

Polymerization of methyl methacrylate to poly(methyl methacrylate) at a modest AIBN concentration(Round 4)

Chemical Engineering 401-02

Team L2: Team Davis

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Abstract

Polymerization is a method used to produce a myriad of materials used for a wide variety of purposes. This paper delineates the way poly(methyl methacrylate) was synthesized using methyl methacrylate with ethylbenzene and ethyl acetate as solvents and using a modest AIBN initiator concentration. The effect of monomer concentration, solvent, and temperature on rate of polymerization was investigated. The effect of monomer concentration was found to be dependent on the ratio of monomer to initiator concentration, meaning that typically, a higher concentration of monomer can be attributed to a higher rate of polymerization. However, this is not always the case. The effect of temperature was found to be proportional to the rate of polymerization. The effect of solvent was seen, as ethylbenzene had a higher rate of reaction than ethyl acetate; ethylbenzene had a rate of about 1.5 times and 1.3 times faster than that of ethyl acetate at 60°C and 70°C, respectively. In addition, the activation energy at a modest AIBN concentration was found to be 74.0kJ/mol. Thirdly, the expansion rates of the monomer to solvent ratio at varying temperatures were investigated and found. Lastly, the dependence of the polydispersity index on the ethyl benzene concentration and on quenching with hydroquinone was found. It was found that at lower concentrations of ethylbenzene the polydispersity index increased and when the reaction was quenched with hydroquinone the polydispersity index was higher.

Introduction

A polymer is a substance that has a molecular structure consisting of a large number of similar units (monomers) bonded together. Polymethyl methacrylate, or PMMA, which is created from repeating units of methyl methacrylate (MMA), is one of the most heavily explored and used polymers today due to its mechanical strength, chemical resistance, and weather resistance¹. PMMA is widely used as an alternative to glass, as it is shatter-resistant and is more transparent than glass itself². More specifically, PMMA is used in the making of hot tubs, sinks, aquariums, and acrylic paints. Another notable characteristic of PMMA is that it is a thermoplastic, meaning that can be used to ensure the effectiveness of lubricating oils and hydraulic fluids, which tend to get viscous when they approach cold temperatures. Dissolving PMMA into these substances can prevent this increase in viscosity and ensure usability. PMMA is also known for its mechanical strength, chemical resistance, and weather resistance².

In this experiment, polymethyl methacrylate was synthesized by dissolving methyl methacrylate in two different solvents, ethylbenzene and ethyl acetate, using a modest AIBN initiator concentration. The dependence of polymerization rate on monomer concentration was assessed by running reactions at three different monomer to solvent ratios at: 60:40, 70:30, and 80:20, with each reaction ratio evaluated at 50, 65, 70, and 75 degrees Celsius using a modest AIBN initiator concentration. Additionally, the activation energy for the polymerization reaction was determined using a modest concentration of AIBN

initiation (0.15% wt). Finally, the relationship between polydispersity index and solvent concentration was established. Molecular weight distributions of PMMA were assessed for certain samples using gel permeation chromatography (GPC).

Background

Kinetics of Polymerization of MMA to PMMA

Polymerization of MMA to PMMA occurs via free radical polymerization, a process that occurs in three steps: initiation, propagation, and termination³. Assumptions for the following schematics include instantaneous initiation and quasi-steady-state. In this lab, 2,2-azobisisobutyronitrile (AIBN) was used as the initiator. Before polymerization can occur, AIBN must be cleaved into two 2-cyanoprop-2-yl molecules, which will provide free radicals to the system^{4,5}. A free radical from 2-cyanoprop-2-yl will attack the double bonded carbon on MMA to form a single bond and another free radical, according to the initiation reaction in Figure 1.

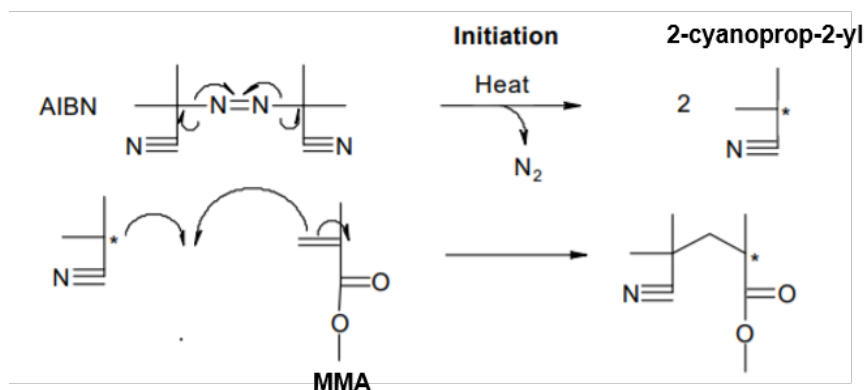


Figure 1: Initiation of MMA to PMMA using an AIBN inhibitor^{4,5}.

During propagation, MMA monomers will continue to be added to the chain until the process is terminated (Figure 2). It should be noted that the propagation step is the rate determining step of the polymerization reaction. Chain termination can occur by one of two mechanisms: termination by combination, or termination by disproportionation (Figure 2)³. In termination by combination, two polymer radicals combine to form a single PMMA molecule³. This type of termination often occurs at low temperatures⁴. Alternatively, termination by disproportion occurs when two growing polymer chains are within close proximity and react to form two polymer molecules. Rather than the two free radicals joining together, one of the free radicals will attack the carbon-hydrogen bond of the carbon atom next to the other carbon radical⁶. The free radical not only acquires one of the electrons from this bond, but also takes

the hydrogen as well. Consequently, the first chain now has no free radicals, and the end carbon shares eight electrons with carbons and hydrogens. Unlike termination by combination, termination by disproportion often occurs at high temperatures⁴. Both termination reactions results in PMMA.

