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ENZYME-INITIATED ADMICELLAR POLYMERIZATION

A Thesis

Presented for the Degree of

Master of Science in Engineering Science

Department of Chemical Engineering

The University of Mississippi

Elaheh Shakeri

May 2021

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ABSTRACT

Admicellar polymerization was developed in the 1980s as an economical method for modifying various surfaces. In admicellar polymerization, a low monomer to initiator (M/I) ratio was traditionally required to overcome this limitation and achieve high polymer conversion when oxygen was present in the headspace and dissolved in the reaction medium. To develop an environmentally friendly, cost-efficient, and feasible deoxygenation and initiation technique, we studied the use of glucose oxidase (GOx) in admicellar polymerization. In this method, GOx acts as the catalyst in the oxidation of β -D-glucose, while consuming oxygen and generating hydrogen peroxide and D-glucono- δ -lactone. There are many advantages of GOx to other deoxygenation techniques. First, GOx is produced in nature by various insects, plants, animals, and fungi; therefore, it is inexpensive and easily accessible. Also, this enzyme has shown persistent activity in aqueous and various organic solvents and has high thermal stability.

We hypothesized that GOx can both deoxygenate and initiate the polymerization system. Deoxygenation occurs by the consumption of oxygen and the formed hydrogen peroxide will initiate the polymerization in the absence of a thermal initiator. We examined the ability of GOx to successfully deoxygenate and initiate the admicellar polymerization of styrene using hexadecyltrimethylammonium bromide (C₁₆TAB) to form admicelles on the surface of silica particles. We compared the initiation performance of GOx to 4,4'-azobis(4-cyanovaleric acid) (V-501) and analyzed its deoxygenation ability compared to nitrogen-purged polymerizations.

The study showed that when the solution was not shaken during the deoxygenation process via GOx, the initiation capacity of GOx was limited, and its corresponding apparent conversions were lower than V-501 initiated admicellar polymerization. However, shaking the vial while the deoxygenation occurs resulted in both a higher conversion and higher equilibrium rate when compared to the thermal-initiated polymerization. After shaking the solution, enzyme-initiated admicellar polymerization reached a final apparent conversion of ~86% after 6 hours. Further, GOx performed exceptionally well as an oxygen scavenger when added to a polymerization system with a thermal initiator present. Low concentrations of GOx ($[GOx]=200$ nM) were able to deoxygenate the reaction medium as well as nitrogen purging and showed similar apparent conversion data of approximately ~80%.

DEDICATION

To Mom and Dad, for their unconditional love and endless support

LIST OF ABBREVIATIONS

M/I	Monomer to Initiator ratio
GOx	Glucose oxidase
CAC	Critical Admicelle Concentration
CMC	Critical Micelle Concentration
PZC	Point of zero charge
I	Initiator
$R \cdot$	Radical
M	Monomer
$P_n \cdot$	Active n-chain polymer
k_I	Initiator decomposition rate constant
k_p	Propagation rate constant
k_t	Termination rate constant
k_d	Desorption rate constant
R_p	Rate of polymerization
[M]	Monomer concentration in solution
$[M]_{ad}$	Monomer concentration in an admicelle
$[R^*]$	Radical concentration based on unit volume of solution

THF	Tetrahydrofuran
FTIR	Fourier-transform infrared
GPC	Gel permeation chromatography
PDI	Polydispersity
M_w	Weight-averaged molecular weight
RAFT	Reversible addition–fragmentation chain transfer polymerization
ATRP	Atom transfer radical polymerization
UV	Ultraviolet
PEGDA	poly(ethylene glycol)diacrylate
AAm	Acrylamide
BAAm	N, N'-methylenebisacrylamide
CTA	Chain transfer agent
VA-044	2,2'-Azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride
HEA	2-Hydroxyethylacrylate
DMAm	N,N-Dimethylacrylamide
MA	Methylacrylic acid
HPMA	N-(2-hydroxypropyl)methacrylamide
Enz-RAFT	Enzyme degassed reversible addition–fragmentation chain transfer polymerization
DP	Degree of polymerization
PET-RAFT	Photoinduced electron transfer reversible addition-fragmentation chain transfer

ICAR-ATRP	initiators for continuous activator regeneration atom-transfer radical polymerization
BMA	n-butylmethacrylate
BA	n-butylacrylate
QCM	Quartz crystal microbalance
LSPR	Localized surface plasmon resonance
C ₁₆ TAB	Hexadecyltrimethylammonium bromide
AIBN	2,2'-Azobis(2-methylpropionitrile)
V-501	4,4'-Azobis(4-cyanovaleric acid)
SAB	Sodium acetate buffer
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
TGA	Thermogravimetric analysis
rpm	Revolutions per minute

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CHAPTER I

1 Introduction

1.1 Precipitated silica modification

Precipitated amorphous silica is a white, powdery material produced by the precipitation of silicate solutions and terminated before xerogel and aerogel growth.¹ Precipitated silica is the second most widely used reinforcer and filler in shoe soles and tractor and off-road tire treads, after carbon black. Silica provides a reduction in heat buildup, high resistance to cutting and chipping, and slower cut growth. These benefits are why silica is commonly used for tractor and off-road tires. High silica loading also leads to lower rolling resistance and superior wet traction. However, the surface of precipitated silica is widely covered by hydrophilic silanol groups (Si-O-H), resulting in strong filler-filler bonds while displaying poor affinity towards hydrocarbon rubbers. Rubber compounds reinforced with silica have low modulus at high elongations, which may be due to the detachment of rubber molecules.² Two main factors determining the final performance of rubber/silica composites are dispersion and interfacial interactions.³ Therefore, the silica surface should be modified to improve the interfacial interaction between the rubber and silica.

Filler surface modification has often been studied to lower the energy of mixing and improve their adhesion and compatibility in composite mixtures. Various surface modification methods have been reported using silica, alumina, and titanium oxide. Further, chemical coupling

agent addition using siloxane, titanate, and zirconate is a common method in industry for such modifications. Coupling agents chemically modify silica surfaces and promote interactions between the hydrophilic silica surface and the hydrophobic rubber phase.⁴ They can also improve the composite's physical properties and strengthen the organic and inorganic boundary layers. However, their high price increases the overall production cost.^{5,6}

A more economical method for modifying various surfaces was developed in the 1980s. This method, called admicellar polymerization, forms an ultrathin (1 to 4 nm) polymer film on a surface.^{7,8} In this technique, the polymer film is formed in surfactant aggregates called admicelles adsorbed onto the substrate surface. Polymerization is initiated, and after the polymerization period is complete, the accessible surfactant is removed by appropriate solvents to expose the polymer films.

Silica particles modified by styrene-butadiene and styrene-isoprene copolymers via admicellar polymerization have been shown to improve rubber physical properties, including decreased cure time, increased tear strength, improved cut growth resistance, and elongation to break, compared to rubbers mixed with unmodified silica.⁶ Precipitated silica has a unique porous structure with significant nano-pores permeating through its structure. Polymer chains are formed within the silica pores as the adsolubilized monomer polymerizes. Therefore, due to the physical interpenetrating network between the polymer and the silica particles, the majority of the polymer formed cannot be removed via solvent extraction. As a result, the modifications of silica's surface characteristics become permanent without chemically bonding the polymer to the substrate.⁶

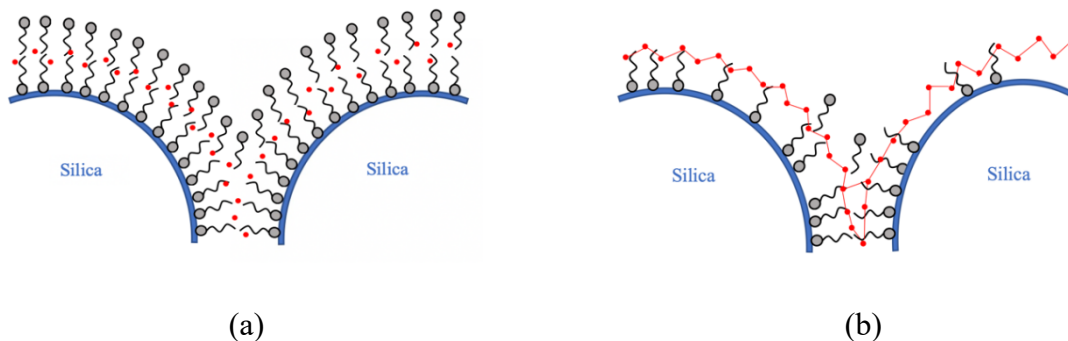


Figure 1.1. Schematic of (a) adsolubilized styrene monomers on silica particles and (b) polystyrene physically bound to silica particles

