Development of Standard Operating Procedure: ADMICELLAR POLYMERIZATION OF POLYSTYRENE THIN FILM (AIBN) ON POLYSCIENCES 30-50μm GLASS BEADS USING CETYLTRIMETHYL-AMMONIUM BROMIDE SURFACTANT

by
David Knox Langford

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Approved By:

Advisor: Dr. Adam Smith

Reader: Dr. John O'Haver

Reader: Dr. Wei-Yin Chen

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Abstract

Poly(1-phenylethene), commonly referred to as Polystyrene, is one of the world's most common polymers. Made from the monomer styrene (ethenylbenzene), this polymer is used in a wide range of products from packing peanuts to disposable cutlery. The method of polymerization used in this research project is called admicellar polymerization. This process consists of four main steps: admicelle formation, adsolubilization, polymerization, and removal of admicelle and polymer.[2,3,5] Admicellar polymerization has a number of advantages over related methods of thin film polymerization including simplicity and low cost of components and process.[4]

Introduction

As shown below in (a) of Figure 1, the first step in the process of admicellar polymerization is admicelle formation, in which a surfactant, a chemical of amphipathic nature with tendency to adsorb at interfaces, lower solid/liquid interfacial tension, and form aggregates in solution, is used to form surfactant aggregates called admicelles on a surface. The admicelle formed on the surface is used as the reaction site for the formation of polymer films from adsolubilized and coadsorbed monomer.4 It should be noted that the majority of the polymerization occurs from adsolubilized rather than coadsorbed monomer.[1] Coadsorbed monomer is adsorbed directly onto the surface rather than adsolubilized within the admicelle. As shown in (b) of Figure 1, once the surfactant has formed the admicelle on the surface, monomer, in this case styrene, is added and allowed to adsolubilize within the admicelle.[4] After adsolubilization occurs, the monomer undergoes polymerization in the presence of an initiator, which can be seen below in part (c) of Figure 1. Typically, an initiator of hydrophilic nature is used so that very little of the initiator enters the hydrophobic admicelle. If allowed to enter the admicelle in large part, the initiator would limit molecular weight growth of the polymer. It should be noted however, that in this project an initiator of hydrophobic nature is used. After polymerization has occurred, the newly formed polymer as well as the adsorbed surfactant can be separated using a variety of methods including extraction via repeated washings with negligible loss of the formed polymer.[1,5]

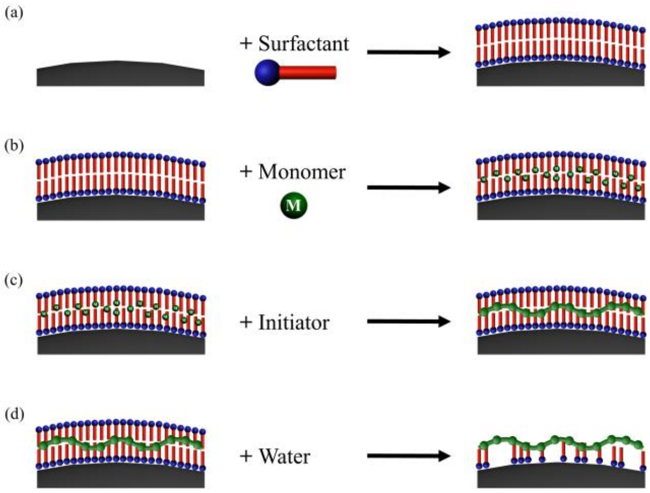

Figure 1. Diagram of Admicellar Polymerization. [3]

The goal of this project was to develop a method of polymerization and separation of polystyrene from the reaction mixture using a reusable and nonporous surface, in this case 30-50μm glass beads. Through the use of a nonporous surface, it has been hypothesized that a more representative sample of polymer can be attained. Previous research on admicellar polymerization has not allowed for detailed characterization of the method due to the frequent use of porous surfaces. While porous surfaces allow for a very high surface area per mass ratio, they also limit the extractability of the polymer.

In industry admicellar polymerization is commonly used to treat materials to improve their properties for applications in other processes. Two major examples of the use of admicellar polymerization are the use of treated silica as a reinforcing rubber filler in tires and the use of coated textiles in hydrophobic clothing. Furthermore, if proven to be an effective means of production, the use of a reusable surface, such as 30-50μm glass beads, could reduce costs for polystyrene production as well as increase the level of sustainability associated with his method of polymerization. While this added benefit potentially can save money, the principle goal of this project was to use a nonporous surface for its ability to, in theory, allow for a sample of higher mass to be extracted. This sample will provide a more characteristic look at the overall process of admicellar polymerization.

