MICROSCALE SYNTHESIS AND CHARACTERIZATION OF POLYSTYRENE: NSF-POLYED SCHOLARS PROJECT

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KEY WORDS: Polystyrene, polymers, film-casting, molecular weight determination, film thickness determination.

PREREQUISITE KNOWLEDGE: The student should be familiar with the care and handling of small amounts of hazardous materials and with simple laboratory techniques normally obtained in a first year chemistry course.

OBJECTIVES: To synthesize a polymer (polystyrene) using laboratory techniques typically introduced in the first year chemistry course. In addition, the concepts of number average molecular weight and weight average molecular weight in polymeric materials, polydispersity, methods of film casting, and film thickness determination are introduced.

EQUIPMENT AND SUPPLIES:

Polystyrene Synthesis:
100 mL corn oil#
1 mL styrene
1-4 mg azobis(isobutyronitrile) commonly called AIBN
2 g Alumina Adsorption 80-200 mesh (Fisher Cat no. A540-500)
50 mL methanol
thermometer#
250 mL beaker#
50 mL beaker
2 small Teflon coated magnetic stir-bars
hot plate equipped with stirring rotor#
small vacuum flask
small vacuum filter funnel
10 X 75 mm test tube
slotted cork
3 Pasteur pipettes

Determination of Molecular Weight by Selective Precipitation (TLC):
Reverse phase thin layer chromatographic plate treated with indicator (Whatman 4803-425)
Polystyrene standards (2K-100K)#
polystyrene sample(s)
5 capillary tubes
1000 mL beaker
plastic ruler
UV lamp#
50 mL graduated cylinder

100 mL stopper glass bottle
Bunsen burner

Film Casting:
0.5g Styrofoam
2 mL chloroform or toluene
1 mL of working solution composed of 40% dichloromethane and 60% diethyl ether
glass rod
watch glass
NaCl or KBr infrared plate
Microspatula or scalpel
glass plate approximately 8 X 8 cm.

Film Thickness Determination:
polymer films of uniform thickness
Infrared Spectrophotometer or Spectrometer#

Quantities are estimated on a per student basis unless otherwise indicated
More than one student may share this equipment

INTRODUCTION: Polystyrene is a familiar polymer with many commercial uses. Its applications range from the clear, high index of refraction, brittle plastic used to form audio cassette and CD cases to the foamed material used in insulated drink cups and packaging material. Polystyrene constitutes 11% of the plastics used in packaging with only High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE) contributing a larger share (1). So much polystyrene is used today, it is one of six common plastics that manufacturers have assigned an identification code. The code helps recycling efforts. Polystyrene's code is (PS code 6).

During the summer and fall of 1992 several new polymeric experiments were developed by the NSF POLYED Scholars for introduction into the chemistry core curriculum. In this presentation one such project will be discussed.

This laboratory project is recommended for a first or second year laboratory course allowing the introduction of polymeric science to undergraduates at the earliest opportunity. The reliability of the experiments which make up this project and the recognition factor of polystyrene, a material we come in contact with everyday, makes the synthesis and characterization of polystyrene a good choice for the introduction of polymerization to undergraduates. This laboratory project appeals to the varied interests of students enrolled in the typical first year chemistry course and becomes an ideal way to introduce polymers to a wide variety of science and engineering students.

In this sequence of experiments, students will:

a. Purify commercially available styrene by removing its inhibitor by small column chromatography.
b. Prepare polystyrene by using different amounts of inhibitors at constant temperature and time.
c. Determine the molecular weights of the synthesized polystyrene by Selective Precipitation (TLC) using a calibration curve obtained from polystyrenes of known molecular weights.
d. Prepare and evaluate polystyrene films formed by casting methods described below.

Procedures for the synthesis have appeared in the literature and several undergraduate laboratory textbooks and manuals (2-5). However, the authors have found several problems with these procedures. This modified procedure is introduced to improve the experiment and make it more applicable to the lower level undergraduate laboratory curriculum.

First, the scale of many referenced procedures is such that students work with larger amounts of the hazardous material styrene than either of the authors felt was necessary. This is consistent with current trends to adapt experiments to microscale in the interest of safety and cost reduction (4,6,7).

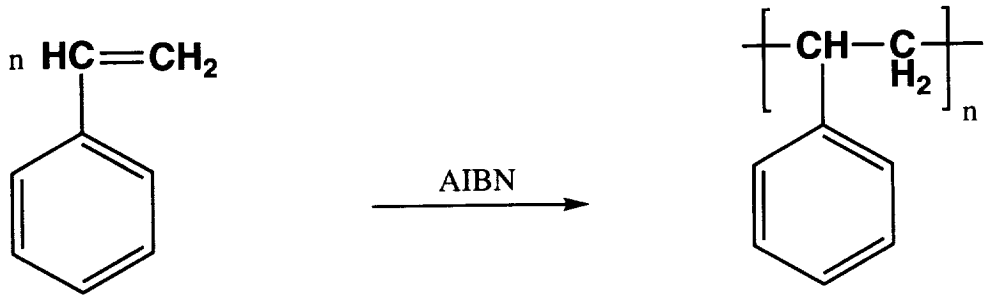
Second, the use of the reagent benzoyl peroxide as an initiator is considered too hazardous for lower level undergraduate laboratories. A suitable substitute is needed to lessen the risk.