1.2 Research Motivation and Objectives

Oxygen sensitivity is one of the main limitations in radical polymerizations. Oxygen is a known inhibitor and radical scavenger due to its two unpaired electrons in its outer shell. These electrons react with monomer radicals and form stable peroxy radicals that compete with the polymerization's propagating radical chain end and extract hydrogen atoms from the polymer backbone to create hydroperoxides.^{9,10} Prematurely terminated polymers with low molecular weight and a lower final conversion are the result of the presence of oxygen in the system.¹¹

In admicellar polymerization, a low monomer to initiator (M/I) ratio was traditionally required to overcome this limitation and achieve high polymer conversion even though oxygen is present in the headspace and dissolved in the reaction medium. As an alternative to adding excess initiator, inert gas purging, sparging, freeze-pump-thaw, the use of a glove box with an inert atmosphere, or Schlenk line techniques are all effective and common methods to deoxygenate the system. However, all these methods are time-consuming, require specific skills and expertise, and are challenging to scale. Additionally, since the monomer has to have been added previously to the system, monomer loss can occur in the case of a volatile monomer.

To develop an environmentally friendly, cost-efficient, and feasible deoxygenation and initiation technique, we studied the use of glucose oxidase (GOx) in admicellar polymerization. In this method, GOx acts as the catalyst in the oxidation of β -D-glucose, while consuming oxygen and generating hydrogen peroxide and D-glucono- δ -lactone. There are many advantages of GOx to other deoxygenation techniques. First, GOx is produced in nature by various insects, plants, animals, and fungi; therefore, it is inexpensive,^{12–14} and easily accessible.¹⁵ Also, this enzyme has shown persistent activity in aqueous and various organic solvents and has high thermal stability.¹⁶

We hypothesize that glucose oxidase will both deoxygenate and initiate the polymerization system. Deoxygenation occurs by the consumption of oxygen, and the formed hydrogen peroxide will initiate the polymerization in the absence of a thermal initiator.^{17–20}

Three different experiments are performed to test the ability of GOx to initiate the polymerization system. In experiments number 1 and 2, glucose oxidase is added to the solution in the absence of a thermal initiator to determine its capability to initiate the admicellar polymerization performed under air and nitrogen, respectively. The data obtained from these two types of experiments are compared to the thermal initiated admicellar polymerizations (number 3).

We plan to determine GOx deoxygenation capacity by adding GOx to a solution with a thermal initiator present and conducting the admicellar polymerization under air conditions (number 4). These experiments are compared to experiments number 5, which are nitrogen-purged admicellar polymerizations in the absence of GOx. Experiments number 6, are performed under air as control admicellar polymerizations in the absence of GOx and a thermal initiator. We hope to incorporate the finding of this study in future research and perform enzyme-initiated reversible addition–fragmentation chain transfer (RAFT) polymerization.

1.3 Thesis Structure

This thesis is organized into five chapters. Chapter 1 is the introduction to the thesis and serves to motivate this research. Chapter 2 provides an overview of pertinent literature to provide the background knowledge required to understand this work presented in the subsequent chapters. Chapter 3 is structured as a journal article and examines the performance of glucose oxidase as the oxygen scavenger and initiator in the admicellar polymerization of polystyrene on silica particles. Chapter 4 summarizes the results and provides recommendations for future work necessary to understand further and perfect enzyme-initiated admicellar polymerization.

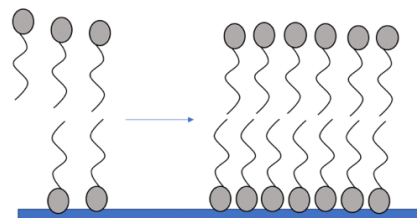
CHAPTER II

2 Background and Literature Review

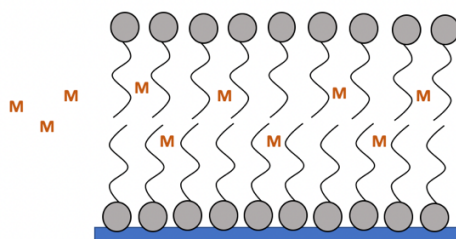
2.1 Introduction to Admicellar polymerization

The chemical and physical compatibilization of components in composite materials is an important area of study. A highly used method is the addition of mineral fillers in polymer composites. The addition of these fillers can improve the composites' mechanical, thermal, and electrical properties.²¹ In admicellar polymerization, surfactant aggregates (admicelles) physically adsorbed onto the substrate surface are used as a polymerization reaction medium.²² The equilibrium bulk surfactant concentration in admicellar polymerization should be above the critical admicelle concentration (CAC), the concentration at which aggregates begin to form, and near, but below, the critical micelle concentration (CMC), the concentration at which micelles form. This ensures the presence of admicelles as loci for polymerization, maximizes the surface concentration of admicelles, and prevents the formation of micelles in the bulk, which would be competing sites for solubilization and thus polymerization.

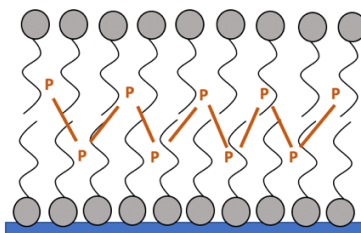
Admicellar polymerization traditionally consists of four main steps (1) the formation of admicelles on the solid substrate, (2) adsolubilization of monomers into the admicelles, (3) polymerization, and (4) washing, as shown in Figure 2.1.²³



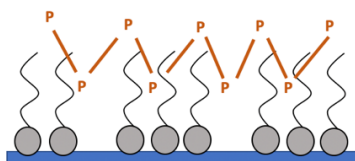
Step 1: Adsorption of surfactants on the solid substrate, Admicelle formation



Step 2: Monomer Adsolubilization



Step 3: Polymerization



Step 4: Washing, Surfactant removal

Figure 2.1. Schematic representation of the four steps of admicellar polymerization

The pH of the solution is adjusted so that the surface will possess the opposite charge of the surfactant headgroup, ensuring adsorption. With increasing surfactant concentration, upon reaching the CAC, admicelles start to form on the surface in a patch-wise and localized manner,^{24,25} which is usually attributed to surface heterogeneity.²⁶ Some researchers believe that the formation of admicelles is a step-by-step process, where a monolayer (hemimicelle) is first formed on the substrate's surface and followed by forming a second layer on top of it.²⁷ However, other

researchers believe that the formation of the bilayer is simultaneous.²⁸ Fluorescence and spin probe studies support the one-step process since the microviscosity and polarity of the aggregates remain constant from Region II through Region III of the adsorption isotherm (Figure 2.2). This observation also suggests that the morphology of the aggregates does not change with the addition of surfactants between Region II and Region III.²⁹ Based on the high microviscosity measured in the adsorbed layer by fluorescence probes, admicelles are highly structured and almost rigid in contrast to the structure of micelles.³⁰

