nanoparticles, 160 mg, were dispersed in 20 mL dry THF during 5 min of sonication. After transfer into a N₂-filled glove box, 10 drops of dimethylchlorosilane initiator, $Cl(CH_3)_2Si(CH_2)_{11}OCOC(CH_3)_2Br$ (light yellow color liquid) was added to the suspension to achieve a 1 mM initiator concentration. The suspension was left in the glove box for the desired amount of time, and the nanoparticles were separated from the suspension via 5 min of centrifugation (5000 rpm), and rinsed with 10 mL dry THF three times. The resulting initiator-modified nanoparticles were dried under vacuum. Due to some loss in decanting following centrifugation, the process yielded about140 mg of initiator-modified nanoparticles.

For alumina membranes, the initiator attachment was performed in a glove box by soaking a UV/ozone-cleaned (10 min) membrane overnight in THF containing 1 mM $Cl(CH_3)_2Si(CH_2)_{11}OCOC(CH_3)_2Br$. The membranes were then rinsed with 5 mL of THF three times and dried under flowing N₂. In a few cases, the alumina membranes were rinsed by flowing 5 mL of THF through the membrane using a peristaltic pump. The two rinsing methods gave no significant difference in the resulting polymer brush film thickness.


Scheme 4.1. Initiator attachment to SiO₂ nanoparticles or alumina membranes.

4.2.2.2 Catalyst Solution

A catalyst stock solution was prepared by adding 0.0596 g (0.6 mmol) of CuCl and 0.0450 g (0.2 mmol), CuBr₂ and 490 μ L (1.8 mmol) of HMTETA ligand into degasses 30.0 mL deionized H₂O. Details of this step is described in (Chapter 3, page 88). The nominal mole ratio in the solution was Cu⁺:Cu²⁺:HMTETA was 3:1:9.

Scheme 4.2. Preparation of nanocomposite membranes by ATRP. The reaction is performed an in oxygen-free glove bag. The pink dots represent nanoparticles, but they are greatly expanded to allow visualization.



4.2.2.3 ATRP

Scheme 4.2 illustrates the polymerization strategy. The monomer solution is prepared by dissolving PEGMEMA-1100, PEGMEMA-475 and PEGDA in water, and adding initiator-modified SiO₂ nanoparticles. The total monomer concentration is 0.75 M. Unless specifically stated, the molar ratio of PEGMEMA-1100, PEGMEMA-475 and PEGDA is 3:3:2. The monomer solution was degassed via four freeze, pump, thaw cycles. Monomer solution and the initiator–modified alumina membrane were transferred into a N₂-filled glove bag containing the catalyst solution. The polymerization mixture was prepared by combining degassed monomer and catalyst solutions in a 9:1 volume ratio to produce a light blue solution containing 0.67 M monomer, 2.0 mM CuCl, 0.60 mM CuBr₂, and 6.0 mM HMTETA. The tops of initiator-modified membranes were immersed in the polymerization solution for designated periods of time, and the resulting polymer films were rinsed with 5 mL DMF three times followed by rinsing with 5 mL of ethanol three times and drying under a N_2 stream. No polymerization occurred on the bottom side of the alumina membrane because the monomer solution did not pass through the membrane during polymerization.

4.2.3 Characterization Methods and Gas Separation Tests

Scanning electron microscopy (SEM) was performed mainly with a JEOL semiin-lens cold cathode field-emission scanning electron microscope (Model JSM-7500F). This microscope operates with an r-filter in signal maximum mode. Some SEM images were obtained using a JEOL 6400V microscope with a LaB6 emitter (Noran EDS). All samples were cracked right after freezing in liquid nitrogen to ensure a clean exposure of the cross-section. The cross-section was then sputter coated with 10 nm of osmium (JEOL 7500F) or 8 nm of gold (JEOL 6400V) prior to imaging.

Nuclear Magnetic Resonance (NMR) spectra of the reaction mixtures were obtained with a Varian Unity±500 superconducting NMR-Spectrometer (500 MHz). Transmission Electron Microscopy (TEM) images were obtained at the Center for Advanced Microscopy using a JEOL100 CXII.

Mixed-gas permeation tests were performed as described in chapter 2 Page 57.

4.3 Results and Discussion

4.3.1 SEM Characterization of Nanoparticle-containing Membranes

SEM images confirm growth of a thick polymer film on top of the alumina membrane. Figure 4.7 shows a cross-sectional image of a nanoparticle-containing film prepared with 0.18 mg/mL SiO₂ nanoparticles in the polymerization solution and a 45-min reaction. The thickness of the poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700)/nanopartices layer is 77.0 \pm 4.3 µm. An expanded view Figure 4.7 (B) suggests that the nanoparticles are embedded in the polymer framework. The diameter of the particles in the image is 200 nm to 2 µm, and this large size is presumably due to the significant polymerization from the 8 nm-diameter, initiator-modified particles. Chen and co-workers previously used nanoparticle size increases as proof of successful polymerization.¹⁹ Figure 4.7 (C) is the cross-sectional image of an alumina membrane modified with a poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) film without embedded nanoparticles, and Figure 4.7 (D) is a higher magnification image of the poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700). As expected, Figure 4.7 (D) does not reveal any particles.



Figure 4.3. (A) and (B) SEM images of cross-sections of polymer films prepared by polymerization of a solution containing 0.25 M PEGMEMA-1100, 0.25 M PEGMEMA-475, 0.17 M PEGDA, 2.0 mM CuCl, 0.60 mM CuBr₂, 6.0 mM HMTETA and 0.18 mg/mL SiO₂ nanoparticles. (C) and (D) are the cross-sectional images of similar films of poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) prepared without nanoparticles.