Third, in order to accommodate the larger scale of the experiment reported in the literature, the inhibitors present in commercially available styrene are usually removed by distillation or extracted with sodium hydroxide prior to the formal laboratory time. Students lose the pedagogical opportunity to remove the inhibitors from their own sample and thus lose the opportunity to understand its presence in the commercially available sample. The inhibitor, typically 10 to 15 parts per million of 4-*tert*-butylcatechol, is present to prevent the styrene from polymerizing in the bottle. The hazards of working with styrene are also minimized by the microscale of this experiment. In addition, some procedures recommended using an excess of benzoyl peroxide to overwhelm the inhibitors present in the polystyrene. Given our reluctance to use benzoyl peroxide, we were even more reluctant to use an excess. The authors feel that the column method suggested by Williamson (4) has the advantages of being small scale, rapid, and introduces chromatography as a method of purification.

Lastly, the time and temperature required for some of the procedures yield product in the form of a solidified glass plug of polystyrene. The formation of the plug shows the consequence of extensive polymerization, but the solidified product is more difficult to characterize by the equipment available in the lower level undergraduate laboratory. The plug often needs to be removed from the reaction test tube by wrapping the test tube in a cloth and shattering both the test tube and the polystyrene plug with a hammer. In addition, the time needed for the polystyrene plug to form uses too much valuable student and instructor time. Conditions are needed that stop the synthesis short of solidification to allow characterization and make more effective use of laboratory time. By purposely stopping the experiment before a solid plug of polystyrene is formed, the reaction yields a solution that is more easily manipulated than the solid plug often seen in bulk polymerization of styrene. The viscous liquid that forms can easily be transferred and precipitated. Precipitation of the polymer in methanol (a non-solvent) illustrates a common method of isolation and purification of a polymer. If a solid plug forms, the student should grind it with a mortar and pestle to obtain a dry powder.

Experience has shown us that the most successful laboratory synthesis experiments are those coupled with an additional goal besides the formation of the product itself. In this synthesis, an additional aspect of polymerization can be illustrated and the pedagogical function of the experiment and the utility of the students' time are enhanced. For example, by using different amounts of initiator in the synthesis, the effect of initiator on the yield can be investigated. Characterization of the polystyrene is accomplished by film casting and identification by infrared spectroscopy.

In this experiment styrene is polymerized in the absence of solvent. Such a reaction is called a bulk polymerization. The polymerization proceeds as a free radical polymerization of styrene initiated by 2,2'-azobis-(2-methylpropionitrile), more commonly known as azobis(isobutyronitrile), AIBN.



The value n is a function of the experimental conditions and will determine the molecular weight of the resulting polymer. The molecular weight and polydispersity of a polymer greatly affect its physical properties and commercial applications. The molecular weight of small molecules is easily defined. The definition of molecular weight for polymers is not as easily defined because each polymeric chain constitutes a molecule and each chain can be of different length. Definitions and methods of molecular weight determination used for small molecules are not directly applicable to polymers.

Molecular Weights for polymers typically range from 5,000 to greater than 1,000,000. Students need to know how molecular weight differs for small and large molecules (polymers) to understand the effect that molecular weight has on the properties of all molecules. The ability of polymer chains to exist in varying lengths gives rise to a distribution of molecular weights within a polymeric sample. Several types of molecular weights have been defined. Two of the more frequently encountered are the **number-average molecular weight** (M_n) and the **weight-average molecular weight** (M_w). The **number-average molecular weight** is defined as the total mass of polymer molecules divided by the total number of moles of molecules present.

$$M_n = \sum_i n_i M_i \,/\, \sum_i n_i \qquad (1)$$

Molecular weights of this type are typically obtained by methods involving effects on colligative properties, GPC (gel permeation chromatography), and end group analysis.

Another definition of molecular weight is **weight-average molecular weight** which is defined as:

$$M_w = \sum_i n_i M_i^2 \,/\, \sum_i n_i M_i \qquad (2)$$

This value can be obtained by light scattering techniques. Due to the square of the M_i term, this value is biased towards the contribution of the higher molecular weight chains.

The ratio of the number-average molecular weight and the weight-average molecular weight is representative of the molecular weight distribution and is referred to as a sample's molecular weight polydispersity.

$$\text{Polydispersity} = M_w/M_n \qquad (3)$$

This value is related to how broadly the chain lengths are distributed in the polymeric sample. When M_w approaches M_n, their ratio approaches 1, and the sample approaches **monodispersity**. Synthetic polymers exhibit varying degrees of **polydispersity**, with

vinyl polymers typically having ratios from 2-10. Many biological macromolecules (polymers) exhibit monodispersity. Determination of the polydispersity of a polymeric sample is important because even small changes in polydispersity can affect the properties of a polymeric sample.