Through research completed in this project in conjunction with research completed by several graduate researchers, it was found that the polymerization and separation method detailed in this thesis were most effective when used in conjunction with a purge and headspace of inert gas during polymerization due to the removal of oxygen. Oxygen has been found to severely reduce the molecular weight of polymer formed in admicellar polymerizations, due to an observed inhibitory effect on initiator performance.[5,6]

The scope of this project was to investigate the efficacy of Polysciences 30-50μm glass beads as a surface for azobisisobutyronitrile-initated admicellar polymerization of polystyrene. The effects of temperature, pressure, mixing duration, reaction time, and the likes thereof were not investigated. However, these factors are certainly significant to the overall polymerization performance and are highly recommended to be investigated in the future. During the process of testing the viability of this method, a new challenge arose which required a new separation method due to the difficulties experiences in separation of the glass bead mixture containing the products of the polymerization reaction. The new method of separation using chloroform was then tested and proven to be effective and thus was incorporated into the standard operating procedure discussed in this thesis.

Experimental

Required Apparatus and Materials

30-50μm glass beads were obtained from Polysciences, Inc (Warrington, PA). CTAB (hexadecyl-trimethyl-ammonium bromide) and AIBN (2,2-Azobisisobutyronitrile) were purchased from Sigma Aldrich (St Louis, MO). Styrene was obtained from Acros Organics (New Jersey) and was passed through a bed of aluminum oxide to remove the inhibitor. Ultrapure water was dispensed from a Millipore Direct-Q 3UV dispenser system (resistivity 18.2□MΩ-cm, 25°C). All other chemicals were purchased from Fisher Scientific (New Jersey) and used as received.

Procedure of Admicellar Polymerization of Styrene

The polymer is made by first mixing the solution of 30-50μm glass beads, CTAB surfactant, and deionized water under normal conditions. After mixing, the solution headspace is degassed with gaseous nitrogen before it is sealed and shaken for 24 hours. Styrene is then added and the vessel is then sealed with a headspace of nitrogen. The mixture is then polymerized in a hot water bath at 70 °C for 24 hours. After polymerization has occurred, the vessel is then transferred to a ring stand at which point the solution is allowed to settle for several hours. A portion of the supernate is then pipetted off and a volume of chloroform is then added to the vessel. The solution is allowed to settle for several hours until any emulsion formed has broken. The aqueous phase is then pipetted off and replaced with DI water and the sample is again allowed to settle. This step is repeated until the aqueous phase shows little indication of remaining surfactant which will be evident due to the amount of bubbles produced and due to the transparency of the phase. Then 90% of the volume of chloroform is allowed to flow through the stopcock at the bottom of the elongated round bottom flask with stop cock to be collected. The collected solution of chloroform containing polystyrene is then placed under Roto-Vap until dry. The dried polymer is then collected and stored.

This method is applicable to the polymerization of polystyrene by using the previously discussed Polysciences 30-50μm glass beads, cetyltrimethyl-ammonium bromide (CTAB) surfactant, AIBN, and chloroform as a separation agent. The effect of purging, washing, and separation were analyzed using thermogravimetric analysis (TGA) to determine weight loss of the product based on temperature.

Table 1: Sample Run for Admicellar Polymerization of Polystyrene.

Vessel	Elongated round bottom flask with stopcock
Substrate (g)	150
CTAB (g)	0.289
Distilled Water (mL)	710
Initiator (AIBN)	AIBN
Initiator Mass (g)	0.0282
Styrene (mL) *Note: Added after degassing	0.295

Temperature (°C)	70

Data Acquisition, Calculations, and Results

Thermogravimetric analysis (TGA) was used to acquire data pertaining to the weight loss of the materials based on decomposition, oxidation, or loss of volatiles. A number of trials were completed with variation in use of nitrogen purge and post-use wash. The results of the trials were conclusive in the fact that both purging and washing have a beneficial effect of the purity of the produced polymer. However, the data acquired in this research project is inconclusive on determining which of the wash/purge combinations is the optimal choice of polymerization performance due to the similarity between the graphed results. As shown below in Figure 2, the results of the TGA experiments are plotted with temperature on the X-axis and mass loss on the Y-axis.