4.3.2 Gas Separations with Nanoparticle-containing Membranes

4.3.2.1 Effect of Nanoparticle Loading on CO₂/H₂ Selectivity and Permeability

The gas permeability of MMMs is traditionally interpreted via a Maxwell model, which uses the theory for electrical conduction through a heterogeneous medium to obtain the exact solution for the conductivity of randomly distributed and non-interacting homogeneous solid spheres in a continuous matrix.²⁰ The Maxwell model (or its refinements) satisfactorily describes MMMs with very permeable fillers such as zeolites.²¹ However, Freeman and coworkers discovered that mixing SiO₂ particles in glassy, amorphous poly(4-methyl-2-pentyne) membranes significantly enhance the permeability and selectivity. The improvement is beyond predictions by the Maxwell model, and the enhancement may stem from free volume generated between the nanoparticles and the polymer.²²

Unlike most nanocomposite membranes, the nanoparticles in my membranes should be anchored to the surrounding polymer due to polymerization from immobilized initiators. The covalently modified nanoparticles may offer more stable MMMs than simple blends, but the effect of covalent grafting on permeability is unknown. With the monomer concentration fixed at 0.67 M, and the monomer composition of 37.5% PEGMEMA-475, 37.5% PEGMEMA-1100 and 25% PEGDA, the amount of nanoparticle loading should depend on the amount of initiator-modified SiO₂ nanoparticles in the monomer solution. We performed a series of experiment that altered the nanoparticle loading in poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) films to find the highest permeability and selectivity for gas separations. Figure 4.4 shows the SEM images of cross-sections of nanocomposite membranes prepared with different amounts of initiator-modified particles. The film thickness measured from SEM images is crucial for calculating gas permeability, which is equal to permeance multiplied by film thickness. For every membrane, at least five thickness measurements from

different areas were performed, and the average value is used for permeability calculations.



Figure 4.4. SEM images of cross-sections of nanoparticle-containing membranes. The nanoparticle concentrations in monomer solutions were 0 mg/mL (A), 0.18 mg/mL (B) and (C), 0.45 mg/mL (D), 0.9 mg/mL (E), and 2.7 mg/mL (F). The film in (B) was grown

from a RC membrane, and all other nanocomposite membranes were grafted from alumina. The black lines indicate the beginning and ending of the grafted polymer film. For samples with seemingly unclear polymer-substrate boundaries, the beginning of the film is determined by checking the difference of layer stability in the electron beam.

Figure 4.5 illustrates the effect of nanoparticle concentration in the monomer solution on the resulting membrane's CO₂/H₂ selectivity. Both selectivity and permeability data represent the average of values from at least two membranes that were prepared under the same condition. Within the region of 0-2.7 mg/mL nanoparticle concentration, CO₂ permeability reached a maximum of 79.0 ± 1.2 Barrer at 0.45 mg/mL. The membranes with 0.18 mg/mL nanoparticles in the monomer solution were synthesized using RC substrates (Figure 4.4). The top of the RC membrane is not as flat as porous alumina (SEM image of a bare RC membrane is in Chapter 3, page 99), and this is perhaps the reason that the permeability varies more on RC than with alumina substrates. Comparing the permeability of nanoparticle-containing membranes with the PEGMEMA-1100-co-PEGMEMA-475-coated membranes ($P_{CO2} = 20$ to 60 Barrers, Chapter 2) and cross-linked PEGMEMA-PEGDA 25% film ($P_{CO2} = 5$ to 15 Barrers, Chapter 3), the permeability of nanocomposite membrane is higher when the concentration of nanoparticles in the monomer solution is 0.45 mg/mL. The CO₂/H₂ selectivity may increase with 0.45-0.9 mg/mL nanoparticles during polymerization, but the scatter in the data prevents a definite conclusion. The fact that mixed gas selectivity is generally smaller than pure gas selectivity. 2^{22} and the pure gas selectivity of PEGMEMA-1100-co-PEGMEMA-475 films is about 13, shows that the maximum selectivity of nanocomposite membrane is almost the same as PEGMEMA-1100-*co*-PEGMEMA-475 film if not larger.



Figure 4.5. The influence of nanoparticle concentration during polymerization on CO_2 permeability (left) and CO_2/H_2 selectivity (right) of membranes coated with poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700). The monomer ratio of PEGMEMA-1100, PEGMEMA-475 and PEGDA is 3:3:2.

Higher concentrations of nanoparticles in polymerization solutions gave decreases in permeability for the nanocomposite membrane. Previous studies of MMMs indicated an increase in permeability of permeate gas due to either an increase of FFV,⁵ and transport through permeable particles such as zeolites.¹² In my case, the nanoparticles embedded in the polymer films are tightly surrounded with covalently grafted polymer, which may lead to different interfaces between nanoparticles and polymers compared to simple blending. As Figure 4.6 (A) and (B) illustrate, the interface between nanoparticles and polymers should contain less voids with grafting from nanoparticles than with blended polymer/nanoparticle films. The size of the free volume around SiO₂

nanoparticles mixed with poly(4-methyl-2-pentyne) ranges from 0.02 nm to 1 nm according to the PALS.^{5,23} Gas transport is very sensitive to the size of the free volume. For example, the kinetic diameters of N_2 and O_2 are 3.64 Å, and 3.46 Å.⁶ Despite a difference in diameter of only 0.18 Å, a small difference in the size of free-volume elements dramtically impacts diffusion.²⁴ Spontak and co-workers studied the effect of embedding of SiO₂ nanoparticles by blending and covalently bonding. The nanoparticles modified with methacrylate on the surface were able to incorporate into surrounding polymer chains. The methacrylate-coated nanoparticles covalently bonded to the polymer decreased CO₂ permeability compare to a film without nanoparticles. However, hydroxyl-terminated nanoparticles did not reduce the permeability as much.²⁵ With polymer covalently linked to the nanoparticles, the inclusion of the particles likely does not increase free volume to enhance permeability. In such a case, the nanoparticle is simply an obstacle for gas permeation. In my study, at high loading the nanoparticles in the films likely acted as obstacles in the permeation pathway. However, there are cases (0.45 mg/mL nanoparticle loading) where the permeability of CO₂ in the nanocomposite film compare is higher than in the corresponding poly(PEGMEMA-1100-co-PEGMEMA-475-co-PEGDA-700) film without nanoparticles (Figure 4.5). At low loadings, the nanoparticles may create some free volume.