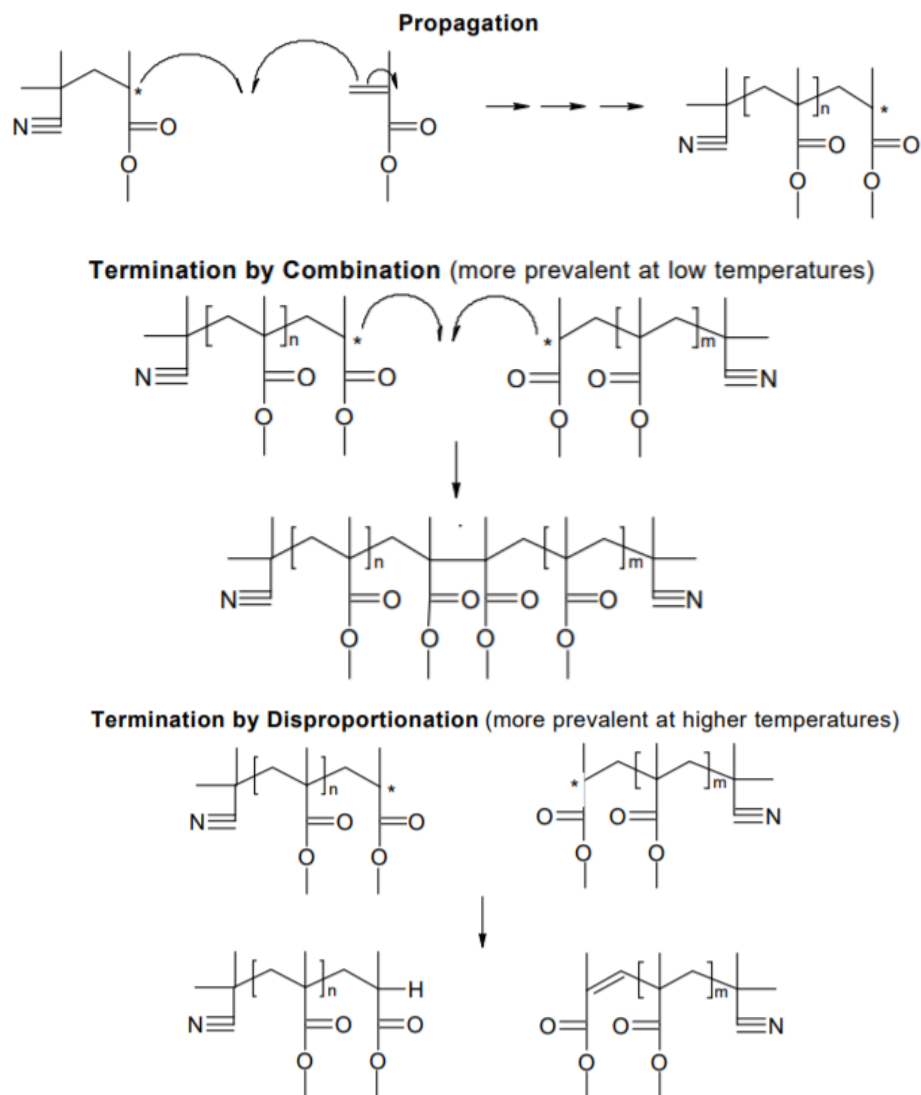


Figure 2: Propagation, termination due to combination, and termination by disproportion of MMA to PMMA^{4,5}.

Once polymerization is complete, the solution needs to be placed in an ice bath then quenched with hydroquinone to stop the reaction. The hydroquinone acts as an antioxidant. Consequently, the free radical on the last monomer unit in the polymer chain reacts with the OH group on the hydroquinone molecule. This free radical will then cycle the benzene ring until it settles on the carbon of the OH group opposite from the OH group is reacted with initially (Figure 3)¹⁴.

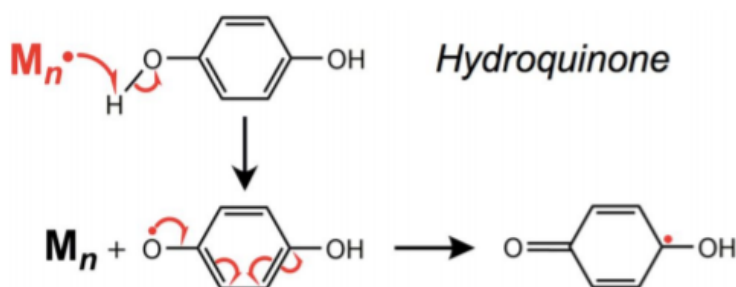


Figure 3: Quenching mechanism of hydroquinone.

Determining Reaction Parameters

In order to determine conversion rate, change in volume of the solution can be related to change in monomer concentration according to Equation 1 where ρ is the density of either the monomer or the polymer, V_0 is the initial volume of the solution, D is the diameter of the glass capillary of the dilatometer, and $[M_0]$ is the initial monomer concentration. The cathetometer was used to observe changes in height as described in the experimental procedure. The assumption that the monomer and solvent mixture is ideal is important in calculating this change in monomer concentration.

$$\Delta[M] = \frac{\pi D^2 [M_0]}{4 V_0 \rho_m \left(\frac{1}{\rho_m} - \frac{1}{\rho_p} \right)} \Delta h$$

Equation 1: Conversion equation that relates the change in volume to the monomer concentration change⁸.

In order to determine the reaction rate constant, the following equation can be used, where R is the reaction rate (which is determined using the dilatometer and cathetometer), k is the reaction rate constant, $[M]$ is monomer concentration, and $[I]$ is initiation concentration. Based on literature values, X is 1, and y is $\frac{1}{2}$ ⁸.

$$R = k [M]^x [I]^y$$

Equation 2: Reaction rate equation⁸

Activation energy can then be determined from a linearized form of the Arrhenius equation where k is the reaction rate constant, E_a is activation energy, R is the ideal gas constant, T is temperature, and A is the frequency factor (Equation 3).

$$\ln(k) = \frac{-E_a}{R} \left(\frac{1}{T} \right) + \ln(A)$$

Equation 3: : Linearized Arrhenius equation used to determine activation energy⁹.

In addition to calculating reaction rate, rate constant, and activation energy, it is important to consider the polydispersity index (PDI) of the PMMA which describes lack of uniformity due to uneven polymer chain lengths¹⁰. PDI is described as a ratio of number average molecular weight (\overline{M}_w) to weight average molecular weight (\overline{M}_n).

$$PDI = \frac{\overline{M}_w}{\overline{M}_n} \quad \overline{M}_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} \quad \overline{M}_w = \frac{\sum_{i=1}^{\infty} W_i M_i}{\sum_{i=1}^{\infty} W_i}$$

Equation 4,5,6: Polydispersity index, number average molecular weight, and weight average molecular weight. N_i is number of chains of particular weight, M_i is weight of the chain, and W_i is molecular weight of the chain¹⁰.