Molecular weight is one of the most important characteristics of a polymer and as previously mentioned, is typically determined by GPC or light scattering techniques. Each of these methods gives meaningful molecular weights but these methods are not accessible to most lower level undergraduate students. An alternative method for determining molecular weight of polystyrene has been reported using Selective Precipitation by thin layer chromatography (TLC) (2,5,8,9). In the TLC procedures, polystyrene samples and standards, over a wide range of molecular weights, are spotted on a reverse phase TLC plate and eluted using a dichloromethane/methanol solution. The R_f is related to the molecular weight of the sample. Using a calibration curve obtained from the polystyrene standards, the molecular weight of the unknown sample is determined.

The coupling of a polystyrene synthesis with a TLC determination was reported by Armstrong (2). Experience has uncovered several problems with these procedures. First, various procedures report that the reproducibility of these methods is very sensitive to the conditions. Yet each procedure requires slightly different conditions. Second, the reverse phase TLC plates are expensive and the cost per student too high for some departments. Third, molecular weights above 100,000 give significantly poorer results than polystyrene samples between 2,000 and 100,000. Many commercial samples of polystyrene have molecular weights above 100,000. Lastly, many polystyrene samples are polydispersed resulting, unfortunately, in a diffuse spot on the TLC plate. The indistinct nature of the spot makes it difficult to assign the "center" and determine the molecular weight.

Our goals for improving this procedure included optimizing conditions, developing a method to recycle any reusable plates, and determining how closely the results obtained by TLC correspond with the molecular weight determined by GPC for the same polystyrene samples. In addition, a method for casting film from the microscale synthesis and assessing its quality was desired.

The experiment discussed in this paper uses thin layer chromatography to determine the molecular weight of polystyrene samples obtained from the microscale bulk polymerization synthesis. The separation of polystyrene by molecular weight is due to selective precipitation of the polymer from the mobile phase. The mobile phase for this elution consists of dichloromethane and methanol. Polystyrene is soluble in dichloromethane and insoluble in methanol. As the chromatogram develops, a solvent gradient is established along the length of the plate. The bottom of the plate is rich in the polymer soluble solvent dichloromethane. As the chromatogram develops, the concentration of dichloromethane decreases and the relative concentration of the non-solvent methanol increases. The less soluble, high polymer weight fractions precipitate first, and as the solvent concentration changes, the lower molecular weights precipitate out at various R_f's.

The developing chamber should be open to the air, away from drafts and without a wick to insure non-equilibrium conditions while the TLC plate is developing. Considerable care must be used in preparing the eluting solvent because even small deviations from the suggested concentrations alter the results. A fresh portion of eluting solvent must be used for each plate because the relative concentration of the two solvents in the reservoir at the bottom of the developing chamber changes during the developing process. A starting concentration of 71% dichloromethane/29% methanol (V/V) as reported by Armstrong (2) gives the best results. This concentration must be maintained to insure reproducibility. A more extensive application of this technique was applied to 47 different samples of polystyrene having molecular weights

between 2,000-100,000. Gel Permeation Chromatographic analysis of the same samples showed a correlation (96%) between the bottom of the TLC spot and the weight average molecular weight determined by GPC. Additional correlation (85%) was observed for the midpoint of the TLC spot and the number average molecular weight. The poorer M_n correlation is attributed to the difficulty determining the midpoint of a spot whose top may be somewhat vague. A similar difficulty is not encountered when determining the bottom of the TLC spot.

A polydispersity index for the polystyrene sample can be calculated based on the ratio of M_w/M_n determined by this method.

There has been much concern in the past over the reproducibility and the cost of this experiment. The key to reproducibility is to keep the conditions as nearly identical as possible from plate to plate. If care is taken, this experiment gives reliable results. One method to minimize variation is to divide a 10 cm X 10 cm reverse phase TLC plate into ten lanes of 1 cm each. Assign the first five lanes to standards and the remaining five lanes to students (See Fig. 1). This allows five students to have identical conditions and results in considerable cost savings.

The ability to form films in high molecular weight compounds is one of the characteristic differences between high and low molecular weight compounds. Under similar conditions, high molecular weight compounds form films where low molecular weight compounds form crystalline deposits or oils. The quality of the films formed from polymeric material is proportional to the molecular weight. The formation of a high molecular weight polymer in a reaction is often confirmed by the formation of a cohesive film. Films may be made by either melt techniques or solution casting techniques (10,11). This procedure discusses two methods of solution casting that are applicable to a wide variety of polymers, and is easily adaptable to the undergraduate laboratory. Finding a suitable solvent is the most difficult part of the technique. A suitable solvent is volatile enough to evaporate in a reasonable amount of time but not too volatile so that the film forms holes, bubbles or precipitates before the film formation is complete.