Figure 4.6. Illustration of the space between nanoparticles and the polymeric matrix embedding the particles. A) The nanoparticles contain grafted polymer prepared by surface-initiated ATRP; B) the nanoparticles are blended in the polymer matrix, there is no covalent bond between nanoparticle and polymer; C) the nanoparticles contain grafted polymer grown by surface-initiated ATRP with lower initiator density.

The elasticity of PEGMEMA-*co*-PEGDA may also affect changes in free volume upon incorporation of nanoparticles in the membrane. According to Pechar and co-workers,⁸ the rigid nature of glassy polymers surrounding nanoparticles creates free volume. In contrast, embedding nanoparticles in rubbery, cross-linked co-polymers may create much less free volume. Base on the T_g of -47 °C for poly(PEGMEMA-475-*co*-PEGDA) wih 50% of each monomer,²⁶ I expect, poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) is also rubbery at room temperature. Thus, the permeability and selectivity poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) may not change greatly upon nanoparticle incorporation.

4.3.2.2 Influence of Nanoparticle Initiator Density on Gas Permeation Through Nanoparticle-containing Films

As Figure 4.6 (A) illustrates, nanoparticles coated with grafted polymer and encapsulated in a cross-linked polymer film may not increase free volume as much uncoated nanoparticles physically blended into a film. However, although the voids between nanoparticles increase with particle loading, eventually the voids will create a non-selective path. A number of recent studies indicated that nanoparticle blending in membranes has this limit,^{5,12} and the unstable nature of such MMMs may be an problem for their application. Perhaps if the nanoparticles had a low density of initiator on the surface, covalent bonds could still stabilize nanocomposite membranes without decreasing the induced increases in free volume (Figure 4.6 (C)). Moreover, the covalently bonded nanoparticles may not create a non-selective path as easily as the blended in nanoparticles.

According to kinetics studies of the reaction of chlorosilanes with SiO_2 surfaces,²⁷ the rate is first order with respect to monochlorotrimethylsilane concentration and hydroxyl group density on the SiO₂ surface. Moreover, after 10 min only 53% percent of the reaction has occurred. Assuming the dimethylmonochlorosilane initiator, $Cl(CH_3)_2Si(CH_2)_{11}OCOC(CH_3)_2Br$, has a similar reaction rate, a 10 min time for initiator attachment to nanoparticles would derivatize only half of the reactive surface hydroxyl groups. The resulting nanoparticles embedded in a polymeric matrix may be more like Figure 4.6 (C) than Figure 4.6 (A). Figure 4.7 shows the SEM images of cross-

sections of nanocomposite membranes prepared using nanoparticles derivatized with initiator for only 10 min. The averaged film thicknesses measured from at least two images (at least eight measurements) were used for the gas permeability calculations.



Figure 4.7. SEM images of cross-sections of alumina membranes coated with a poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) film containing nanoparticles. The polymerization solution contained 0.25 M PEGMEMA-1100, 0.25 M PEGMEMA-475, 0.17 M PEGDA, 2.0 mM CuCl, 0.60 mM CuBr₂, 6.0 mM HMTETA and SiO₂ nanoparticles. The concentrations of nanoparticles in the monomer suspension were 0.18 mg/mL (A) and 1.35 mg/mL (B). The polymerization time was 30 min.

Figure 4.8 shows permeability and selectivity data for nanoparticle-containing poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) membranes prepared with SiO₂ nanoparticles reacted with initiators for 6 h (squares) or only 10 min (triangles). The similarity between the two types of membranes may occur because at high initiator density, steric constraints prohibit ATRP from occurring at all initiation sites. Thus the two types of nanoparticles may contain similar densities of chains grafted to the surface. Data from Kim et al. suggest that ATRP uses only 10% of the initiators in monolayers on gold.²⁸



Figure 4.8. The effect of initiator attachment time on CO_2 permeability (left) and CO_2/H_2 selectivity (right) of porous alumina membranes coated with poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) nanoparticle-containing films. The open circles indicate membranes prepared with SiO₂ nanoparticles reacted with silane initiator for over 6 hr, and the open triangles indicate membranes prepared with SiO₂ nanoparticles reacted with

Figure 4.9 is the summary of CO₂/H₂ selectivity and CO₂ permeability data from this

section. The black line indicates the upper bound of CO_2/H_2 separations given by Freeman. Unfortunately, although the nanoparticle-containing membranes approach the upper bound, they do not cross it.



Figure 4.9. The upper bound $line^{29}$ of CO₂/H₂ separations and data for membranes composed of alumina coated with poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) nanoparticle-containing films. Filled diamonds represent nanocomposite membranes synthesized with nanoparticles reacted with initiator for 6 h, and open triangles represent corresponding membranes with nanoparticles reacted with initiator for only 10 min.