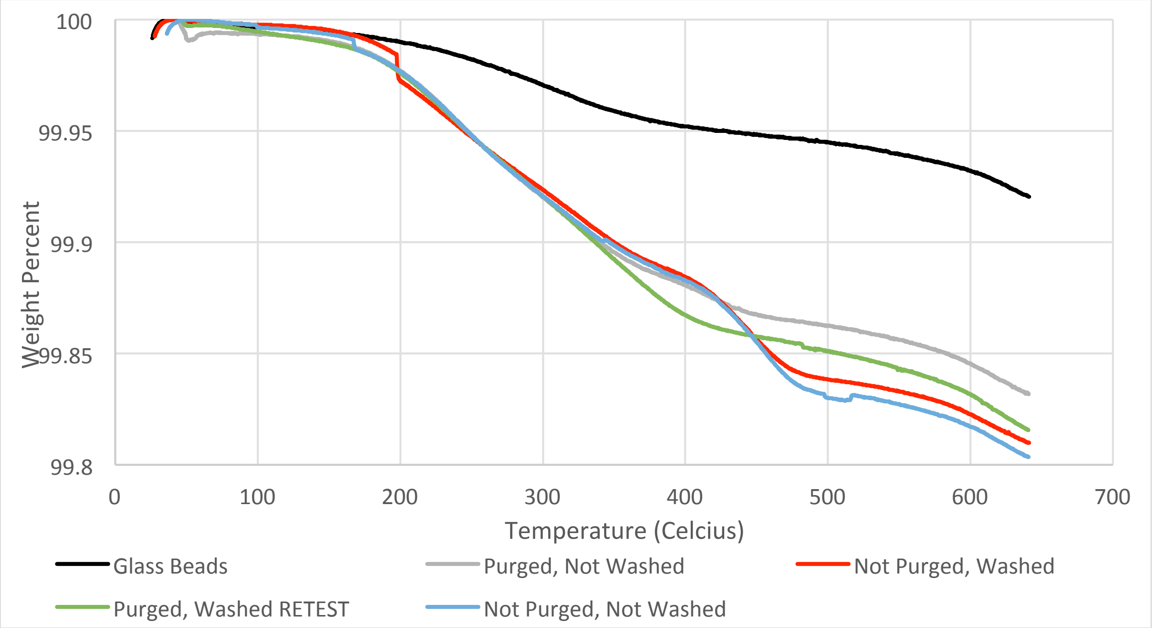

Figure 2. Graph of TGA Results for Polymerization on Polysciences Glass Beads Purging and Wash Trials.

During the acquisition of TGA data for the washing/purging trials, it was found that the polymer was very difficult to extract from the glass bead mixture. In an attempt to extract a high percentage of produced polymer, a new separation method using chloroform was investigated and used in lieu of the typically used Soxhlet extraction. Knowing that polystyrene will preferentially dissolve in chloroform rather than water, it was hypothesized that polystyrene could be more effectively separated by allowing chloroform and the aqueous reaction mixture to phase separate. Shown below in Figure 3, two trials were completed using the chloroform separation method. Trial one and two were the same in terms of reagent ratios and amounts, degassing time and pressure, polymerization time, vessels, and apparatuses used. The difference between trial one and two was that in trial two after allowing the chloroform to settle and phase separate in the elongated round bottom flask, nearly all the aqueous phase was removed and replaced with fresh DI water until, after settling, the aqueous phase appeared clear. Whereas in trial one, only a portion (~100 mL) of the aqueous supernatant was removed and replaced with chloroform prior to settling and extraction. The results shown in Figure 2 indicate that a much higher percentage of polystyrene was present in Trial 2 when compared to Trial 1. It should be noted that in the analysis of the TGA results, weight loss below 150 °C was considered to be due to water loss. Weight loss between 200 °C and 300 °C was attributed to decomposition of CTAB. Weight loss above 300 °C was attributed to the polystyrene decomposition and assumed to be representative of the amount of polystyrene.