Polystyrene is a glass at room temperature. A piece of clear brittle polystyrene produces sharp edges when broken. If the film is thick enough, it will appear brittle. When warmed in boiling water, the glass transition temperature of 100°C is approached. At the glass transition temperature, polystyrene undergoes a characteristic change from a glass to a flexible thermoplastic. Above the glass transition temperature, T_g, polymer chains have enough energy to undergo conformational changes, resulting in a more flexible polymer. Flexibility on the macroscopic scale is related to torsional mobility on the molecular level (10).

There are several options available in this experiment. The effect of initiator concentration on yield and molecular weight distribution can be determined by running identical reactions using three different initiator concentrations. Each student can be assigned all three concentrations or only one of the three variations. The class results are then pooled to determine the effects of initiator concentration on yield and molecular weight distribution.

PROCEDURE: Microscale Bulk Polymerization of Styrene

Safety Statements:
Styrene is a hazardous chemical with an unpleasant odor. Work in the hood at all times and avoid skin contact with this chemical. The flammability of this chemical should also be respected. There should be no open flames in the vicinity.

Waste Disposal:
All the alumina used to remove the inhibitors from the styrene should be placed in a jar labeled styrene contaminated alumina. All organic solvents should be disposed of in properly labeled waste containers.

Equilibration of Constant Temperature Bath:

1. Fill a 250 mL beaker 1/3 full with oil and place a magnetic stirring bar in the beaker.
2. Heat the oil bath to 80°C on a hot plate equipped with a stirring rotor. In the interest of time, the oil bath may be turned on and equilibrated prior to the beginning of the laboratory period.

Preparation of Styrene: Removal of Inhibitors in Styrene

1. Prepare the mini-column by placing a small glass wool plug in the bottom of a Pasteur pipette and fill it one half full with alumina.
2. Place the mini-column in a hood and add styrene drop wise to the top of pipette. It takes about 4 minutes to elute 2 mL of styrene. If it takes much longer than 4 minutes, the styrene may be contaminated with some polymeric material and very little monomeric styrene will be collected in a reasonable amount of time. A new bottle of styrene should be substituted.

Preparation of Polystyrene:

3. Weigh 0.250 g of freshly eluted styrene and 1, 2 or 4 mg of the initiator, AIBN, in a 10 X 75 mm test tube.
4. Cover the test tube(s) with a slotted cork.
5. Place the test tube(s) in the oil bath at the same time and record time and temperature.
6. Remove the test tubes from the oil bath after 45 minutes.
7. Pour the reaction mixture, immediately after removal from the oil bath, into a beaker containing 20 mL stirred methanol. A white precipitate should settle out.

7a. If the product is difficult to pour, add a small amount of toluene (~0.5 mL) to dissolve it and then pour as described in 7 into 40 mL of methanol.

8. Continue to stir in methanol for another 10-20 minutes.
9. Vacuum filter the solid polymer and wash with methanol several times.
10. Air dry the polymer or dry the polymer in a vacuum oven at room temperature until constant weight.
11. Weigh and save the polymer in a vial. Yields may be calculated on dried samples.

Plot % yield of polymer vs. mg of AIBN and note the effect of initiator concentration on the yield of polystyrene.

The polystyrene may be characterized by infrared spectroscopic identification of a film cast on glass, water, or a NaCl or KBr plate and the molecular weight distribution may be determined by selective precipitation (TLC) or GPC techniques.

PROCEDURE: Determination of Molecular Weight by Selective Precipitation

Safety Statements:
Dichloromethane and methanol are hazardous solvents. Avoid skin contact and breathing of the vapor. Do not look directly at the UV lamp.

Waste Disposal:
Dispose of all organic solvents in a properly labeled container. Dispose of all glass waste in a properly labeled container.