4.4 Conclusions

Surface-initiated ATRP of PEGMEMA-1100, PEGMEMA-475 and PEGDA in the presence of initiator-modified SiO_2 nanoparticles gave a membrane with covalently embedded nanoparticles. The nanoparticles introduced in the polymer film did not promote the CO_2/H_2 selectivity or CO_2 permeably significantly. Further studies of grafting density on the nanoparticles suggests that the free volume is not affected by the initiator density on the nanoparticles, at least at high density (>0.5). However, there may be an effect at much lower initiator density.

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Chapter 5 An Investigation of the Rapid Surface-initiated Polymerization of PEGMEMA

In chapters 3 and 4, studies of poly(PEGMEMA-1100-*co*-PEGMEMA-475) and poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) brushes showed an unusually rapid growth of these films from porous alumina. A 30-min surface-initiated polymerization often yields 100 µm-thick films. This chapter examines possible reasons for these remarkable growth rates. I simultaneously grow brushes on both sides of porous alumina to prove that the fast polymerization is not due to precipitation. Film thickness increases non-linearly with monomer concentration, showing that the process is not a simple first-order polymerization. Kinetic studies of in-solution polymerization of poly(PEGMEMA-1100-*co*-PEGMEMA-475) and poly(PEGMEMA-475) that the most probable reason behind the rapid polymerization is that a high concentration of PEGMEMA-1100 alters solvent polarity to enhance catalyst activity.

5.1 Introduction

5.1.1 Growth of Thick Polymer Films from Porous Alumina

Chapters 3 and 4 discussed the synthesis of cross-linked poly(PEGMEMA-*co*-PEGDA) and nanoparticle-containing poly(PEGMEMA-*co*-PEGDA) films from porous supports. Remarkably, when grown from porous alumina, these films are as thick as 200 μ m (Figure 5.1) after just 30 – 45 min of polymerization. In many previous studies, surface-initiated polymerization of other monomers yielded films with thicknesses of

only a few nm in a similar time.¹ Huang and co-workers reported a rapid polymerization of poly(*tert*-butyl acrylate) brushes, but the ellipsometric thickness of the film on SiO₂ was still only 200 nm after 20 min of polymerization.² A few studies reported "rapid", surface-initiated ATRP (SI-ATRP) of PEG-based monomers. Xu and coworkers polymerized PEGMEMA-360 from oxidized silicon to achieve a film thickness of 38 nm in 4 h.³ All of these thicknesses are several orders of magnitude lower than the thicknesses of the poly(PEGMEMA-1100-*co*-PEGMEMA-475) films that I prepared on porous alumina with a 30-min polymerization. An understanding of the exceptionally fast PEGMEMA polymerization from porous alumina is vital for reducing the thickness of membrane skins to improve membrane permeance.



Figure 5.1. SEM images of cross-linked poly(PEGMEMA)-based films grown from porous alumina. (A) poly(PEGMEMA-*co*-PEGDA), PEGDA molar fraction of 25%. (B) poly(PEGMEMA-*co*-PEGDA) film with SiO₂ nanoparticles, PEGDA mole fraction of 10%. (C) poly(PEGMEMA-1100-*co*-PEGMEMA-475) The total monomer concentration in the polymerization solution was 0.67 M, and 0.34 M for (C); catalyst concentrations were CuCl- 2 mM, CuBr₂- 0.67 mM and HMTETA- 6 mM. Polymerization times were 120 min for (A) and 30 min for (B) & (C).

At least three factors might contribute to the exceptional thickness of poly(PEGMEMA) on alumina. (1) The high porosity of the alumina may lead to a much higher amount of immobilized initiator than the formation of initiator monolayers on flat surfaces such as oxidized silicon wafers. However, a recent study of poly(N-isopropylacrylamide) (PNIPAM) growth from initiators on flat and etched silicon wafers suggested that the increased surface area of the etched wafer did not enhance the rate of

ATRP.⁴ (2) Formation of polymer in solution and subsequent precipitation on the face of the membrane could yield thick films. (3) The monomer/water mixture may provide a solvent that is especially favorable to ATRP. Armes showed that the presence of water sometimes enhances the rate of ATRP, presumably because the solvent favors the Cu(II) form of the catalyst to promote the formation of active chains.⁵ After briefly reviewing aqueous ATRP below, this chapter examines whether precipitation or solvent effects might account for the extremely rapid growth of poly(PEGMEMA-1100-*co*-PEGMEMA-475) brushes from porous alumina.

5.1.2 Aqueous ATRP

ATRP can occur in neat monomer, in a solution,⁵ or in a heterogeneous system (e.g., an emulsion).⁶ "Various solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide, and others were used for different monomers."⁷ Coca et al. reported the first aqueous ATRP. Polymerization of 2-hydroxyethyl acrylate (HEA) at 90 °C for 12 hr gave 87% conversion with $M_n = 14,700$ and a polydispersity index (PDI, M_w/M_n) of 1.34. Compared with neat polymerization, the reaction rate was slightly slower (90 °C polymerization for 10 hr in neat monomer gave 92% conversion) and the PDI (1.2 for neat polymerization) was higher.⁸ Armes later reported aqueous ATRP of a carboxylate-containing monomer. After polymerization for 10 h at 90 °C, sodium methacrylate

conversion reached 70-80% with a PDI of 1.2-1.3.⁹ The Armes group also reported aqueous ATRP of PEGMEMA-408 (also called methoxy-capped oligo(ethylene glycol) methacrylate, OEGMA in the original reference). Compared to neat monomer, the presence of water accelerated the ATRP significantly. With the same concentration of catalyst, 2.2'-bipyridine and CuCl, the aqueous polymerization reached 90% monomer conversion in 20 min, whereas the neat polymerization required 15 h for comparable conversion. The PDI resulting from aqueous polymerization was also slightly lower than for the neat monomer: 1.15-1.30, and 1.30 respectively.^{5,10} According to Wang and Armes, this accelerating effect of water may occur because a) the catalyst is very active in polar solvent; and b) "since OEGMA is a sterically congested monomer, its termination rate constant is several orders of magnitude lower than that of conventional methacrylates, which is expected to lead to improved living character."⁵ Ye and Narain studied ATRP of N-isopropylacrylamide (NIPAM) in water and water-organic solvent mixtures. At room temperature, NIPAM ATRP in organic solvents follows wellcontrolled first-order kinetics, but in both water and water-organic solvent mixtures (organic:water 4:1 or 3:1) the polymerization is very rapid and shows significant termination. However, when performed at 0 °C, the aqueous polymerization yields molar masses that increase linearly with conversion and pseudo-first-order kinetics.¹¹