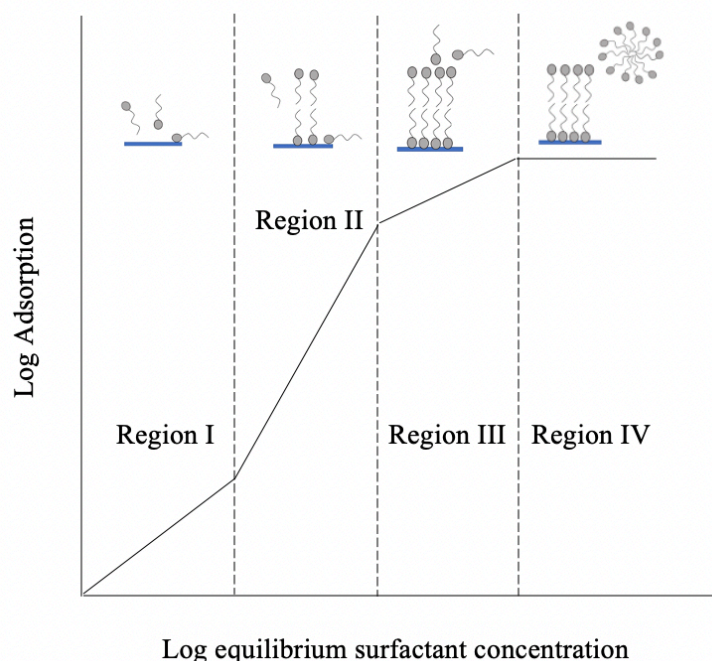


Figure 2.2. Schematic diagram of ionic surfactant adsorption isotherm

Pinacyanol chloride is a widely used dye to detect the formation of surfactant aggregates in solution. Pinacyanol has a red color in aqueous solutions while forming a blue color when dissolved in an organic environment. At surfactant concentrations below the CMC and above CAC, and thus in the absence of micelles, dye's addition will result in a red solution and blue substrate, showing that the adsorbed aggregates provide an organic microenvironment for the dye

to solubilize into. However, it should be noted that above the CMC value, the addition of dye will result in a purple solution which is the combination of red and blue. The color purple indicates the formation of some micelles, but not enough to completely solubilize all the red dye in the micelle core.³¹

The optimum conditions for the adsorption of the surfactant on the substrate must be determined for each specific system. The point of zero charge (PZC) is an important factor for each substrate, as it represents the pH value in which the electrophoretic mobility is zero. Surfactant adsorption will occur when the surfactant substrate bears the opposite charge to the surfactant headgroup. Thus, for a given substrate, you must balance the factors of substrate solubility versus pH with the ability to choose different surfactants. For example, in the case of CaCO_3 , the PZC value at room temperature is approximately 11.4, which means that at pH's below 11.4 that the surface of CaCO_3 is positively charged, and an anionic surfactant will adsorb on this substrate.³² Anionic surfactants tend to adsorb better at lower pH values. However, CaCO_3 will decompose into carbon dioxide and water in acidic aqueous solutions. Therefore, these two factors are used to adjust the pH value to an optimum value. After determining the surfactant and adsorption pH value, the adsorption isotherm of the surfactant on the substrate must be determined to calculate the CAC and CMC values of the system and determine the appropriate equilibrium surfactant concentration.

Solution pH can affect the surface charge density and significantly change the hydrophobicity of the surfactant if the ionic headgroup does not dissociate. Other factors affecting surfactant adsorption include the temperature of the solution and the addition of electrolytes. Increasing temperature will usually decrease the adsorption of ionic surfactants but may increase nonionic surfactants' adsorption as the system nears the cloud point of the surfactant.³³

Temperature changes for ionic surfactant systems will usually have a smaller impact than changes in the solution's pH. The addition of electrolytes will increase the adsorption of surfactants on oppositely charged surfaces and reduce the CAC and CMC by shielding headgroup repulsive forces.³⁴

Surfactant adsorption is also affected by varying surfactant structure, such as changing the hydrophobic tail's length or using a surfactant with a branched chain.³⁵ Gemini surfactants have higher surface activity and lower surface tension and CMC values than monomeric surfactants. Also, while the two hydrophobic tails will interact more prominently with neutral or oppositely charged surfaces, the hydrophilic heads will be packed more tightly, which results in a more stable interfacial film on the substrate reducing surfactant desorption.^{36,37}

Step 2: Adsolubilization of the monomer in the admicelles

After admicelle formation is achieved, sparingly soluble monomers are introduced into the system. Based on the polarity of the monomer, three different sites have been proposed for adsolubilization; the headgroup region, the so-called palisade region, and the admicelle core. Nonpolar compounds such as alkanes adsolubilize only in the hydrophobic core of the admicelles. In contrast, compounds with intermediate polarity may solubilize both in the core and in the palisade region of the admicelles. Highly polar compounds will be found only near the interface of the charge headgroups and the bulk solution.³⁸ For instance, alcohols and fluromonomers tend to adsolubilize in the headgroup region.³⁹ The adsolubilization sites in the admicelles are different for aromatic monomers than for alcohols and alkanes, which led to the three-site adsolubilization model suggested by Behrends et al.⁴⁰

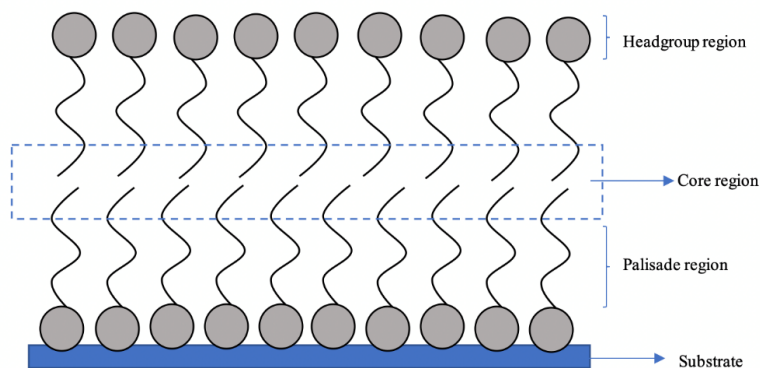


Figure 2.3. Schematic of the adsolubilization regions in admicelles

Adsolubilization of monomers has been shown to increase the adsorption of the surfactant on the substrate below the CMC values.^{28,38} For nearly insoluble monomers, their hydrophobic behavior towards water is similar to the amphiphile tails of the surfactant. Therefore, the monomer's presence is a cooperative force to increase the adsorption and stabilize the bilayer structure. The addition of long-chain alcohols will significantly lower the CMC for more ionic surfactants and increase adsorption, sometimes by a factor of as high as 50. The impact differs with alcohols of different chain length⁴¹.

Step 3: Polymerization

Initiators are typically added to the system during adsolubilization. Polymerization is then typically started by increasing solution temperature to the cause initiator cleavage. To study the kinetics of admicellar polymerization, the polymerization mechanism must be known. Based on the analogy between admicellar polymerization and emulsion polymerization, Wu et al.⁴² compared the polymerization of styrene on alumina with sodium dodecyl sulfate as the surfactant and sodium persulfate as the thermal initiator to the Smith-Ewart theory of emulsion polymerization.⁴³ Three major similarities were observed between these two polymerization techniques: (1) water-soluble sodium persulfate was used as the thermal initiator, (2) the diameter

of the alumina powders (between 100 and 1000Å) is in the range of emulsion particles, and (3) admicelles are assumed to be the main location for the admicellar polymerization reaction which correlates the micelle's role in the emulsion polymerization. Therefore, admicellar polymerization can be considered as a form of free radical polymerization, and the mechanism can be represented as below:⁴⁴

Initiation:



Propagation:

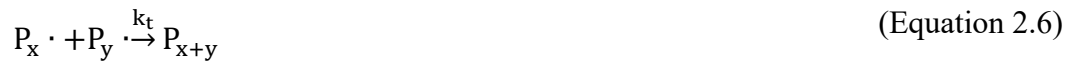


Or in general:



Termination:

- a. Combination of active polymers in an admicelle:



- b. Desorption of radicals into the aqueous phase:



Based on the reactions mentioned above, the rate of polymerization in the admicelles can be expressed as:

$$R_p = -\frac{d[M]}{dt} = k_p [M]_{ad} [R^*] \quad (\text{Equation 2.8})$$

Step 4: Washing

After the polymerization period is complete, based on the monomers and surfactants used in the process, appropriate solvents such as water, methanol, ethanol, or a mixture of solvents are used to remove accessible surfactant. To verify the formation of the polymer and analyze its characteristics, the polymer film is extracted from the surface of the substrate. The extraction is performed by a solvent such as tetrahydrofuran (THF) via various methods. Early methods included manually shaking or stirring the washed solution in the solvent for multiple days to ensure a homogenous mixture. The solvent solution was then analyzed by ultra-violet (UV) visible spectrophotometry, and the spectrum was compared to either the original solvent or to known samples of the polymer dissolved in the same solvent.^{45,46} In the case of admicellar polymerization of styrene on cotton, the fibers were boiled in THF to remove the polymer film. After the extraction, the solvent was evaporated, and the polymer was analyzed by Fourier-transform infrared (FTIR) spectrometer and gel permeation chromatography (GPC).⁴⁷ In recent studies, the most common method for polymer removal has been Soxhlet extraction. The extraction is performed for 48 to 72 hours. Depending on the polymer, it is either precipitated in the solvent by water, dried off, and then analyzed separately, or the extracted solution is analyzed directly.⁴⁸⁻⁵¹