1. Prepare 100 mL of 71:29 stock solution of dichloromethane/methanol by pipetting 71 mL of dichloromethane in a clean, dried stoppered bottle and adding 29 mL of methanol. Mix the solution thoroughly and keep stoppered when not in use. This stock solution is enough for 2 separate slide developments, as 50 mL is needed for each.
2. Using a pencil, very gently, without disturbing the adsorbent, draw a baseline across the width of the TLC plate, 1 cm from the bottom of the plate.
3. Prepare a capillary spotter for each standard or sample that will be examined. Using capillary tubing, draw out the tubing into a fine narrow spotter using a Bunsen burner.
4. Place the plate on a piece of wide ruled paper. This allows for easy visualization of lanes on the TLC plate. If care is taken during the spotting procedure, 10 lanes can easily be run on a 10 cm plate without risk of overlap. This allows for several permutations of standards and samples on the same plate. Typically, 5-7 standards are needed for the calibration curve, leaving 3-5 lanes for samples to be analyzed. The standards and samples should have molecular weights between 2,000 and 100,000 and be prepared by dissolving 5 mg of polystyrene in approximately 1 mL of dichloromethane.
5. Place a standard or sample spot 1 cm from the bottom of the plate in the center of a lane. Care should be taken to avoid overloading the plate at any one site. Check the standards and sample spots with the UV lamp. Care should be taken not to overload the spot but make sure the spots can be clearly visualized under the UV lamp. As the spot develops, the material spreads out and leaves a very diffuse spot after development.
6. Place 50 mL of the stock solution in a clean and dry 1,000 mL beaker. This amount of solvent should be sufficient to cover the bottom of the 10 cm X 10 cm reverse phase TLC plate without being above the spots. Place this beaker or an equivalent developing chamber in a location free of drafts. Do not allow the solvent to sit too long in the developing chamber.
7. Place the TLC plate in the developing chamber gently. Lean the plate against the side of the beaker so that the plate only touches the beaker at the top and the bottom. Do not cover.
8. Do not disturb the plate while it is developing. Remove the plate when the solvent comes within 5 mm of the top of the plate and gently mark the solvent front.
9. Place the TLC plate under a UV lamp. Circle each spot with pencil and record the distance from the baseline to the bottom, the midpoint, and the top of each spot. (See Fig. 1).
10. Determine the R_f of each of the recorded points for each spot by dividing the distance from the baseline by the distance from the baseline that the solvent traveled.
11. Plot log MW of each standard versus R_f for the bottom and the midpoint of each corresponding spot. Obtain 2 calibration curves (See tables 1 and 2). The results of each should correlate best with a second power polynomial fit. If access to a curve fitting program is limited, a reasonable linear fit may be obtained using graphs of Log MW versus R_f bottom and R_f midpoint.
12. Using the calibration curves produced in step 11, determine the molecular weights of the bottom and midpoint for each of the unknown polystyrene samples.
13. Under the conditions discussed above, the molecular weight derived from the bottom of a spot correlates with the weight average molecular weight (M_W) for the sample. The molecular

weight derived from the midpoint of the spot correlates with the number average molecular weight (M_n) for the sample.

14. Calculate the polydispersity index for each sample by dividing M_w by M_n.

PROCEDURES: Film Casting

Safety Statements:
The solvent used to cast the film is hazardous and the procedure should be carried out in the hood.

Waste Disposal:
Dispose of all organic waste in a properly labeled container.

Method 1. Traditional Film Casting on Glass

This method requires significantly more samples than methods 2 and 3 and may not be suitable for small samples. The following procedure is adapted for a polystyrene sample.

1. Place approximately 0.5 g of pieces of polystyrene in a test tube and add 2 mL of chloroform or toluene. Stir until completely dissolved.
2. Pour the viscous solution near the edge of a glass plate. Spread the solution out by rolling a glass rod or Pasteur pipette, whose edges have been wrapped in a layer of tape to allow for a space between the rod and the glass plate, once across the surface of the solution in an effort to form a film of uniform thickness. Allow the solvent to slowly evaporate in the hood. Complete drying may take overnight.
3. Remove the film by lifting the edge of the film from the glass using a sharp instrument (a knife, microspatula, or scalpel). If the film does not lift off the glass surface, the glass plate may be partially submerged in a pan of water and the film should float off the glass plate. Allow the film to air dry after excess water has been removed by gently patting with a paper tissue.
4. Examine the film and assess its quality. Does it appear uniform? Are there any weaknesses or holes in the film? Is it flexible?
5. The film may be mounted on a cardboard holder and its infrared spectrum obtained. If the film is uniform in thickness, then interference fringes will be evident and the film thickness may be calibrated.

Method 2. Film Casting on Water

This method is applicable to small samples and limited to polymers which dissolve in solvents or mixtures of solvents that are immiscible and less dense than water. The following procedure is adapted for a polystyrene sample.

1. Prepare a working solution by dissolving approximately 10 mg of the polystyrene sample in 1 mL of a 40% dichloromethane/60% diethyl ether (V/V) solution. Allow the polystyrene sample to completely dissolve.
2. Add a small amount of water to a clean watch glass to make a puddle approximately 5 cm in diameter. As an alternative, half fill a small recrystallizing dish with water.
3. Add the entire polystyrene solution dropwise to form a layer on top of the water.
4. Observe the surface of the water closely. Almost immediately a film will begin to form. After several minutes the film should have set enough to allow for a qualitative evaluation of the film. If it proves cohesive enough, gently remove the film from the surface of the water and place on a paper towel to dry for 10 minutes. Using the alternative procedure, a glass microscope slide may be dipped under the fragile film in the recrystallizing dish, and raised at an angle to aid in removal of the film from the surface of the water.
5. Examine the film and assess its quality. Does it appear uniform? Are there any weaknesses or holes in the film? Is it flexible?
6. The film may be mounted on a cardboard holder and an infrared spectrum obtained.

Method 3. Film Cast Directly on Warm NaCl or KBr Plates

This method is applicable to solutions of polymeric materials with low molecular weight which do not form quality films and for microscale samples.

This method usually yields the poorest quality films because the polymeric material often precipitates on the plate prior to film formation. If this occurs, substitute a room temperature salt plate to see if this improves the film quality. Fortunately, even if the film quality is poor, an infrared spectrum may be recorded and the material characterized by this method.