Finally, the chain transfer coefficient of polymerization of MMA to PMMA can be assessed. Chain transfer is a polymerization reaction that by which the activity of a growing polymer chain is transferred to another molecule. The chain transfer coefficient is a ratio of the chain transfer rate constant to propagation rate constant¹¹. Therefore, a higher chain transfer coefficient translates to increased radical transfer between molecules. The chain transfer coefficient can be determined using a simplified version of the Mayo equation where DP_n is the number average degree of polymerization, DP_{n0} is the number average degree of polymerization for polymer produced under the same conditions in the absence of added chain transfer agent, $[S]$ is the concentration of added chain transfer agent, and $[M]$ is the concentration of added monomer.

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_s \frac{[S]}{[M]}$$

Equation 7: Modified Mayo equation¹¹

Gel Permeation Chromatography

In order to determine PDI and molecular weight distribution, gel permeation chromatography was used. In gel permeation chromatography, molecules are separated based on their effective size in solution. The PMMA was dissolved in THF and is injected into a continually flowing stream of solvent in a mobile phase¹². Toluene is also added to the mixture in order to serve as a reference value in the refractive index reading. This mobile phase flows through millions of highly porous, rigid, stationary particles in a packed column. Smaller species will move through and exit the column more quickly than larger species. This process results in a molecular weight distribution curve¹².

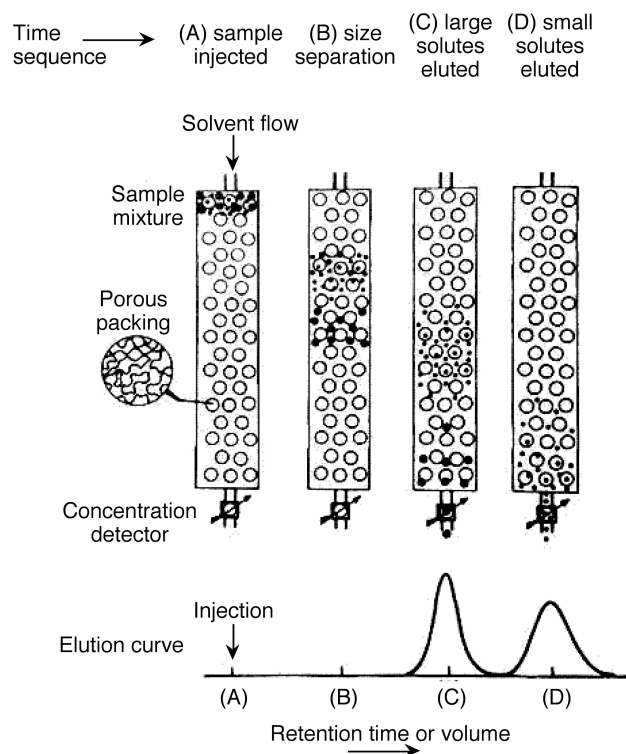


Figure 4: A schematic of GPC¹³

Design of Apparatus

The relevant equipment used in this laboratory included two dilatometers and two cathetometers (Figure 5). A dilatometer is a U-shaped glass tube which includes a reaction bulb on one side of the U-tube. The glass tubing of dilatometer 20 had a diameter of 1.64 mm, while the glass tubing of dilatometer 5 had a slightly smaller diameter of 1.62 mm. As shown below, one end of the U-tube is shorter than the other. The shorter end of the dilatometer can be connected to vacuum suction in order to fill or empty the device. When polymerization occurs in

the dilatometer, the polymer will crawl down the capillary tube on the longer side of the U-tube. This decrease in height can be recorded using a cathetometer.

The cathetometer can be read with the help of a telescope assembled about six feet opposite the dilatometer. The telescope can be adjusted so that the polymer meniscus is in sight once polymerization begins. The telescope can then be focused so that the cross hairs of the cathetometer are in view. As the polymer travels through the glass capillary of the dilatometer and passes the crosshair of a certain height, the height of the telescope can be decreased by one centimeter until the polymer reaches the crosshair of the new height. Time points can be recorded each time the polymer reaches the crosshair of a certain height. This process can be repeated for twenty heights in order to determine reaction rate of polymerization. Caution was taken not to lean on the table the cathetometers were on, as the telescope needs to be kept at a steady level in order to obtain accurate reaction rate data.

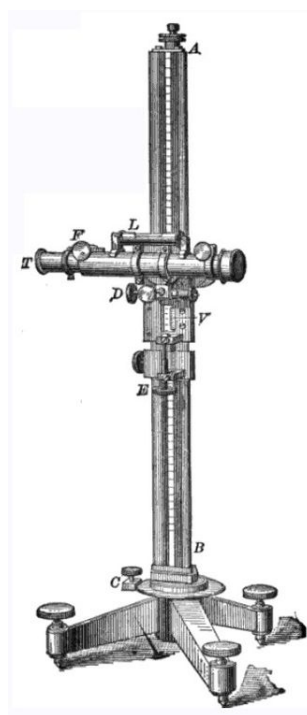
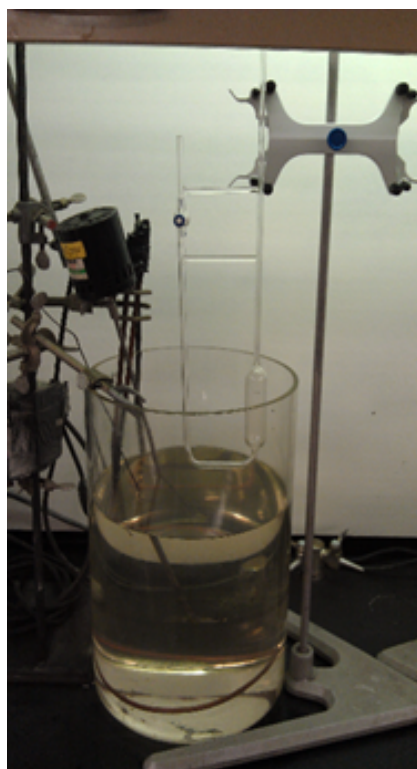


Figure 5: Dilatometer in oil bath (left) and cathetometer (right)^{14,15}.