2.2 Effect of Oxygen on Admicellar Polymerization

Historically, a disadvantage of admicellar polymerization was the low M/I ratio required to achieve an effective conversion of monomer to polymer when oxygen is present in the headspace and dissolved in the solution. While this ratio is reported to be above 500 or even greater

than 1000 in some emulsion polymerization cases,^{52,53} a low M/I, typically below 15, was necessary for admicellar polymerization, which greatly increased the cost of the process.^{6,45,54–60} Oxygen is a known inhibitor and radical scavenger due to its two unpaired electrons in its outer shell. These electrons react with monomer radicals and form stable peroxy radicals that compete with the polymerization's propagating radical chain end and extract hydrogen atoms from the polymer backbone to create hydroperoxides.^{9,10} Prematurely terminated polymers with low molecular weight and a lower final conversion are the result of the presence of oxygen in the system.¹¹ Sparging the solution with inert gases in admicellar polymerization is not a practical option since it will cause foaming of the surfactants and the loss of volatile monomer. Several studies have analyzed the effect of removing oxygen by purging the headspace of the reaction vessel with inert gases.^{22,51,61–65}

2.2.1 Degassing by inert gases

Lai et al.²² were the first to utilize nitrogen purging in admicellar polymerization. Based on their research, if poly(tetrafluoroethylene) polymerization on alumina is performed under the nitrogen atmosphere, the final conversion increased drastically from 7% to 35% when the initiator concentration was increased a hundred-fold. However, the study does hypothesize that though the concentration of the surfactants is below the CMC when the initiator concentration is at its highest (2.5 wt. %), polymerization is believed to occur in the bulk solution due to the murky appearance of the supernatant.

Similar results have been observed while coating the surface of glass fibers with polyethylene in a nitrogen-purged environment. Weight loss and ethylene pressure drop measurements during the adsolubilization and admicellar polymerization confirm that when the

concentration of initiator is doubled and tripled, the total conversion of monomer to the polymer at the interface as well as the bulk increases,⁶⁴ which is in agreement with the results of Lai et al.²². While studying the admicellar polymerization of methyl methacrylate on calcium carbonate particles in a nitrogen-purged reactor, Seul et al.⁶² demonstrated incomplete conversion at low initiator concentrations ($[I] = 0.79 \times 10^{-3} \text{ mol/L}$) and calcium carbonate coagulation as the initiator concentration is increased ($[I] = 6.32 \times 10^{-3} \text{ mol/L}$). As a result, an optimum concentration of $[I] = 1.58 \times 10^{-3} \text{ mol/L}$, (M/I value of 225) was determined to achieve 100% conversion in five hours while avoiding coagulation of the substrate in the solution. The effect of initiator concentration in a nitrogen-purged environment has also been studied in the admicellar polymerization of methyl methacrylate on aluminum pigments. A maximum weight loss of 24% was reported while altering the M/I ratio from 9 to 114.⁶¹

To fully understand the effect of oxygen on free radical admicellar polymerization and its influence on the polymer properties such as polydispersity and molecular weight, a comprehensive study on the admicellar polymerization of polystyrene on silica particles with three different M/I ratios was conducted under air and a nitrogen-purged environment.⁵¹ This study demonstrates that as oxygen was removed from the headspace of the reaction vessel, high conversions were achieved with high M/I ratios. The findings of the study are summarized in **Table 2.1**.

Table 2.1. Apparent monomer to polymer conversion (%), weight-averaged molecular weight (M_w , g/mol) and, polydispersity (PDI) of extracted polymer for deoxygenated and control admicellar polymerization of polystyrene on silica initiated by AIBN.⁵¹

M/I molar ratios	Deoxygenated			Control		
	Apparent conversion (%)	M_w (g/mol)	PDI	Apparent conversion (%)	M_w (g/mol)	PDI
15	91	3.7×10^5	2.1	94	1.7×10^5	2.1
150	88	8.5×10^5	1.6	57	7.1×10^5	1.7
1000	80	1.8×10^6	1.2	11	N/A	N/A

2.2.2 Enzyme degassing

Inert gas purging, freeze-pump-thaw, the use of a glove box with an inert atmosphere, or Schlenk line techniques are all effective methods to deoxygenate the system. However, these methods are often time consuming, require specific expertise, may result in monomer loss, and challenging to scale. To address these issues, scientists have proposed using enzymes as a green and inexpensive technique for removing oxygen from reaction environments. GOx is of particular interest among enzymes due to persistent activity in aqueous and various organic solvents and its inexpensive cost¹²⁻¹⁴ and high thermal stability¹⁶. GOx has been isolated from the fungus *Aspergillus niger* and is widely used to determine the glucose present in body fluids, raw vegetables, and various food products.¹⁰ This enzyme consumes oxygen and generates D-glucono- δ -lactone and hydrogen peroxide while oxidizing β -D-glucose and, therefore, can be used as an oxygen scavenger and initiator¹⁷⁻¹⁹ (Figure 2.4).

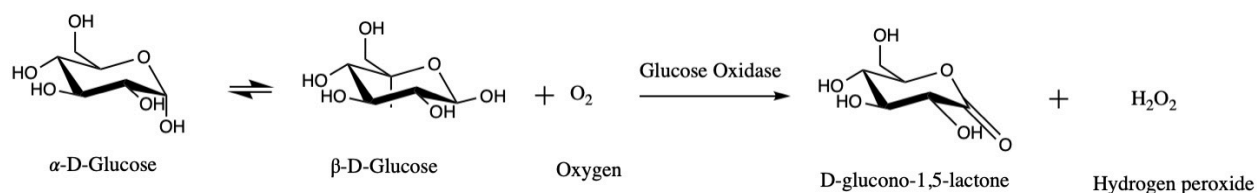


Figure 2.4. Reaction scheme of glucose oxidation catalyzed by glucose oxidase

While enzyme degassed admicellar polymerization has not yet been performed, GOx and other enzymes such as horseradish peroxidase^{66,67} have been utilized in other controlled radical polymerization techniques such as photoinitiated free radical polymerization, reversible addition–fragmentation chain transfer polymerization (RAFT), and atom transfer radical polymerization (ATRP).

2.2.2.1 Photoinitiated Free Radical Polymerization

Yagci et al. was the first group to utilize GOx in the capacity of an oxygen consumer in photoinitiated free radical polymerization.¹⁰ They developed a UV curing system based on an enzyme degassed free radical polymerization containing photoinitiators. They demonstrated that with the addition of GOx and glucose to the system, higher monomer conversion and increased polymerization rate are observed for the polymerization of poly(ethylene glycol) diacrylate (PEGDA) and acrylamide (AAm)/N, N'-methylenebisacrylamide (BAAm) in the presence photoinitiators. Also, while comparing the enzyme-degassed polymerization to the polymerization performed with nitrogen saturation, it was observed that due to the biological activity of GOx, the rate of the enzyme-assisted polymerization was higher while showing similar conversion values.