1. Dissolve the sample in an appropriate solvent.
2. Add the solution to the center of a NaCl or KBr plate that has been warmed in a 60°C oven. The solvent will flash evaporate leaving behind a film residue of the polymeric material.
3. After the plate is dried, record the infrared spectrum.

PROCEDURE: Determination of the Thickness of a Polymer Film by the Interference Fringe Technique (12)

1. Place the polymer film in the sample beam of an infrared instrument and record its spectrum from 4000 cm^{-1} to 400 cm^{-1}.
2. Determine if any wavy interference pattern emerges in the spectrum. Such a pattern emerges ONLY if the film is of uniform thickness.
3. Using the interference pattern, the thickness of the film can be calculated using the following equation:

$$d = \Delta m/2n(v_1-v_2) \qquad (4)$$

where:

- d = thickness of film in cm
- Δm = a whole number of complete fringe maxima (or minima) in the interval from u_1 to u_2.
- v_1 = frequency at which first maximum (or minimum) occurs, in cm^{-1}.
- v_2 = frequency at which last maximum (or minimum) occurs, in cm^{-1}.
- n = the index of refraction for the film.

INSTRUCTOR'S NOTES:

This sequence of experiments can be done in teams of two students.

Microscale Bulk Polymerization of Styrene

The mechanism of the free radical polymerization of styrene can be found in the section on polymers and/or vinyl polymerization in any undergraduate organic chemistry text.

The AIBN and Styrene should be keep in the refrigerator when not in use.

The styrene contaminated alumina and pipettes should be placed in a beaker labeled **styrene contaminated alumina and pipettes** and left in the hood until it can be disposed of properly as hazardous waste.

The synthetic experiment should be performed in the hood. Each student is only manipulating one test tube and/or pipette column so that all students should be accommodated in the various

hoods. Styrene is extremely flammable and toxic so encourage the use of gloves when handling the monomer. The polymer does not exhibit these health hazards. The difference in toxicity between the monomer and polymer illustrate just one of the many differences between these two compounds.

Benzoyl peroxide is traditionally used to initiate free radical polymerization of styrene, but the explosive hazard of this chemical is considered too risky for a first year experiment. The substitution of AIBN proved acceptable and significantly less hazardous for undergraduates.

All reactions were run with and without a nitrogen purge. The yields without the nitrogen purge were higher and were believed to be due to the loss of monomer during the purging process. The presence of oxygen does not seem to adversely affect the outcome of the free radical reaction on a microscale, although a small induction period is needed before any polymeric material can be isolated.

It is essential the oil bath (corn oil, cooking oil) be equilibrated before the beginning of the lab. I provide settings on various hot plates that should equilibrate close to 80°C. If the temperature goes much higher than 80°C, the polymerization will yield a solid plug of polymer. This material, although polystyrene, is not easily manipulated by equipment available to first and second year students. The precipitation of the polymer in methanol is a classic method for handling polymeric material. Polystyrene is soluble in toluene and dichloromethane but not in methanol or diethyl ether. If a student does form a polystyrene plug (temperature too high or heated too long) and it does not easily slide out of the test tube, try adding a small amount of toluene to dissolve the polymer. If that does not work, then the only method opened to them is to wrap the test tube in a towel and crack it open with a hammer. Unfortunately it is often difficult to differentiate between the silica glass of the test tube and the organic glass of polystyrene when it is all commingled in pieces on the paper towel.

Once precipitated, the polystyrene is filtered using a vacuum filtration setup. The white powder (it does not precipitate as a transparent, amorphous glass) is polystyrene. The yields are obtained by weighing the product. By combining students' data, the class can determine if there is any correlation between the amount of initiator used and the yields obtained. If vacuum filtration is not possible, then gravity filtration can be substituted. This reaction is a chain-growth polymerization and as such will always have monomer present until polymerization is complete. Therefore the precipitation, and, if possible, the filtration (vacuum or gravity) should be done in the hood to minimize the amount of styrene introduced into the laboratory.

Further Extensions: Variation of yields and molecular weight distribution with temperature may be investigated. The authors investigated 60°, 70° and 80°C and found that 80°C gave the highest yields.

Molecular Weight Determination by Selective Precipitation

The characterization by TLC is straightforward. The TLC is best run in the hood in a 1 L beaker that is clean. Soap residue interferes with the separation and gives uninterpretable results. Once the students have obtained the R_fs of both the midpoints and the bottoms of all spots they should plot the results using a plot program, if they have access to one, or using graph paper. A correlation coefficient of 1.0 was obtained for a second order polynomial fit, whereas correlation coefficients of .96-.99 were obtained for a linear fit of the same data (See Tables 1 and 2). This method of determination of molecular weight of polystyrene is applicable to all polystyrene samples whose molecular weight falls between 2,000-100,000. Samples whose molecular weight falls outside this window give significantly poorer correlations with their corresponding GPC data.