Experimental Procedure

Pre-Lab Technical Request Form

Before each lab period, a technical request form (TRF) was filled out. The TRF specified chemicals used, oil bath temperatures (ranging from 50 to 75 degrees Celsius), and preparation of molecular sieves¹⁴.

Monomer Preparation: Methyl Methacrylate

The following procedure was used to prepare MMA for the polymerization reaction. ~0.6 g of sodium hydroxide (NaOH) was combined with 300 mL of distilled water (H₂O) in a 1000 mL flask. 300 mL of monomer was then measured out in the fume hood. Next, the monomer was transferred from a beaker into an inverted flask, with the stopcock closed. 100 mL of NaOH solution was added. The mixture was shaken for 1 minute to thoroughly mix the solutions. Setting the flask down, the mixture was allowed to separate into its organic and aqueous phases, and the aqueous phase was decanted out the bottom. The previous steps were repeated twice. After the third wash, 1 g of molecular sieves was added to the inverted flask. The flask was shaken for 2 minutes. With a Buchner funnel and filter paper, the MMA solution was poured over the paper to filter out the sieves. The solution was then refrigerated.

Run Solutions:

The following steps in the run solutions section were done under a fume hood. The three monomer:solvent ratios used during this experiment were 60:40, 70:30, and 80:20. Monomer solution and solvent (ethylbenzene or ethyl acetate) were measured out according to the desired ratio. The total volume of the mixture summed to 100 mL. Monomer and solvent were combined into a 250 mL beaker. The AIBN initiator of 0.15 weight percent with respect to monomer was measured out and added to the solution. A magnetic stirrer was utilized and the solution was mixed thoroughly¹⁴.

Dilatometer Filling

The dilatometer was used to monitor the polymerization reaction in the oil baths. It was vital that the dilatometer was filled with the monomer solution with no bubbles in the tubing. The vacuum pump was used to suck the reaction mixture into the dilatometer. After this, the bottom of the dilatometer was lifted out of the reaction mixture. The vacuum pump was turned on to allow for air to be sucked into the dilatometer. This was done to provide space for the expansion of the monomer solution when the bulb was placed into the bath and prevent spilling

of the reaction mixture into the bath. If there were any bubbles in the solution, the vacuum was turned off and the process of filling the dilatometer was restarted. The measurement of the end of the long end and to the bottom of where the solution in the dilatometer ends is taken. This was used to calculate the expansion rate of the polymerization reaction¹⁴.

Experimental Runs

The polymerization reactions were run by placing the dilatometer in an oil bath at the desired temperature. The filled dilatometer was placed in the desired oil bath and the timer was started to measure the amount of time it took for the solution to reach the top of the long end of the dilatometer. The distance covered by the solution was also documented. The reaction bulb was completely submerged in the bath. If the temperature was too hot, auto-acceleration could have occurred. A paper towel hat was used to catch the overflowing polymer solution as it continued to expand after it reached the top of the dilatometer. The cathetometer was set to line with the dilatometer and was monitored until the polymer solution began to shrink. Once the meniscus reached the cross hairs, the timer was started. The cathetometer was then moved down the pole to 1cm below the previous height. When the meniscus reached the crosshairs again, the time was recorded. This process was done until the meniscus dropped about 20 cm. After height drop was achieved, the dilatometer was removed from the oil bath and the outside was wiped clean of the oil¹⁴.

Polymer Isolation/Dilatometer Clean-Up

The reaction solution was placed in a beaker in an ice bath immediately after this step. This was achieved by attaching vacuum hose to the Erlenmeyer flask with a drilled cap. The hose was attached from the cap to the short end of dilatometer. The vacuum was turned on and the solution was collected in the beaker. 50 mL of cyclohexane was added to the solution in the ice bath to precipitate the polymer, which was allowed to sit for about 10 minutes. While waiting, the dilatometer was immediately cleaned with successive runs of water and acetone to avoid clogging. After 10 minutes, the polymer was vacuum filtered and dissolved in 50 mL of toluene. 150 mL of methanol was added to a large, separate beaker, and stirred with a magnetic stirrer. The polymer solution was dropped in the methanol in increments of 30 mL. The polymer precipitated out as white powder and was filtered with a small Buchner funnel. The polymer was then scraped off the filter paper and added to a clean vial¹⁴.

Gel Permeation Chromatography

The polymer was then analyzed with GPC to determine the polymer make up. A 3 mg/mL solution of the polymer in THF is needed. The solution was filtered with a 0.45 micron pore sized PTFE filter directly into the GPC autosampler vial and sealed. The autosampler vials must have a septum in the cap in order to be compatible with the GPC instrument¹⁴.

Clean-Up Procedure

All glassware was cleaned with acetone and dried with pressurized air. Any reaction waste was disposed of in a hazardous waste container. After, at least 1 mg of hydroquinone inhibitor per 70 mL of reaction solution was added to container. This step was conducted to prevent auto-acceleration of the reaction. Paper products such as filter paper and paper towels were allowed to dry in the hood before being disposed of in a small waste basket provided in the hood. The collection container from the vacuum was emptied and cleaned¹⁴.

Safety Information

Hazardous waste labels were filled out with the chemical name. All chemicals were mixed and opened in the fume hood. Caution was taken around oil baths because of the high temperature of them. The safety data sheets were inspected thoroughly for each chemical that was used in this lab. The max temperature of the heating bath did not exceed 115 degrees Celsius. To avoid auto-acceleration at all times, a stopping solution was used at the end of each trial. A stopped flask was not heated and acetone was not used with hot glassware because of its low boiling point ¹⁴.

Table 1: List of reactions ran. All reactions ran were ran with AIBN 0.15 wt% with respect to the monomer.