2.2.2.2 Reversible addition–fragmentation chain transfer (RAFT) polymerization

The first report of the incorporation of glucose oxidase in RAFT was in 2014 when GOx was utilized in very low concentrations (200 nM) to deoxygenate the solution fully. GOx also produced sufficient amounts of hydrogen peroxide for the horseradish peroxidase enzyme also present in media. Horseradish peroxidase can create free radicals that promote the dynamic growth of the polymer chains in the presence of hydrogen peroxide.⁶⁸ The same research group incorporated their previous data into RAFT polymerization and produced polymers from various hydrophilic monomers in organic solvent mixtures of methanol and dioxane using 4 μ M GOx and low concentrations of an initiator (2.5 mM) in a stirred vial.⁶⁹ While the optimum temperature for GOx is 35°C, it retains its enzymatic activity at higher temperatures (50°C) for up to 8 hours and, therefore, can even be used for the enzyme-degassed RAFT (enz-RAFT) polymerization of monomers with low propagation rate coefficients such as HPMA. Excellent conversion and high-end group fidelity are observed for enz-RAFT polymerizations and a degree of polymerization (DP) up to 400 for acrylates and acrylamides and up to 200 for methacrylates and methacrylamides has been reported.⁷⁰ These features combined with the advantages of GOx, such as its low cost and robustness in various solvents, promote enz-RAFT polymerization as a feasible large-scale industrial method that can be performed in an open vessel. However, this study has experimentally proven that enz-RAFT polymerization cannot be initiated solely by GOx or hydrogen peroxide without the presence of a suitable initiator.⁶⁹ A summary of their findings can be found in **Table 2.2**.

Table 2.2. Examples of enzyme degassed RAFT polymerizations with various monomers and in organic solvent mixtures.⁶⁹

Monomer	Solvent (v/v %)	[M]/[CTA]	[VA044] (mM)	GOx (μ M)	Time (h)	Conversion (%)
HEA	Methanol (20%)	25	0	1	20	9
HEA	Methanol (20%)	25	0	4	2.3	6
HEA	Methanol (15%)	55	2.5	4	4	98
DMAm	Methanol (15%)	50	2.5	4	4	96
MA	Methanol (15%)	50	2.5	4	20	<99
HPMA	Methanol (15%)	43	2.5	4	20	<99

The activity of GOx remains high and consistent throughout the polymerization period and can be utilized to prepare homopolymers and any combination of block copolymers. GOx can successfully remove the injected oxygen at each step when a fresh batch of monomers is introduced to the solution and produce homopolymers and block copolymers with high monomer conversion and low polydispersity (<1.2).^{70,71} The performance of GOx enz-RAFT has been further analyzed in ill-defined and complex solvents such as whiskey, cognac, and fermentation broth. Narrow polydispersity and good control over molecular weight were observed when the target DP was set as moderate, and the GOx showed great robustness and tolerance towards the antioxidants found in dark liquors and wine.⁷² GOx performs best in slightly acidic environments with an optimum

pH of 5.1; however, if the pH is reduced to under 3, lower conversion or even termination of the polymerization might be observed due to the instability of GOx.⁷³

Photoinduced electron transfer-reversible addition-fragmentation chain transfer (PET-RAFT) can also benefit from GOx to be performed in a metal-free oxygen-tolerant open-to-air environment. Thick polymer brushes up to 100 nm can be generated over large area substrates in a short period (2 h) using enzyme degassed PET-RAFT. The retardation of GOx enzymatic activity by residual minerals and salts present in deionized (DI) water was also proven in this study, and when nanopore water (MilliQ) was substituted, the thickness of the polymer brush doubled.⁷⁴

DNA-polymer conjugates derived from acrylamide (DMA, NAM) and acrylate (HEA, OEGA) monomers and DNA-diblock copolymers have also been synthesized by thermal initiated enz-RAFT.⁷⁵ However, while consuming oxygen, GOx produces H_2O_2 which interacts with dithiobenzoate- and trithiocarbonate-based CTAs in a Fenton-like reaction. In this process, new radicals and chains are generated. To neutralize these effects and transform H_2O_2 into inert species sodium pyruvate is added to the solution.

2.2.2.3 Atom transfer radical polymerization (ATRP)

The first report of an oxygen-tolerant well-controlled ATRP was published by Enciso et al.⁷⁶ In this study, the deoxygenation of an initiator for continuous activator regeneration atom-transfer radical polymerization (ICAR ATRP) of block copolymers and protein-polymer hybrids by GOx was analyzed. Significant discoveries were made in these experiments, which were set in an aqueous solution. The diffusion of oxygen in the solution was shown to be of great importance. If the experiments were performed under stirring in an open vessel, no polymerization occurs due to the constant oxygen diffusion into the reaction. Therefore, either the experiments should be

performed in capped containers or under no stirring to avoid this issue. Also, while the polymers generated by ICAR ATRP in the presence of GOx and glucose had low polydispersity (PDI=1.27), their average molecular weights were one-fourth the theoretical values. This difference has been attributed to the presence of H_2O_2 in the solution after the oxygen consumption. As mentioned before, the addition of sodium pyruvate converts hydrogen peroxide to CO_2 , acetate, and water, which does not interfere with the propagation chains and eliminate the generation of new chains.⁷⁷

The synthesis of hydrophobic polymers in miniemulsion⁷⁸ and ab initio emulsion systems^{78,79} via ATRP with GOx and sodium pyruvate has also been investigated. High conversion, great control, and low dispersity were observed for the miniemulsion ARGET ATRPs of n-butyl methacrylate (BMA) and n-butyl acrylate (BA) when $GOx = 2\mu M$. Similar results were also observed while polymerizing BMA in an emulsion solution that has been deoxygenated by glucose oxidase. A conversion of 60% was determined after 4 h while the polymer's molecular weight was an exact match of the theoretical value with a low polydispersity ($D=1.15$).⁷⁸ A summary of their findings can be found in **Table 2.3**.

Table 2.3. Miniemulsion ARGET ATRP of BMA and BA using GOx deoxygenating system.⁷⁸

Monomer	Polymerization time (h)	Conversion (%)	Theoretical molecular weight (g/mol)	Average molecular weight (g/mol)
BMA	6.5	89	35600	32400
BA	20	71	25700	25300

GOx degassed surface-initiated ATRP has also been shown to be an effective method to produce large-scale polymer brushes while also improving the fouling resistance of antifouling polymer brushes. The absence of oxygen due to the presence of the enzyme in the solution eases

the use of monitoring techniques such as quartz crystal microbalance (QCM) and localized surface plasmon resonance (LSPR) during the surface-initiated polymerization.¹⁴

CHAPTER III

3 Enzyme-Initiated and Deoxygenated Admicellar Polymerization of Polystyrene on Silica particles

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3.1 Abstract

One of the main limitations to radical polymerization systems is their intolerance to oxygen. To overcome this limitation in admicellar polymerization, low monomer to initiator (M/I) ratios, typically below 15, have been required to achieve high conversion and high molecular weight polymer. In this study, we introduced glucose oxidase to initiate and deoxygenate the admicellar polymerization of styrene on the surface of porous silica particles. In this method, GOx acted as the catalyst in the oxidation of β -D-glucose, while consuming oxygen and generating hydrogen peroxide and D-glucono- δ -lactone. Deoxygenation occurs by the consumption of oxygen, and the formed hydrogen peroxide will initiate the polymerization in the absence of a thermal initiator. There are many advantages of GOx to other deoxygenation techniques. First, GOx is produced in nature by various insects, plants, animals, and fungi, therefore, it is inexpensive and easily accessible. Also, this enzyme has shown persistent activity in aqueous and various organic solvents and has high thermal stability. Results show that low concentrations of GOx

([GOx]=200 nM) were able to successfully deoxygenate and initiated admicellar polymerization and reach high apparent conversions in the absence of a thermal initiator.

3.2 Introduction

Admicellar polymerization was developed in the 1980s as an economical method to modify various surfaces. In this technique, an ultrathin (1 to 4 nm) polymer film is formed in surfactant aggregates called admicelles adsorbed onto the substrate surface.^{7,8} Polymerization is initiated, and after the polymerization period is complete, the accessible surfactant is removed by appropriate solvents to expose the polymer films. Admicellar polymerization has been used as an effective method to modify and improve the surface characteristics of various solid substrates, such as silica^{1,36,48,80,81}, rubber^{55,82-86}, cotton^{47,58,59,87-89}, glass fiber^{45,64,65,90}, cellulose^{49,91,92} and different carbon structures^{63,93-96}.