From their results, students should be able to determine the M_n, M_w and the polydispersity of their polystyrene sample. By combining students' data, the class can determine if there is any correlation between the amount of initiator used and the molecular weight obtained. As the concentration of initiator increases, the yield of polystyrene should increase. More initiator means more chains started. There should be a corresponding decrease in the molecular weight obtained. There is an inverse square root relationship between the molecular weight and the initiator concentration. It is the authors' observations that students do not get precise enough results to support this mathematical relationship, but correlating trends are observed. The physical justification for this relationship lies in the frequency of termination steps. With more initiator present, more chains start, resulting in more chains termination steps, which causes the average molecular weight to stop increasing.

Recycling of the reverse phase TLC plates results in a significant cost reduction. Recycling can be easily accomplished with only minor modifications in the procedure. These modifications are time costly, as the student is required to spend more time using the UV lamp. The laboratory directors will determine which procedure best serves their needs. Reverse phase TLC plates can be recycled by a method discussed in a separate procedure (13).

Film Casting

Another aspect of this experiment is to examine the relationship between molecular weight and film quality. Film formation is dependent on molecular weight. To form a film, polymer chains must be of sufficient length to have a large amount of chain entanglements. The longer the chains (the higher the molecular weight) and more extensive the entanglements, the stronger the film. For these samples, the students will see film formation on the surface of the water. When they try to remove their samples they will find that the film is extremely fragile and may not maintain its integrity. For comparison, samples of polystyrene made from packing peanuts can be made in a similar manner. These films are normally stronger than the student samples because they are made from polystyrene of higher molecular weight. If a film can be lifted from the surface of the water and placed on a paper towel to dry it can be suspended in the infrared beam and a spectrum obtained. This spectrum should be identical to the polystyrene film in the calibration strip including the distinctive 1601 cm^{-1} peak.

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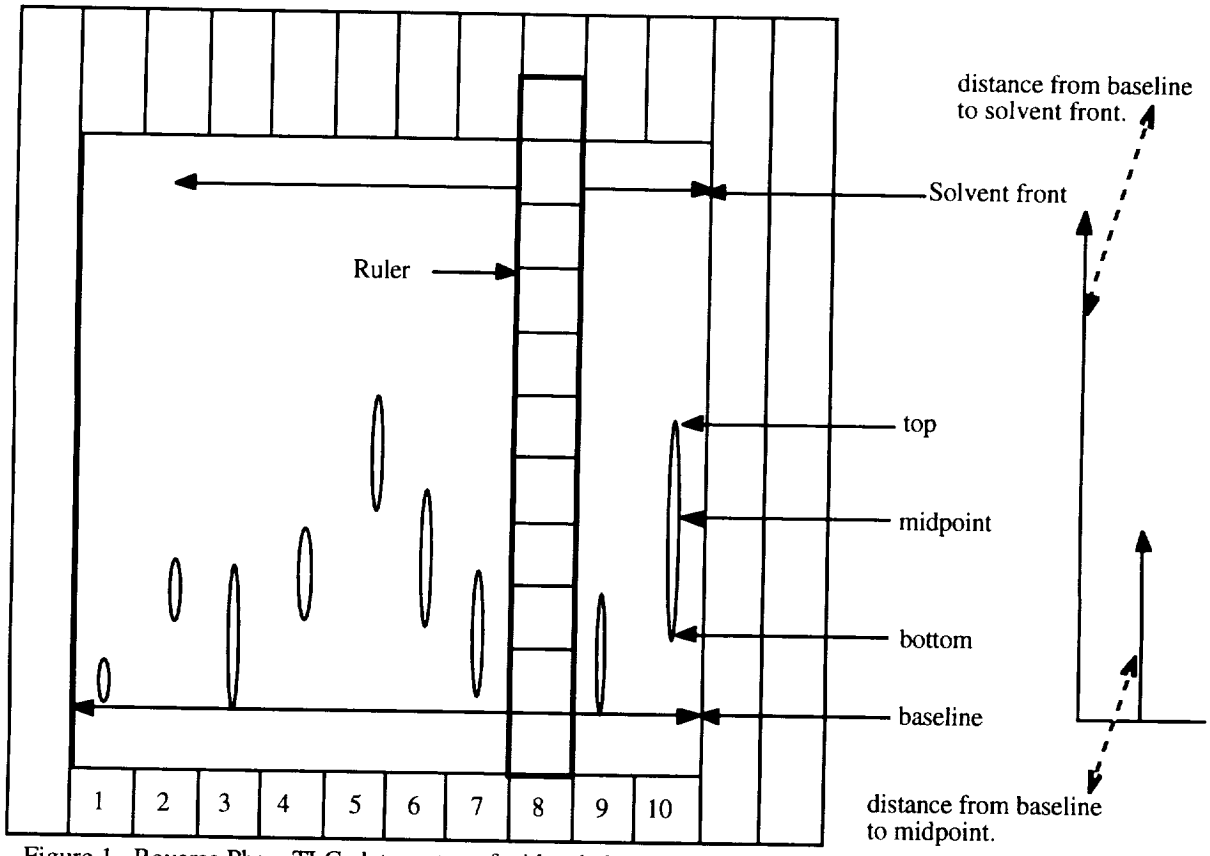

Figure 1. Reverse Phase TLC plate on top of wide ruled paper. The paper serves as a guide for sample lanes. Rf is calculated by dividing the distance travelled by the spot by the distance travelled by the solvent front.