Solvent	Ratio of MMA: Solvent (ml:ml)	Temperature (°C)
Ethyl acetate	60:40	60
Ethyl acetate	60:40	70
Ethyl acetate	70:30	60

Ethyl benzene	60:40	60
Ethyl Benzene	60:40	70
Ethyl benzene	60:40	75
Ethyl benzene	70:30	70
Ethyl benzene	70:30	75
Ethyl benzene	80:20	50
Ethyl benzene	80:20	60
Ethyl benzene	80:20	70
Ethyl benzene	80:20	75

Results and Discussion

The first objective of this project was to determine the monomer concentration, effect of temperature, and solvent on the rate of reaction. Firstly, the rate of conversion from methyl methacrylate to poly methyl methacrylate can be visually seen in both figures 6 and 7. Figure 6 shows the non-normalized conversion of monomer to polymer versus time when using an ethylbenzene solvent and 0.15 weight percent with respect to the monomer. As can be deciphered from the graph, it appears that the rate of reaction increases as the ratio of monomer to solvent increases. In Figure 7, the data was normalized by scaling by the amount of monomer used in order to compensate for different amounts of polymer occupying different volumes in the dilatometer. This figure provides a different result; it shows that the rate does increase from the 60:40 to 70:30. However, the 80:20 ratio has a lower rate than the 70:30 ratio. This can be explained by the twofold property of the polymerization reaction stated in the paper written by Baldwin (1963). In this paper, Baldwin states that as the ratio of monomer to initiator

concentration decreases, the rate of reaction increases to the peak rate, but also approaches zero when the ratio of monomer to initiator increases. This is as a result of there not being enough initiator for the monomer. Therefore, as can be seen in Figure 7, the 70:30 ratio of methyl methacrylate to ethylbenzene has the fastest rate and this can be explained by the twofold property of polymerization reactions¹⁶. The same trend can be seen in Figure 8 and Figure 9; even though the un-normalized data seems to show a faster rate for the 70:30 monomer to ethyl acetate ratio compared to the 60:40. In Figure 9, it is visible that the 60:40 has a slightly higher rate of conversion than the 70:30.

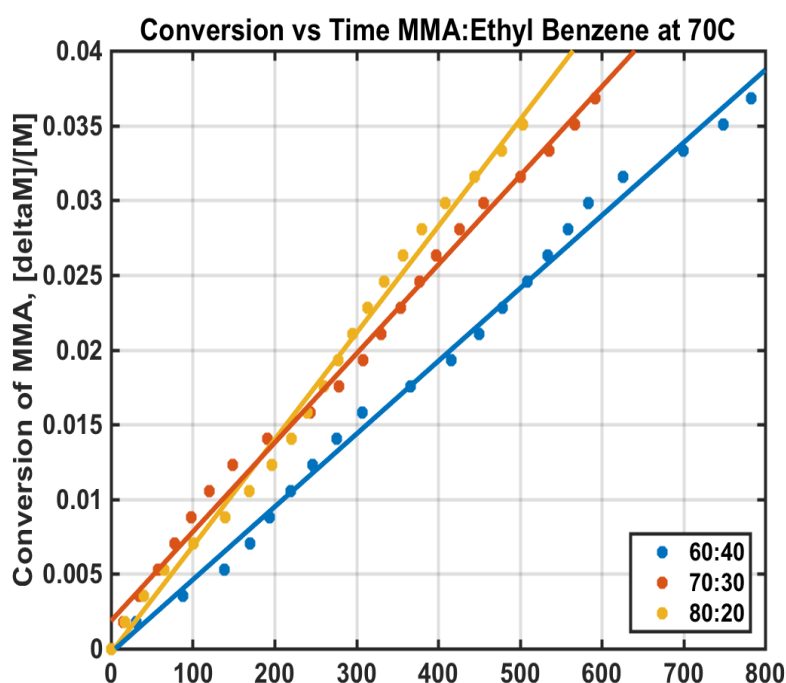


Figure 6: Conversion vs Time of varying Methyl methacrylate and Ethyl benzene ratios at 70°C

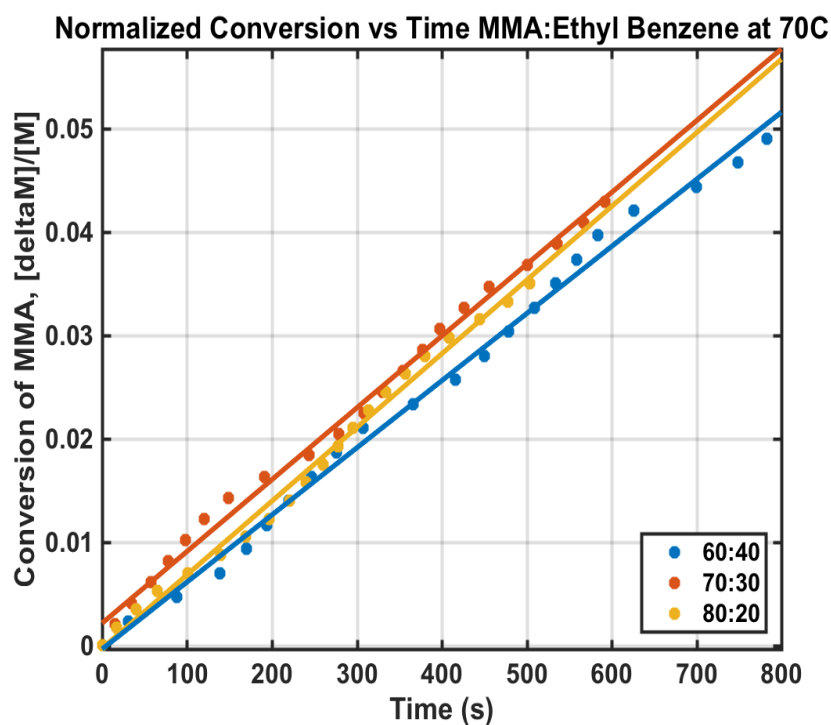


Figure 7: Normalized Conversion vs Time of varying Methyl methacrylate and Ethylbenzene ratios at 70°C