Precipitated silica is the second most widely used reinforcer and filler in shoe soles and tractor and off-road tire treads, after carbon black. Silica provides a reduction in heat buildup, high resistance to cutting and chipping, and slower cut growth. High silica loading also leads to lower rolling resistance and superior wet traction. However, the surface of precipitated silica is widely covered by hydrophilic silanol groups (Si-O-H), resulting in strong filler-filler bonds while displaying poor affinity towards hydrocarbon rubbers. Rubber compounds reinforced with silica have low modulus at high elongations, which may be due to the detachment of rubber molecules.² Two main factors determining the final performance of rubber/silica composites are dispersion and interfacial interactions.³ Therefore, the silica surface should be modified to promote interactions between the hydrophilic silica surface and the hydrophobic rubber phase.⁴ Silica particles modified by styrene-butadiene and styrene-isoprene copolymers via admicellar polymerization have been

shown to improve rubber physical properties, including decreased cure time, increased tear strength, improved cut growth resistance, and elongation to break, compared to rubbers mixed with unmodified silica.⁶

One of the main limitations to radical polymerization systems is their intolerance to oxygen. Oxygen is a known inhibitor and radical scavenger due to its two unpaired electrons in its outer shell. These electrons react with monomer radicals and form stable peroxy radicals that compete with the polymerization's propagating radical chain end and extract hydrogen atoms from the polymer backbone to create hydroperoxides.^{9,10} To overcome this limitation in admicellar polymerization, low monomer to initiator (M/I) ratios, typically below 15, have been required to achieve high conversion and high molecular weight polymer.^{6,45,54-60} To fully understand the effect of oxygen on free radical admicellar polymerization and its influence on the polymer properties such as polydispersity and molecular weight, a comprehensive study on the admicellar polymerization of polystyrene on silica particles with three different M/I ratios was conducted under air and a nitrogen-purged environment. This study demonstrated that as oxygen was removed from the headspace of the reaction vessel, 88% and 80% apparent conversions were achieved with M/I ratios of 150 and 1000, respectively.⁵¹

Various methods such as inert gas purging, sparging, freeze-pump-thaw, the use of a glove box with an inert atmosphere, or Schlenk line techniques can all effectively deoxygenate the system; however, they are all considered time-consuming, require specific skills and expertise, and are difficult to scale. Additionally, since the monomer had to be added previously to the system, loss of monomer can occur. To address these issues in solution polymerizations, scientists have utilized enzymes as a green and inexpensive technique for removing oxygen from reaction environments. GOx is of particular interest among the enzymes due to persistent activity in

aqueous and various organic solvents and its inexpensive cost^{12–14} and high thermal stability¹⁶. GOx has been isolated from the fungus *Aspergillus niger* and is widely used to determine the glucose present in body fluids, raw vegetables, and various food products.¹⁰ This enzyme consumes oxygen and generates D-glucono- δ -lactone and hydrogen peroxide while oxidizing β -D-glucose and, therefore, can be used as an oxygen scavenger and initiator.^{17–20}

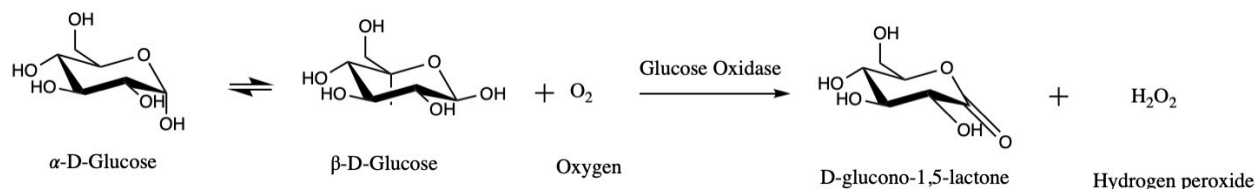


Figure 3.1. Reaction scheme of glucose oxidation catalyzed by glucose oxidase

It has been reported that very low concentrations of GOx (as little as 200 nM) could fully deoxygenate the system and consume all of the dissolved oxygen.⁶⁸ Therefore, GOx has been successfully utilized to deoxygenate controlled radical polymerization systems such as photoinitiated free radical polymerization,¹⁰ reversible addition–fragmentation chain transfer polymerization (RAFT)^{68–75}, and atom transfer radical polymerization (ATRP).^{14,76–79} GOx has also been utilized as a source of initiation in polymerization reactions. The hydrogen peroxide produced in the oxidation of glucose degrades in Fenton-type reactions and generates hydroxyl radicals. Hydroxyl radicals can initiate radical polymerization.^{17–20}

Herein, we examined the ability of glucose oxidase to successfully deoxygenate and initiate the admicellar polymerization of styrene using hexadecyltrimethylammonium bromide ($C_{16}TAB$) to form admicelles on the surface of porous silica particles. We compared the initiation performance of glucose oxidase to 4,4'-azobis(4-cyanovaleric acid) (V-501) and analyzed its deoxygenation ability compared to nitrogen-purged polymerizations. Results indicated that low

concentrations of GOx ($[GOx]=200$ nM) were able to fully deoxygenate and initiate the admicellar polymerization system while yielding high monomer to polymer apparent conversions.

3.3 Methods and Materials

3.3.1 Chemicals and Materials

Precipitated silica Hi-Sil 233 (N_2 BET surface area of 135 m^2/g) was obtained from PPG Industries. Hexadecyltrimethylammonium bromide $\geq 98\%$ ($C_{16}TAB$) was purchased from Sigma Aldrich and recrystallized in ethanol before use. 4,4'-Azobis(4-cyanovaleric acid) $\geq 98\%$ (V-501), 2,2'-azobis(2-methylpropionitrile) 98% (AIBN), D-(+)-glucose $\geq 99.5\%$, glucose oxidase (Type X-S, lyophilized powder, 100,000 -250,000 units/g solid, without added oxygen), sodium acetate buffer (SAB) solution (pH 5.2 ± 0.1 ($25^\circ C$), 3M, 0.2 μm filtered) and, tetrahydrofuran $\geq 99.5\%$ (anhydrous, inhibitor-free) was purchased from Sigma Aldrich. Styrene 99% (Extra pure, stabilized with 10 to 20 ppm p-tert butylcatechol, Acros Organics) was obtained from Fisher Scientific and passed through a bed of silica gel and aluminum oxide to remove the inhibitor. Methanol (HPLC grade) was also purchased from Fisher Scientific. Deionized water with a resistivity of 18.2 $M\Omega \cdot cm$ at $25^\circ C$ was used for all experiments. All chemicals were used as received unless stated otherwise.

3.3.2 Model development

To determine the initiation and deoxygenation capacity of glucose oxidase, six different types of experiments were conducted in this study. A summary of these experiments can be found in **Table 3.1**.

Table 3.1. Summary of the experiments performed in this study

Experimental Investigation	Initiator	Enzyme	Solution headspace	
			Air	Nitrogen
Number 1	-	+	+	-
Number 2	-	+	-	+
Number 3	+	-	+	-
Number 4	+	+	+	-
Number 5	+	-	-	+
Number 6	-	-	+	-

(+ means presence and – means the absence of the chemical or condition in the admicellar polymerization system)

Number 1 through 3 were performed to analyze GOx's initiation capability. In experiments number 1 and 2, glucose oxidase is added to the solution in the absence of a thermal initiator to determine its capability to initiate the admicellar polymerization performed under air and nitrogen, respectively. The data obtained from these two types of experiments were compared to the thermal initiated admicellar polymerizations (number 3).

The deoxygenation capacity was determined by adding GOx to a solution with a thermal initiator present and conducting the admicellar polymerization under air conditions (number 4). These experiments were compared to the experiments number 5, which were nitrogen-purged admicellar polymerizations in the absence of GOx. Experiments number 6, were performed under air as control admicellar polymerizations in the absence of GOx and a thermal initiator.

3.3.3 Solution Preparation and Admicellar Polymerization

For the admicelle formation, C₁₆TAB, silica, and water were added to the vial with ratios based on the adsolubilization and adsorption data reported by Dickson and O'Haver.⁹⁷ In this study, 10 g of silica and 0.99 g (2.7 mmol) of C₁₆TAB were added to 150 mL of water in a 250 mL flask to form admicelles on the silica surface and equilibrate at a bulk concentration of CTAB of ~90% of the CMC (CMC ~950 μ M).⁹⁸

When the experiments were performed with the presence of a thermal initiator, 0.052 mmol of V-501 or AIBN was added to the solution to achieve a M/I ratio of 100. At low M/I ratios (~15), enough initiator is present to overcome the presence of oxygen. However, at higher M/I ratios, the effect of oxygen is more apparent since the number of initiator fragments decreases significantly with oxygen present in the headspace.