Aqueous ATRP is very convenient for synthesis of water-soluble polymers. Perruchot et al. successfully polymerized poly(PEGMEMA) from the surface of SiO_2 nanoparticles.¹² Later, Wang and co-workers performed similar SI-ATRP from Au nanoparticles. They successfully grafted poly(PEGMEMA) on Au nanoparticles through a DNA-modified initiator.¹³ A few recent studies of (poly(2-dimethylamino)ethylmethacrylate) (PDMAEMA) and PEGMEMA block copolymer films binding with DNA through polyanion-polyanion electrostatic forces. The binding of active DNA indicated the block-copolymer has some potential of gene delivery applications.^{14,15}

5.2 Experimental

5.2.1 Chemicals and Materials

PEGMEMA monomers with $M_n = 475$ Da (PEGMEMA-475), and $M_n = 1,100$ Da (PEGMEMA-1100) as well as PEGDA M_n =700 Da were obtained from Aldrich. All monomers contain both 100 ppm 4-methoxyphenol and 200 or 300 ppm 2,6-di-*tert*-butyl-4-methylphenol as inhibitors and were used as received. Proton NMR spectra show that the average numbers of ethylene oxide units in PEGMEMA-475, and PEGMEMA-1100 are 8.8, and 23.1, respectively (Figure 2.1).¹⁶ 2-Bromoisobutyryl bromide (BiBB) (98%), CuCl (99.995%), CuBr₂ (99.999%), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%) were purchased from Aldrich, and deionized water was obtained using a Millipore system (Milli-Q, 18.2 MΩ•cm). Triethylamine (TEA) and DMF (99.8%) were purchased from Jade Scientific and used as received. THF was distilled over sodium metal with benzophenone. The porous alumina substrates were Anodisc membrane filters (25 mm disks with 0.02 μm surface pores) purchased from Whatman. Silicon (100) wafers were obtained from NOVA Electronic Materials. Silane initiator, $Cl(CH_3)_2Si(CH_2)_{11}OCOC(CH_3)_2Br$,¹⁷ and a water-soluble initiator, $CH_3(OCH_2CH_2)_3OCOC(CH_3)_2Br$,⁵ were prepared by literature methods. A gas cylinder containing 50% CO₂ and 50% H₂ was purchased from Praxair.

5.2.2 Polymerization

5.2.2.1 Initiator Attachment

Initiator attachment to both alumina membranes and oxidized silicon wafers was performed by soaking UV-Ozone cleaned (15 min) substrates in 1 mM dimethylchlorosilane initiator, $Cl(CH_3)_2Si(CH_2)_{11}OCOC(CH_3)_2Br$, in THF overnight. The membranes were then rinsed with 5 mL THF three times and dried with flowing N₂. In a few cases, the alumina membranes were rinsed by flowing 5 mL THF through the membrane using a peristaltic pump. The two rinsing method made no significant difference in the thickness of the resulting polymer brush.

5.2.2.2 Catalyst Solution

A catalyst stock solution was prepared by adding 0.0596 g (0.6 mmol) of CuCl and 0.0450 g (0.2 mmol), CuBr₂ and 490 μ L (1.8 mmol) of HMTETA ligand into degasse 30.0 mL deionized H₂O. Detail of this step is described in (Chapter 3, page 88). The nominal mole ratio was Cu⁺:Cu²⁺:HMTETA was 3:1:9.

5.2.2.3 SI-ATRP

The monomer solution was prepared by dissolving the desired amount of monomer in water and degassing via four freeze, pump, thaw cycles. Monomer solution and initiator-modified alumina membranes were transferred into the N₂-filled glove bag with the catalyst solution. The polymerization mixture was prepared by combining degassed monomer and catalyst solutions in a 9:1 volume ratio to produce a light blue solution containing 0.67 M monomer, 2.0 mM CuCl, 0.60 mM CuBr₂, and 6.0 mM HMTETA. The initiator-modified membranes were immersed in the polymerization solution for designated periods of time, and the resulting polymer films were rinsed with 5 mL DMF three times followed by 5 mL of ethanol three times and drying under a N₂ stream.

5.2.2.4 Solution ATRP

Monomer solutions were prepared similarly to solutions for SI-ATRP, except that water-soluble initiator, CH₃(OCH₂CH₂)₃OCOC(CH₃)₂Br, was added to the monomer solution before freeze, pump, thaw cycles. The catalyst solution was added to degassed monomer solution to start the polymerization. The reaction mixture was vigorously stirred. Catalyst concentrations were the same as in surface-initiated polymerization.

5.2.3 Characterization Methods

Scanning electron microscopy (SEM) was performed mainly with a JEOL semiin-lens cold cathode field-emission scanning electron microscope, model JSM-7500F, operating with an r-filter in signal maximum mode. Samples were sputter coated with 10 nm of Osmium prior to imaging. A few SEM images were obtained with a JEOL 6400V instrument with a LaB6 emitter (Noran EDS). The samples for the JEOL 6400V were coated with 8 nm of gold before of imaging.