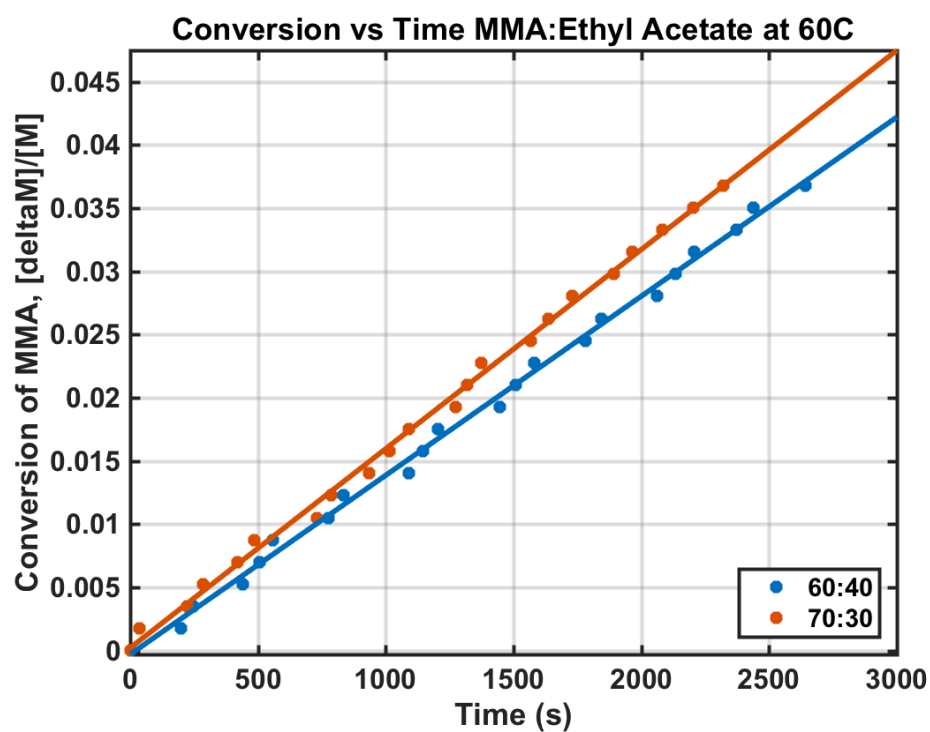


Figure 8: Conversion vs Time of varying Methyl methacrylate and Ethylacetate ratios at 60°C

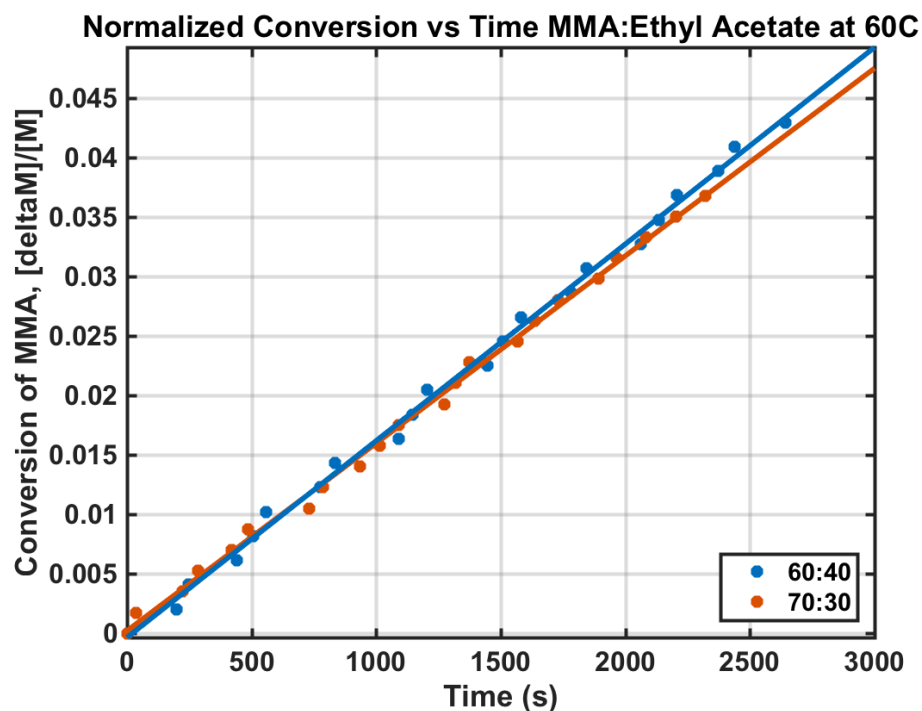


Figure 9: Normalized Conversion vs Time of varying Methyl methacrylate and Ethyl Acetate ratios at 60 °C

The effect of temperature and solvent on reaction rate can be elucidated by Figure 10. As can be seen in the graph, the rate of reaction increases as temperature increases. This follows kinetic intuition that as temperature increases there is an increase in the number of high energy collisions. Meanwhile the rate of conversion also varies with the solvent being used. As can be seen in both Figure 10 and Table 2, the rate of reaction at the same temperature for the different solvents are distinctly different. It can be seen that the ethylbenzene solvent has a higher rate of conversion. This can be attributed to the fact that ethylbenzene has a higher chain transfer coefficient than ethyl acetate. The chain transfer for ethylbenzene and ethyl acetate are 13.5×10^{-5} and 1.35×10^{-5} , respectively, at 60°C. The higher chain transfer coefficient means that more termination reactions occur thus leading to a faster rate of conversion. From Table 2, the rate of reaction of ethylbenzene was faster than that of ethyl acetate by 1.5 times and 1.3 times at 60°C and 70°C respectively.

Table 2: Rates of reaction of 60:40 methyl methacrylate and varying solvent at varying temperatures

Solvent used	Temperature (°C)	Rate (mol/(ml*s))	Rate ratio
Ethyl Benzene	60	2.20e-05	1.5
Ethyl Acetate	60	1.42e-05	
Ethyl Benzene	70	4.87e-05	1.3
Ethyl Acetate	70	3.65e-05	