If the addition of enzyme was needed, 2.7 g (100 mM) Glucose as the enzyme substrate and 4.8 mL (200 nM) of GOx and sodium acetate buffer solution were mixed in the solution. The rate of oxygen consumption by GOx is expected to be in equilibrium with oxygen diffusion from the atmosphere within 10 min.⁶⁹ Therefore, the mixture was left at room temperature for 10 minutes for the enzyme to deoxygenate the solution fully. GOx is not soluble in pure water, and therefore 1 mg GOx was solubilized in 1mL of a 50 mM SAB with a pH of 5.1. The purchased SAB solution (3M) was diluted with water, and the pH was adjusted by Sodium hydroxide (NaOH) or Hydrochloric acid (HCl).

When the experiments were performed in the absence of oxygen, the headspace of the flask was purged with nitrogen for 30 minutes. 0.52 mmol (0.54 g) of styrene was then added to yield a 2:1 molar ratio of styrene to adsorbed surfactant. After the addition of styrene, the solution was mixed at 150 rpm for 3 hours for the styrene monomers to be adsolubilized into the admicelles.

The samples were then immersed in a 70°C water bath. The polymerization was terminated after the desired reaction time by immersion in a cold-water bath and by introducing air into the samples.

The solution was then centrifuged to separate the silica particles from the aqueous solution. The modified silica particles were then washed with 2 L of 1:1 (v/v) methanol and water mixture, followed by 3 L of water. The supernatant was decanted and dried at ~100°C overnight before analysis. Polystyrene was recovered from modified silica by Soxhlet extraction with refluxing THF for 48 hours followed by precipitation in water. The extracted polymer was then rinsed with water and dried before analysis.

3.4 Characteristics

3.4.1 Thermogravimetric analysis (TGA)

The polymer amount formed on each modified-silica sample was measured by a TA Instruments Q500 thermogravimetric analyzer (TGA). To calculate the apparent conversion of monomer to polymer, each sample was heated from room temperature to 600 °C at a rate of 20 °C/min under a nitrogen atmosphere. The weight loss observed below ~150 °C was attributed to the water loss from the samples. The decomposition temperature of C₁₆TAB is reported to be 237.3°C.⁹⁹ Therefore, the weight loss between 200 and 300°C was assumed to be the loss of residual C₁₆TAB remaining on the modified silica particles. Finally, the temperature loss above 300°C was attributed to the loss of polystyrene formed on the silica surface. Based on material balance, if all of the styrene (0.54 g) forms polymer on the silica particles (10 g), a weight loss percentage of 5.1% would be observed in the TGA profile above 300°C. As a result, the apparent conversion for each sample was calculated by the equation below:

$$\rho_{\text{app}} = \frac{\text{Percent Weight Loss above 300}^\circ\text{C}}{5.1\%} \quad (\text{Equation 3.1})$$

3.5 Results and Discussions

3.5.1 Initiation of Admicellar polymerization via Glucose oxidase

To analyze the effect of the enzyme, 2.7 g of glucose and 100 mM of GOx were added to the mixture of water, C₁₆TAB, silica, and initiator (V-501 or AIBN) with ratios mentioned in the previous section. The solution was left for 10 minutes at room temperature to degas. Then it was mixed for three hours and immersed in a 70 °C water bath for the predetermined time before the polymerization was terminated by introducing air to the samples and immersing them in a cold-water bath. After the samples were washed and dried, they were analyzed by the thermogravimetric analyzer. **Figure 3.2** compares the TGA profiles of untreated silica, modified silica, polystyrene, and C₁₆TAB.

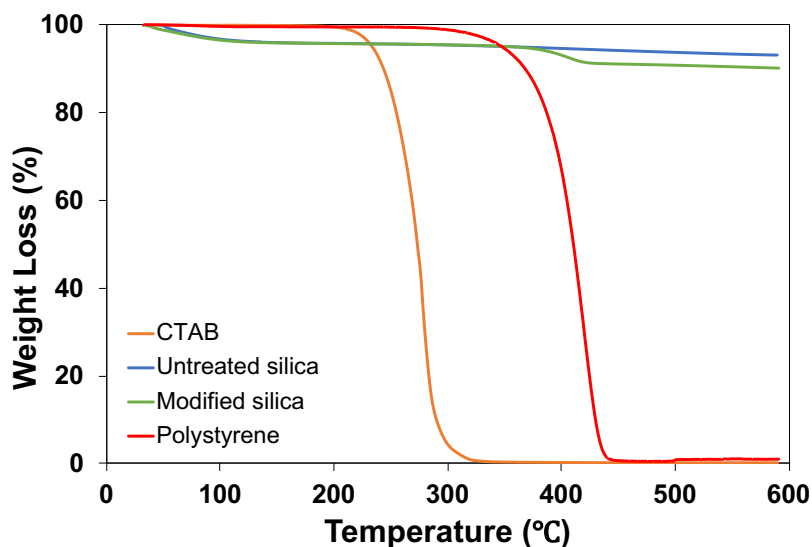


Figure 3.2. TGA profile for untreated silica (blue), modified silica (green), polystyrene (red), and C₁₆TAB (orange)

AIBN and V-501 have a half-life of 5 and 10 hours at 70 °C, respectively.¹⁰⁰ Based on previous admicellar polymerization reactions initiated by AIBN and V-501, equilibrium is reached after 6 hours of polymerization time.⁵¹ Therefore, the polymerization was terminated after 6 hours.

As observed in **Figure 3.3**, an apparent conversion of ~54.5% and ~48.8% after polymerization time of 6 hours was reported for the modified silica particles initiated by AIBN and V-501, respectively. We had hypothesized that the hydrogen peroxide produced in the oxidation of glucose by glucose oxidase initiated the reaction before the adsorption of styrene into the admicelles was complete. As a result, polymerization had occurred at the solution's interface, and the formed polymer was lost in the washing process.

In the second set of experiments, we added the enzyme after the 3-hour shaking process to ensure the adsorption step was complete. After the six-hour polymerization time was completed in the water bath, the polymerization was terminated. TGA was performed on washed and dried samples. For these experiments, an apparent conversion of ~86.4% and ~76.4% above 300 °C was reported for the modified silica particles with AIBN and V-501 as the thermal initiator present, respectively. The results demonstrated that for admicellar polymerizations, GOx should be added to the reaction medium after the adsorption of the monomer was complete to ensure that the polymers were formed within the admicelles.

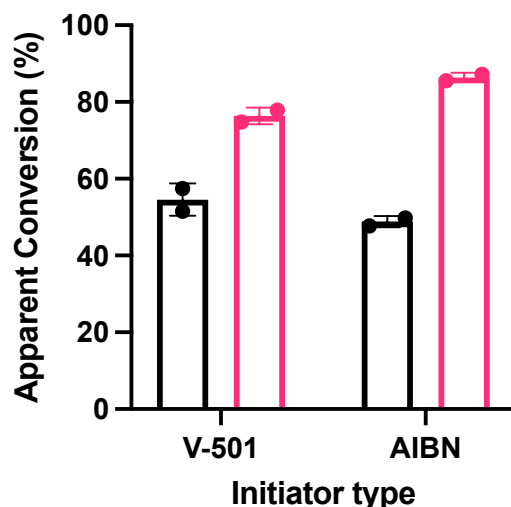


Figure 3.3. Apparent conversion versus initiator type in admicellar polymerization after 6 hours of polymerization time with the presence of GOx (“black” addition of enzyme before mixing, “pink” addition of enzyme after mixing)

To further support the hypothesis that GOx can initiate admicellar polymerization via glucose oxidation, the experiments were performed in the absence of a thermal initiator under air and nitrogen atmosphere. The effect of GOx on the kinetics of admicellar polymerization was examined by determining the apparent conversion at varying polymerization times (0 to 24 hours).