Nuclear Magnetic Resonance (NMR) spectra of the reaction mixture were obtained with a Varian 500 MHz superconducting NMR-Spectrometer operating at 499.738 MHz and interfaced with a Sun Microsystems Ultra5 UNIX console.

Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC was performed at 35 °C in DMF using a PLgel 20 μ m MIXED-B column at a flow rate of 1 mL/min. Two detectors were used: a Waters R410 differential refractometer and a Waters 996 photodiode array. The concentration of the polymer samples was approximately 1 mg/mL, and each solution was filtered through a Whatman 0.2 μ m PTFE filter before injection. Molecular weights are reported relative to monodisperse polystyrene standards.¹⁸

5.3 Results and Discussion

5.3.1 Does Precipitation Increase Film Thickness

Precipitation of polymer on the membrane might explain the exceptionally high film thicknesses on porous alumina. However, NMR spectra of the monomer solution after growth of the poly(PEGMEMA-1100-*co*-PEGMEMA-475) (PPEGMEMA) from the surface show that little polymer is present in solution. (The only initiator is that attached to the substrate.) In the spectrum in Figure 5.2, there is no signal at 1 ppm, so the signature peak of CH₃ from the polymerized methacrylate backbone is absent. Strong signals from the alkene protons (5.62 and 6.0 ppm) indicate the presence of extensive monomer in the solution. This experiment is not definitive proof, however, that there is no precipitation because if polymer were extremely insoluble, it would not remain in solution. Nevertheless, the extent of polymerization in solution is minimal.



Figure 5.2. NMR spectrum of the monomer and catalyst mixture (contains CuCl, CuBr₂ HMTETA, PEGMEMA-1100 and PEGMEMA-475) after surface-initiated polymerization from a porous alumina membrane. The absence of a PPEGMEMA signal in region \boldsymbol{b} and the large peak \boldsymbol{a} for PEGMEMA show that there is little polymer in solution.

Typically, we grow poly(PEGMEMA-1100-*co*-PEGMEMA-475) brushes with the alumina in a holder that exposes only the top surface of the membrane (Figure 5.3, left). In this apparatus, precipitating polymer should settle on the membrane. To better examine whether precipitation contributes to film thickness, we also mounted the membrane in the middle of the reaction mixture (Figure 5.3, right) and compared the films thicknesses on the two sides of the membrane. As Figure 5.4 shows, exposing only the top face of the membrane to the polymerization solution yields a thick films only on

the top face of the membrane. In contrast for the membrane in the middle of the polymerization solution, thick films form on both sides of the membrane. Precipitation should not increase the thickness of the film on the bottom of the membrane because the precipitate should settle on the bottom of the reaction vessel not on the membrane. Nevertheless, these films are still 48 µm thick after 15 min of reaction.



Figure 5.3. Illustration of different positions of an initiator-modified alumina substrate in a monomer-catalyst mixture during polymerization. On the left only the top of the membrane is exposed to monomer and catalyst, whereas on the right both sides are exposed to the solution



Figure 5.4. SEM images of the cross sections of membranes modified with poly(PEGMEMA-1100-*co*-PEGMEMA-475) brushes. The condition for polymerizations are [CuCl]=2 mM, [CuBr₂]=0.67 mM, [HMTETA]=6 mM, and PEGMEMA-

1100:PEGMEMA-475=1:1, monomer total concentration is 0.34 M. (A) Only the top side of the membrane was exposed to the monomer solution (B) Both sides of the membrane were exposed to the monomer solution.

Figure 5.5 compares the film thicknesses on the top and bottom faces of a number of membranes modified by polymerization with times ranging from 10 to 30 min. The poly(PEGMEMA-1100-*co*-PEGMEMA-475) brush thickness increased with polymerization time, and the difference in the film thickness on the top and bottom face of the membrane is typically less than a factor of 2. Note that the alumina membrane has different pore sizes on each side. The pore size on the top is 0.02 μ m, and that on the bottom is 0.2 μ m. This difference in pore size might explain the small differences in thickness of the membranes. Overall, the high thickness of films on the bottom face of the membranes suggests that precipitation is not responsible for the exceptionally high film thickness.



Figure 5.5. Evolution of poly(PEGMEMA-1100-*co*-PEGMEMA-475) thickness with polymerization time for films grown from both the top and bottom faces of initiator-modified porous alumina. The diamonds indicate the side of the membrane facing up, and the circles represent the side facing down. The error bars indicate the standard deviation of multiple SEM thicknesses on at least two membranes prepared under identical conditions. The conditions for polymerization were [CuCl]=2 mM, [CuBr₂]=0.67 mM, [HMTETA]=6 mM, and PEGMEMA-1100:PEGMEMA-475=1:1, total monomer concentration is 0.17 M.

5.3.2 The Effect of Monomer Concentration on Film Thickness

In controlled polymerization (minimal termination), the reaction rate is proportional to the monomer concentration.¹⁹ To investigate the kinetics of PEGMEMA polymerization, I grew poly(PEGMEMA-1100-*co*-PEGMEMA-475) brushes from porous alumina using total monomer concentrations ranging from 0.04 to 0.34 M. The relative molar ratio of PEGMEMA-1100 and PEGMEMA-475 was 1:1 and the

polymerization time was 30 min. Figure 5.2 shows some representative SEM images of film cross-sections, and I determined film thicknesses using at least two images (5 measurements) for a given film.