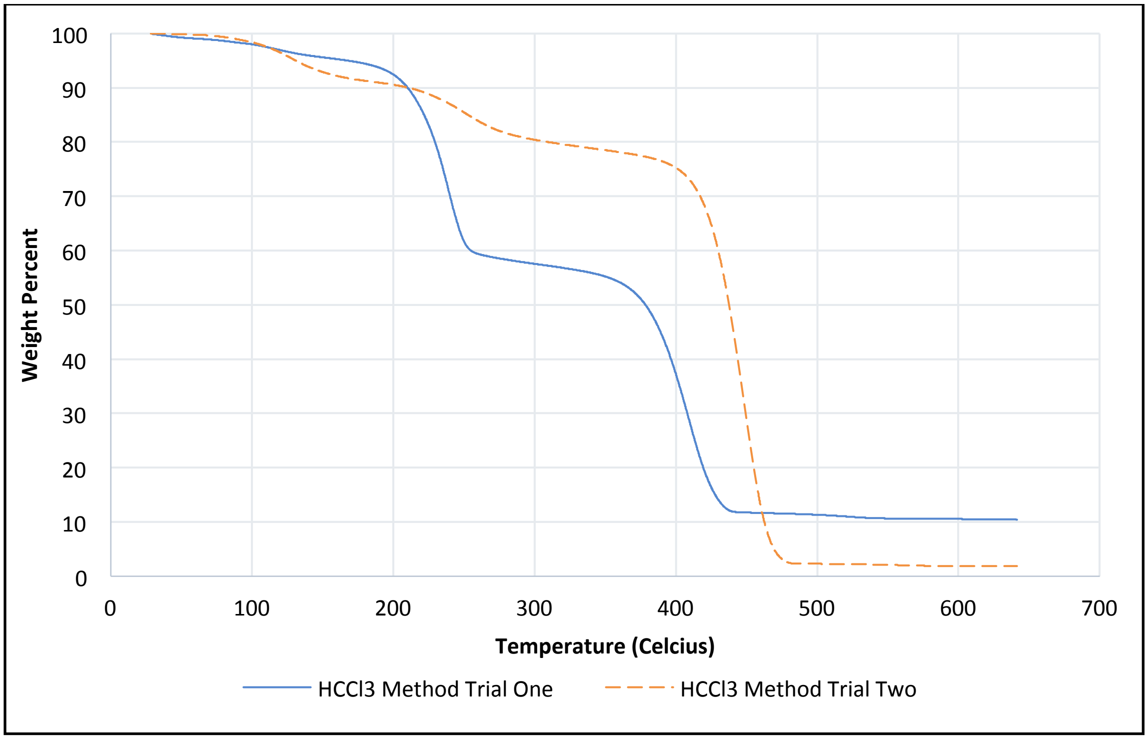

Figure 3. Graph of TGA Results for Polymerization on Polysciences Glass Beads Chloroform Separation Method Trials.

From these results, it can be seen that the chloroform separation method is an effective method of extracting a relatively high purity sample of polystyrene from the post-admicellar polymerization glass bead mixture. It is highly recommended that the method be adhered to in the form used in Trial two which can be found in full in the attached appendix.

The overall result of this research project was the development of the standard operating procedure for the method of conducting the AIBN-initiated admicellar polymerization of polystyrene on 30-50μm glass beads using cetyltrimethyl-ammonium bromide surfactant and chloroform. While the results of this study do not conclusively indicate that a representative sample can be taken using this method, it is likely possible to do so if given the appropriate resources and time. Due to obvious time constraints, research on this project will likely be continued under the supervision of another researcher. However, it is recommended that further investigation and trials be completed using this standard operating procedure in an effort to take a more representative sample for the goal of further characterizing and understanding the process of admicellar polymerization through.

Interferences and Potential Error

Throughout the experiment a number of potential errors can occur due to a variety of reasons including contamination, measuring, and operating conditions. The primary source of error is likely contamination due to leak during the mixing, purging, shaking, and polymerization stages. To prevent contamination in the mixing stage, it is critical to ensure that the vessel (elongated round bottom flask with stopcock) has been cleaned thoroughly with a cleaning regiment of acetone, methanol, and DI water in this order. Furthermore, the inside of the vessel should be scrubbed with a wire brush to debride any remaining polymer or surfactant that may be adhered to the inner wall. To prevent contamination during the purging stage, copper wire should be used to secure the rubber stopper thus reducing the chance for a potential leak. Additionally, when introducing the gaseous nitrogen to the headspace via needle, be prepared to quickly insert the second needle allowing the gas in the vessel to escape rather than allowing accumulation which would lead to a pressure increase great enough to eject the stopper. To reduce the risk of error during the shaking phase, it is recommended that the vessel be wrapped in a protective layer of bubble wrap in case the restraints loosen in such a way that the shaking apparatus can impact the vessel causing damage and potential leaking. During the polymerization stage, the most likely source of error is leaking while under the solution of the hot bath. This is likely to occur as a result of the rubber stopper expanding under the temperature in the hot bath. To mitigate the chance of contamination, it is recommended that parafilm be used to cover both openings of the vessel. Additionally, the regulators on nitrogen cylinders, the fume hoods, and the stock of reagents and solvents should be tested periodically to ensure accuracy.