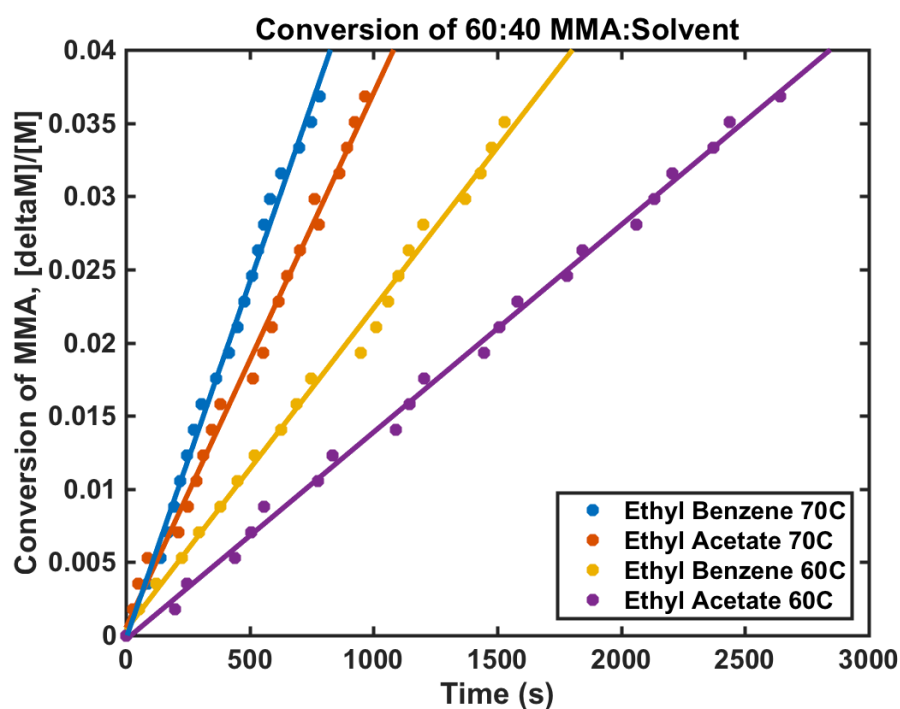


Figure 10: Conversion vs Time of 60:40 ratio Methyl methacrylate and Ethylbenzene/ Ethyl acetate at varying temperatures

The second objective of this project was to determine the activation energy at a modest AIBN concentration, which was 0.15 wt% with respect to monomer. In the Figure 11, the activation energy of 80:20, 70:30, and 60:40 monomer to ethyl benzene solution mixtures were plotted comparatively to one another. The range of activation energies calculated during the course of the project were from 74.0 kJ/mol, 41.9 kJ/mol and 66.4 kJ/mol respectively to the

monomer to ethylbenzene ratios stated previously. The literature value for this reaction corresponded to 80.04 kJ/mol¹⁷. Results from previous groups include: 74.1 kJ/mol⁷, 24.1 kJ/mol¹⁸ and 77.95 kJ/mol¹⁹.

As stated previously, the calculated energies were differed with the monomer to ethylbenzene ratio. The 80:20 ratio was the closest to the literature value, while the 70:30 and 60:40 ratios were quite different from the literature values. It can be inferred from the graph that the 80:20 ratio provides the most accurate result because its activation energy was determined using the largest temperature difference, while the 70:30 provides the largest difference between the literature value and the result. Therefore, it can be deduced that the 80:20 ratio's activation energy of 74.0 kJ/mol is the most accurate because of its relative closeness to the literature value and its large temperature distribution used to calculate it.

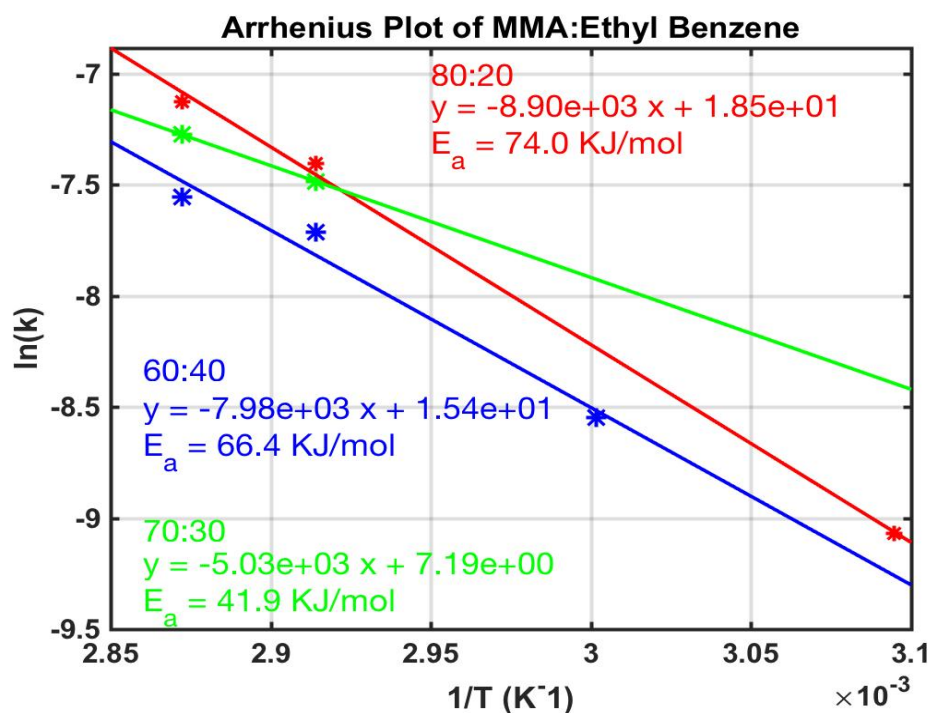


Figure11: Arrhenius plot of Methyl Methacrylate and Ethyl benzene at varying ratios

The third objective of this project was to quantify the rate of expansion of the monomer. As can be seen in Figure 12, the volumetric expansion of the monomer can be seen to increase as temperature increases. This plot shows the rate of both ratios. As can be seen on the graph, the 70:30 ratio has a higher rate of expansion at all temperatures. This is a result of ethylbenzene

having a slightly higher volumetric expansion coefficient of $0.00103^{\circ}\text{C}^{-1}$, while methyl methacrylate has a volumetric expansion coefficient of $0.001^{\circ}\text{C}^{-1}$ ¹⁸. Therefore, this graph offers an avenue to be able to predict the rate of expansion through a dilatometer at a certain temperature at these ratios of methyl methacrylate to ethylbenzene.