Figure 5.6. SEM images of poly(PEGMEMA-1100-*co*-PEGMEMA-475) films grafted from porous alumina. The monomer concentrations and film thicknesses are A) 0.34 M, $150.0 \pm 9.2 \,\mu\text{m}$, (B) 0.17 M, $93.7 \pm 2.7 \,\mu\text{m}$, (C) 0.084 M, $19.7 \pm 1.2 \,\mu\text{m}$ and (D) 0.042 M, $775 \pm 120 \,\text{nm}$. The monomer concentration is the sum of PEGMEMA-1100 and PEGMEMA-475. The monomers were present in a 1:1 ratio, and polymerization times were 30 min.

Figure 5.3 shows film thickness as a function of the total monomer concentration.

The film thickness increases faster than expected as the monomer concentration increases.

In particular, when the monomer concentration doubles from 0.077 to 0.17 M, the film

increases 5 fold, from 19.7 to 100 μ m. Higher concentrations of monomers likely alter the polarity and viscosity of the reaction mixture to accelerate the reaction.



Figure 5.7. Thicknesses of poly(PEGMEMA-1100-*co*-PEGMEMA-475) brushes as a function of monomer concentration. The brushes were grown for 30 min from initiators immobilized on porous alumina. The monomer concentration is the sum of the two monomers, which were present in a 1:1 ratio. The error bars indicate the standard deviation of multiple thickness measurements on at least two membranes prepared under identical conditions, [CuCl]=2 mM, [CuBr₂]=0.67 mM, [HMTETA]=6 mM, and PEGMEMA-1100:PEGMEMA-475=1:1. The polymerization time was 30 min in all cases.

5.3.3 In-solution Polymerization of PEGMEMA

To help us understand the rapid, surface-initiated polymerization of poly(PEGMEMA-1100-*co*-PEGMEMA-475) from porous alumina, we also examined
polymerization from initiators in solution. Table 5.1 summarizes results from in-solution polymerizations that employed the same monomer and catalyst concentrations as the surface-initiated polymerization. The only variation with respect to polymerization from a surface was the monomer:initiator ratio, which of necessity was much lower than in surface-initiated polymerization. All solution reactions were quenched by bubbling air through the samples for 30 s.

Table 5.1. Characterization of the polymer resulting from copolymerization of PEGMEMA-1100 and PEGMEMA-475 initiated by $CH_3(OCH_2CH_2)_3OCOC(CH_3)_2Br$ The reaction was catalyzed by [CuCl]- 2 mM, [CuBr₂]- 0.67 mM and [HMTETA]- 6 mM, in water at room temperature. Each monomer initially was present at 0.34 M. The conversions are calculated via integration of the NMR signals from the –CH₃ group on the polymethacrylate back bone and the vinyl protons of the unreacted monomer.

Monomer: Initiator	Reaction Time (min)	Conversion %	M _n by GPC	PDI
300:1	30	99.0	203000	5.71
300:1	2	83.9	216000	2.61
1600:1	20	~0	1100	-
200:1	0.5	89.8	112000	2.31
200:1	3.5	93.0	166000	2.92

The conversion data show that the reaction is very rapid. For the 200:1 monomer: initiator ratio, the reaction is 90% complete in 0.5 min. However, PDI values >2 show that the resulting polymers have a broad range of molecular weights. This suggests a relatively uncontrolled reaction, where either polymerization is much faster than initiation and/or significant termination occurs. When the monomer:initiator ratio was

1600:1, the reaction did not yield significant amounts of polymer. This might occur in part because we did not remove the inhibitors from the monomers. The monomer: inhibitor ratio is 480:1, so the ratio of inhibitor to initiator was 3:1 in the solution with a 1600:1 monomer: initiator ratio. Notably, the reaction was much faster when the monomer: initiator ratio decreased from 300:1 to 200:1. A higher initiation efficiency combined with a larger amount of initiator may increase the polymerization rate. However, the M_n value did not drop drastically on going to from a monomer:initiator ratio of 300:1 to 200:1, which suggests that the initiation efficiency did not change by even a factor of 2.

In a study by Armes and co-workers, ATRP of PEGMEMA (contains repeating PEO units) in water (catalyzed by CuCl and bpy) was much faster than polymerization of neat monomer. We performed copolymerization of PEGMEMA-475 under the same conditions (Table 5.2, reaction 1 lists the conditions).⁵ and compared the results with polymerization of PEGMEMA-475 using the catalyst we employed in surface-initiated polymerization (Table 5.2, reaction 2). Additionally, we copolymerized PEGMEMA-475 and PEGMEMA-1100 (Table 5.2, reaction 3). We examined the kinetics of the polymerization by periodically taking a small aliquot from the reaction mixture, quenching the polymerization by bubbling with air for 30 s, and subsequently examining the aliquot NMR spectrum.

Table 5.2. Different conditions for PEGMEMA polymerization initiated by $CH_3(OCH_2CH_2)_3OCOC(CH_3)_2Br$ in solution. Reactions 1 and 2 employed PEGMEMA-475 as the monomer, but reaction 3 used equimolar PEGMEMA-475 and PEGMEMA-1100 with the total monomer concentration listed.

Reaction	Monomer (mM)*	Monomer:Initiator Ratio	CuCl (mM)	CuBr ₂ (mM)	Ligand (mM)
1	1634	33:1	49	0	bpy, 90
2	1634	33:1	2	0.67	HMTETA, 6
3	336	200:1	2	0.67	HMTETA, 6

* The monomer concentration for reaction 3 is limited because the maximum PEGMEMA-1100 monomer concentration is 0.9 M in pure monomer.



Figure 5.8. Evolution of monomer conversion with time for polymerization of PEGMEMA-475 (diamonds-bpy catalyst, reaction 1, and circles-HMTETA catalyst, reaction 2) and a PEGMEMA-1100, PEGMEMA-475 mixture (triangles, reaction 3). Table 5.2 lists the reaction conditions.