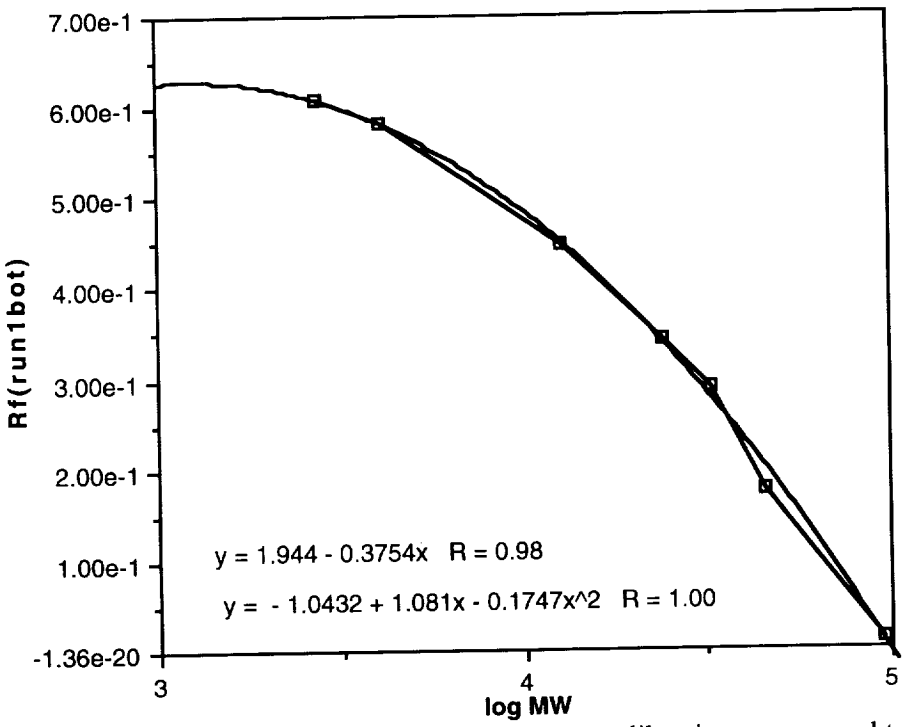

Table 1. Plot of log MW vs. R_f bottom which serves as a calibration curve used to calculate the number average molecular weight using Rf values obtained by TLC. Correlation coefficient for first order fit is .98, and for a second order polynomial fit is 1.

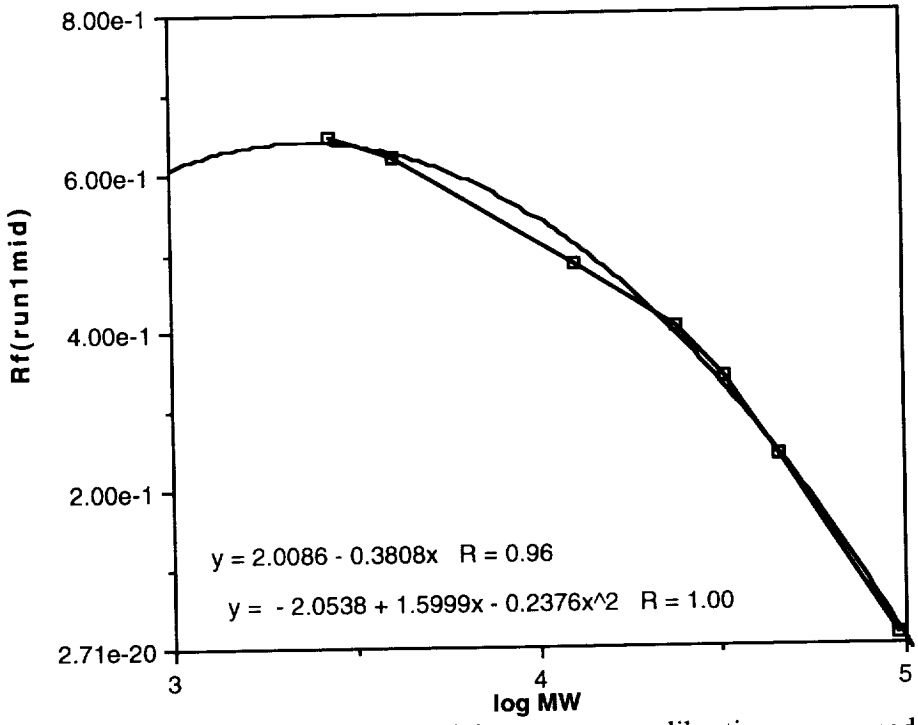

Table 2. Plot of log MW vs. R_f midpoint which serves as a calibration curve used to calculate the weight average molecular weight using Rf values obtained by TLC. Correlation coefficient for first order fit is .96, and for a second order polynomial fit is 1.

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