As observed in **Figure 3.4**, polymerization occurs in the presence of GOx and air and reaches a maximum of ~57% apparent conversion. However, when the headspace of the solution is purged with nitrogen, the oxidation of glucose does not take place, and negligible polymer is formed on the silica surface (apparent conversion of less than 5%).

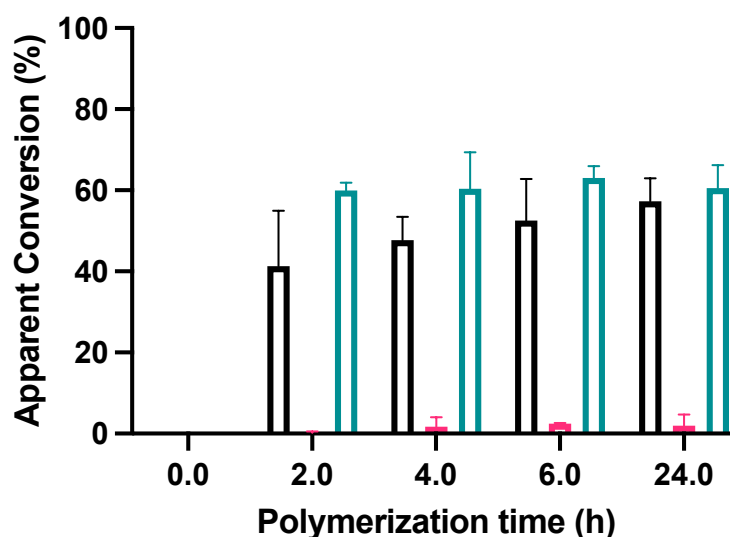


Figure 3.4. Apparent conversion versus polymerization time in admicellar polymerization (“black” GOx, no Initiator, air atmosphere, “green” no enzyme, V-501, air atmosphere, “pink” GOx, no initiator, N₂ atmosphere)

When enzyme-initiated admicellar polymerization was compared to the polymerization initiated by V-501, the conversion in the presence of GOx was lower at the earlier polymerization times. Nevertheless, as the polymerization time progressed, the conversion increased due to oxygen consumption and better distribution of hydrogen peroxide. At last, enzyme-initiated

admicellar polymerization was able to achieve a final conversion similar to the thermal-initiated polymerization.

While a higher concentration of GOx might have resulted in higher apparent conversions, increasing the GOx concentration more than 200 nM was not feasible for the substrate, surfactant, and solvent ratios set for our experiments. Since GOx is not soluble in water, it must be solubilized in a 50mM SAB before the addition to the mixture. Increasing the final GOx concentration to, for example, 2 μ M, would require the addition of 70.6 mL of the 1 mg/mL mixture of GOx/SAB in the solution. This high quantity would change the CAC and CMC of the solution and interfere with the admicelle formation, adsolubilization, and polymerization.

Further, we attempted to improve the apparent conversion percentage by shaking the solution during its deoxygenation via GOx. We hypothesized that with shaking, the hydrogen peroxide formed during the oxidation of glucose is distributed better in the solution, which will result in higher apparent conversions.

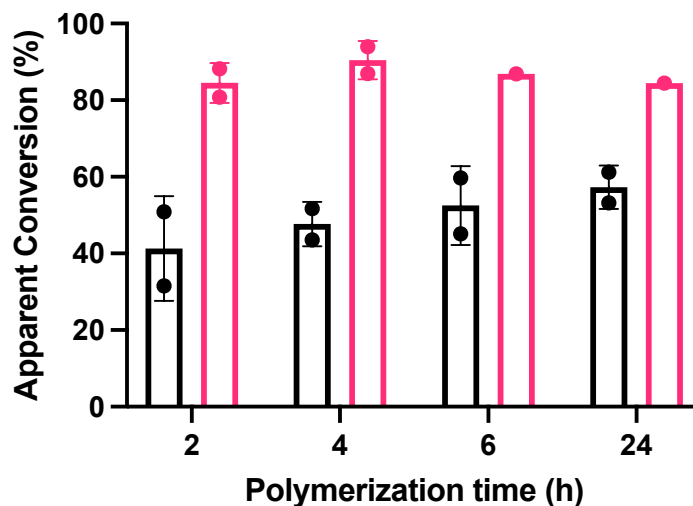


Figure 3.5. Apparent conversion versus polymerization time in admicellar polymerization with the presence of GOx (“black” no shaking during deoxygenation, “pink” shaking during deoxygenation)

As observed in **Figure 3.5**, significant improvement in the apparent conversion was observed when the solution was shaken. Shaking the vial at 150 rpm for 10 minutes while the deoxygenation occurs resulted in both a higher conversion and a higher equilibrium rate. At a polymerization time of 2 hours, the not-shaken solution reached an apparent conversion of ~40%, while the shaken solution reported an apparent conversion of ~82%. Also, with shaking, enzyme-initiated admicellar polymerization reached a final apparent conversion of ~86% after 6 hours.

3.5.2 Deoxygenation of Admicellar Polymerization via Glucose oxidase

To study the deoxygenation ability of GOx, the experiment performed with the GOx and V-501 were compared to experiments initiated with V-501 and purged with nitrogen.

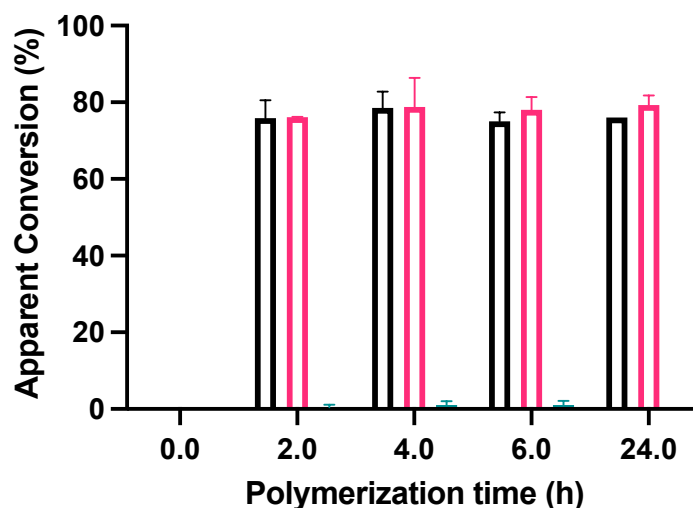


Figure 3.6. Apparent conversion versus polymerization time in admicellar polymerization (“black” no enzyme, V-501, N₂ atmosphere, “pink” GOx, V-501, air atmosphere, “green” no enzyme, no initiator, air atmosphere)

Based on the data obtained from the TGA analysis shown in **Figure 3.6**, GOx performed exceptionally well as an oxygen scavenger and deoxygenated reaction medium. The

deoxygenation via GOx performed as well as purging the samples with nitrogen, both resulting in a final conversion percentage of approximately ~80%. A control polymerization reaction was also performed in the absence of GOx and V-501, which resulted in no monomer to polymer conversion.

3.6 Conclusions

In previous studies, high monomer to polymer conversions in admicellar polymerization were either achieved by low M/I ratios or by deoxygenating the headspace of the solution via nitrogen purging. We hypothesized that low concentrations of GOx have the capacity to both initiate and deoxygenate the polymerization system. The study showed that when the solution was not shaken during the deoxygenation process via GOx, the initiation capacity of GOx was limited, and its corresponding apparent conversions were lower than V-501 initiated admicellar polymerization. However, shaking the vial when the deoxygenation occurs resulted in both a higher conversion and higher equilibrium rate when compared to the thermal-initiated polymerization. After shaking the solution, enzyme-initiated admicellar polymerization reached a final apparent conversion of ~86% after 6 hours. Further, GOx performed exceptionally well as an oxygen scavenger when added to a polymerization system with a thermal initiator present. Low concentrations of GOx ($[GOx]=200$ nM) were able to deoxygenate the reaction medium as well as nitrogen purging and showed similar apparent conversion data of approximately ~80%.

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**Publications
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E. Shakeri, J. H. O'Haver, A. E. Smith, *"Enzyme-Initiated and Deoxygenated Admicellar Polymerization of Polystyrene on Silica particles"*

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