Figure 5.8 shows monomer conversion versus time for the reactions in Table 5.2. Under similar conditions, Armes achieved 80% conversion in 24 min, Mn=12500, PDI=1.2,⁵ and I obtained 95% conversion in 22 min, Mn=16100, PDI=1.36). Note that the monomer PEGMEMA-475 contains 1.5 more PEO units than the PEGMEMA that Aarmes reported. Comparing the rates of reactions 1 and 2, the HMTETA catalyst system (circles) gives lower rates than the bpy catalyst for polymerization of PEGMEMA-475. Note that the concentration of Cu^I for the HMETEA catalyst system is about 10 times less than the Cu^I concentration in the bpy system. GPC gives PDI values of 1.34 and 1.40, for polymerization of PEGMEMA-475 from the bpy and HMTETA catalysts, respectively. This result suggests that the rapid polymerization of poly(PEGMEMA-1100-co-PEGMEMA-475) from the surface was probably not simply due to the high activity of the HMTETA catalyst. However, the presence of PEGMEMA-1100 in the monomer mixture increases the initial polymerization rate by an order of magnitude or more (triangles, Figure 5.8). PEGMEMA-1100 has a very long PEO side chain that swells in aqueous solution, and the monomer itself might serve as a solvent that accelerates polymerization. Future studies will investigate polymerization of PEGMEMA-475 in the presence of oligo ethylene glycol to see if this increases polymerization rates. We suspect that changing the polarity of the solvent increases the activity of the catalyst to give a rapid, uncontrolled polymerization. Chapter 2 described surface-initiated growth of poly(PEGMEMA) films with three monomers that had different PEO side chain lengths (PEGMEMA-300, PEGMEMA-475, and PEGMEMA-1100) using a catalyst solution prepared in DMF. The resulting polymerization rate from

Au did not reveal a dramatic impact of monomer side chain length on film thickness. The combination of water and PEGMEMA is likely necessary to see the dramatic increase in polymerization rate.

5.4 Conclusion

This chapter discussed why the synthesis of poly(PEGMEMA-1100-*co*-PEGMEMA-475) films from porous alumina yields unusually thick films (100 μ m in 30 min). This rapid polymer brush growth is several orders of magnitude faster than previous results.² NMR results indicate that the reaction mixture did not polymerize greatly in solution, and precipitation does not appear to contribute to film growth. By altering the monomer concentration and comparing in-solution polymerization with work from other groups, we think the most probable reason for the extremely rapid surface-initiated polymerization is a change in the solvent characteristics for aqueous solutions containing large amounts of PEGMEMA-1100. However, the details behind acceleration of the polymerization need further study.

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Chapter 6 Summary and Future Work

This thesis discussed a few topics centered CO_2/H_2 separation membranes developed on porous substrates. Chapter 1 introduced the topic of hydrogen economy, and the separation techniques for CO_2 and H_2 . Additionally, this chapter also introduced solution-diffusion model, which provided the guide of material selection for reverseselective CO_2/H_2 separation membranes. Atomic Transfer Radical Polymerization (ATRP) is a robust method of developing a selective skin, and is used for all the studies of this entire thesis. Thus, a summary of ATRP mechanisms and each component is gathered in chapter 1 as well.

Chapter 2 is represented the development on grafting a poly(ethylene glycol methyl ether methacrylate) PEGMEMA-1100 and PEGMEMA-475 copolymer film from porous alumina surface. The copolymer film successfully stopped PEGMEMA-1100 side chain from crystallization without compromising the selectivity. Reflectance FTIR data was used to study the film composition, and the how the composition affects the gas separation properties.

Chapter 3 experimented the development of poly(PEGEMEMA) and poly(PEGMEMA-1100-*co*- PEGMEMA-475-*co*-PEGDA-700) cross-linked co-polymers. By cross-linking, the nanocomposite membranes are prepared by introducing surface-

initiated SiO_2 nanoparticles. Chapter 4 focused on this nanocomposite membrane, how it is prepared and the gas separation properties are tested.

Chapter 5 is an investigation of an ultra-rapid polymerization of PEGMEMA-1100 and PEGMEMA-475 in aqueous media. The polymer film thickness is usually about 100 μ m from 30-45 min of polymerization. A few controlled experiments were performed to approach the reason of this ultra-fast polymerization. With more understanding of the polymerization kinetics, thinner poly(PEGMEMA) films could be prepared in the future for fast CO₂/H₂ separation.

With the work presented in this thesis the reported reverse-selective polymeric membranes in the literature, I now want to propose some future work in this area. The first is the nanocomposite membranes with covalently bonded nanoparticles embedded. As discussed in chapter 4, the main reason that the nanoparticles failed to enhance the permeability and selectivity could be the elasticity of rubbery poly(PEGMEMA-1100-*co*-PEGMEMA-475-*co*-PEGDA-700) film is rubbery. Kalakkunnath and co-workers studied the impact of the cross-link segments on the polymer's transition temperature.¹ Thran reported the fraction of free volume (FFV) impact on gas separation properties in glassy polymer.^{Lin}, H. & Freeman, B. D. *J. Molec. Structr.* **2005** 739, 57-74. Freeman and Lin provided a detailed material selection guide for reverse-selective gas separation membranes.³ Glassy polymer that is suitable for CO₂/H₂ separation combined with SI-ATRP on nanoparticles is promising in increasing the FFV and increase in the permeability and selectivity.

The other meaningful approach of study reverse-selective gas separation membrane is find a better support that is of less cost and ready to be packed in large spiral wound modules. At the same time, evaluation of membranes' gas separation properties in high temperature and high humidity conditions are very important.

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References

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