Safety

Due to the inherent danger of all laboratory work, proper personal protective equipment (i.e. lab coat, goggles and nitrile gloves) should be worn at all times throughout the duration of the experiment. All stages of the experiment in which volatile chemicals (styrene, chloroform, acetone, AIBN, etc.) are open to the air should be performed under a fume hood. Inhalation of any of these chemicals can result in a wide range of negative health effects.

It should be noted that periodic exposure to styrene in humans can result in cancer as well as negative central nervous system effects which can manifest with symptoms such as headache, fatigue, depression, delayed reaction time, poor memory, and hearing loss.[7]

Additionally, chloroform exposure can result in similar central nervous system effects. Chloroform causes skin irritation and may cause chemical burns of the eyes, skin, and respiratory linings. Furthermore, it may act as a depressant causing fatigue, dizziness, nervousness, euphoria, loss of coordination, hallucinations, and possibly coma and death.[8]

During the cleaning phases, it should be kept in mind that ethanol and acetone have autoignition temperatures of 363 °C and 465 °C, respectively. Due to this, the glass beads should be washed well with water before placing the beads into the muffle furnace for drying.[9]

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Appendix

SOP Listed Procedure

1. Determine amount of polymer desired and calculate needed amounts of reagents. Using analytical balance, weigh the ingredients and place them in the elongated round bottom flask with stopcock (except styrene and chloroform).
    1. Secure rubber stopcock in the closed position using copper wire for additional support.
    2. Purge the sample with gaseous nitrogen.
        - a. Degas the sample headspace under a fume hood.
        - b. Turn on the nitrogen air flow (~10 PSI, ~50 mL/min), place the degassing needles through rubber stoppers and put a needle for excess pressure release. Degas for 30 minutes.
    3. Remove the copper wire and add the desired amount of styrene. Replace the stopper and degas for approximately 3 seconds. Quickly pull out the outlet needle and then the degas needle. Again, secure the stopper with copper wire.
    4. Place the elongated round bottom flask with stopcock into the shaker and shake for 24 hours, allowing the contents to mix well.
        - a. Note: Be sure that the vessel is positioned in such a way as to avoid any contact with the shaking tray to prevent damage or destruction of the glassware and shaker.

5. Pre-heat the water bath to desired temperature for one hour prior to polymerization time.
6. Place the closed vessel in a hot water bath at the appropriate temperature for 24 hours.
    a. Note: The rubber stopper may expand overtime in the hot bath. To avoid spilling or contamination, use Parafilm to cover both openings of the vessel.
7. After the polymerization time has concluded, remove the sample from the bath and place it on a ring stand under a fume hood.
8. Puncture the stopper with a needle to introduce air, and allow the contents within the vessel to settle.
9. Pipette off approximately 100mL amount of the supernate and add approximately 100mL of chloroform to the sample.
10. Allow the solution to settle for several hours until any emulsion formed has broken. This can be observed when the solution has separated into two distinct phases.
11. Pipette off the aqueous (top) phase and replace with Deionized water. Allow the sample to settle again.
12. Repeat Step 13 until the aqueous phase shows no indication of remaining surfactant.
    a. Note: This can be observed when, given time, the water no longer becomes clouded and no bubbles form when adding DI water or stirring.

13. Collect 90% of the added chloroform by allowing the bottom phase to flow through the stopcock exit.
14. Place the collected solution under Roto-Vap until completely dry.
15. Collect, mass, and label the polymer.
16. Dispose of any waste in the correctly labeled carboys and thoroughly clean all glassware and instruments used in the completion of the experiment.
17. Clean the glass beads with acetone, ethanol, then water and allow to dry in muffled furnace at ~500 °C to ensure the organics are no longer on the beads. Store in appropriately labeled container.