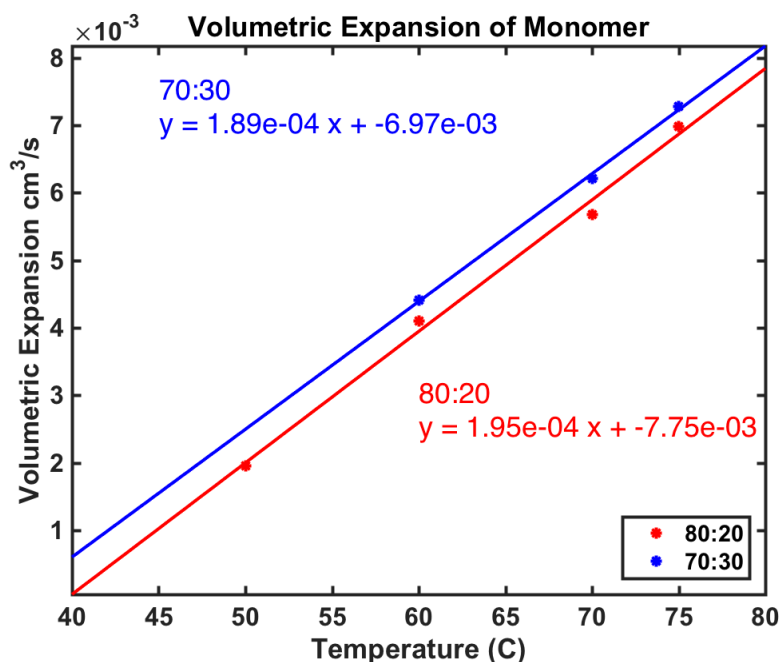


Figure 12: Volumetric expansion rate vs Temperature of varying Methyl methacrylate and Ethylbenzene solutions

Lastly, the fourth objective of this project was to establish the dependency of PDI on ethylbenzene concentration and to determine whether quenching the reaction with hydroquinone affects the PDI. In Table 3, it can be seen that as the ethylbenzene concentration decreases from the 60:40 to the 80:20 ratio at the same temperature the PDI increases. This can be accredited to the chain transfer coefficient. As a result of decreasing concentration of ethylbenzene, there are less chain termination reactions thus leading to a larger dispersity of a measure of the distribution of molecular mass in a given polymer sample. As can be seen in Table 3, the 70:30 ratio doesn't fall into the trend of increasing PDI with decreasing temperature. However, from the results of Rhys (2017); it was observed that increasing temperature led to increased PDI. Therefore, it can be inferred from paper that the reason for a lower PDI in the 70:30 ratio is as a result of a lower temperature²⁰. Lastly, it can be observed that hydroquinone does affect the PDI. This makes intuitive sense; when the solution is cooled and then hydroquinone is added, it stops the reaction.

Consequently, there is less polymerization and termination reactions that can occur afterwards, therefore leading to a more disperse distribution of molecular weights in the monomer.

Table 3: PDI vs Concentration of Ethylbenzene

MMA/ Ethylbenzene	Hydroquinone added	Mw	Mn	PDI	Concentration of Ethylbenzene (mol/l)	Temperature (°C)
60/40	No	2.56E+05	1.81E+05	1.41	3.3	70
70/30	No	2.05E+05	1.48E+05	1.39	2.4	60
80/20	Yes	2.28E+05	1.52E+05	1.50	1.6	70
80/20	No	2.37E+05	1.63E+05	1.46	1.6	70

Conclusion

As can be seen in Figure 6 and 7, the monomer concentration affects the rate of polymerization. However, the effect of monomer concentration has a twofold property where a low ratio of monomer concentration to initiator concentration leads to a decreasing rate of polymerization and where a very high ratio of monomer to initiator also leads to a decreasing rate of polymerization. The temperature was also seen to affect the rate of polymerization, with the highest temperature having the highest rate. Additionally, the solvent affects the rate of polymerization. From Figure 10, it shows that ethylbenzene has a higher rate at each temperature than ethyl acetate. This result can be attributed to the higher chain coefficient of ethylbenzene. The activation energy found at a modest AIBN concentration at 0.15 wt% with respect to monomer was found to be 74.0 kJ/mol, which was very close to the literature value. Lastly, concentration of ethylbenzene and quenching the reaction with hydroquinone was seen to have an effect on the PDI. It can be seen from table one that PDI increases with decreasing solvent ratio as a result of less chain transfer reactions occurring as there is less solvent to help this occur. Quenching the reaction with hydroquinone can be seen to increase the PDI since it stops the reaction once added thus preventing possible termination reactions occurring afterwards.

Recommendations

1. When filling the dilatometer, be sure to leave space for the expansion of the monomer when it is put into the oil bath
2. Clean as the experiment is being done. Leave about 45 minutes for final clean-up.

Word count: 3472

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Notation

Symbol	Definition	Units
$[M_0]$	Initial Monomer Concentration	mol/L
$[M]$	Monomer Concentration	mol/L
π	Pi	Unitless
D	Diameter of Glass Capillary of Dilatometer	cm
V_0	Initial Volume of Solution	L
ρ_m	Density of Monomer	g/cm ³
ρ_p	Density of Polymer	g/cm ³
h	Height	cm
R	Reaction Rate	(mol/L*s)
k	Reaction Rate Constant	Experimentally Determined
$[I]$	Initiator Concentration	mol/L
E_a	Activation Energy	kJ/mol
R	Ideal Gas Constant	J/K*mol
T	Temperature	Celsius
A	Frequency Factor	1/s
PDI	Polydispersity Index	Unitless
M_w	Average Molecular Weight	g/mol
M_n	Weight Average Molecular Weight	g/mol
W_i	Molecular Weight of the Chain	g
N_i	Number of Chains of Particular Weight	Unitless
M_i	Weight of the Chain	g/mol
DP_n	Number Average Degree of Polymerization	Unitless
DP_{n0}	Number Average Degree of Polymerization for Polymer	Unitless

	Produced Under the Same Conditions in the Absence of Added Chain Transfer Agent	
[S]	Concentration of Added Chain Transfer Agent	mol/L
C _{Ss}	Chain Transfer Coefficient	Unitless

Appendix

Sample MATLAB code

60:40 MMA:Ethyl Benzene at 60 degrees

```
time = [0 52.53 122.09 228 295 383 452 521 626 689 748 948 ...
        1011 1061 1102 1144 1201 1369 1431 1479 1530];

%height = linspace(62,42,21);
l=linspace(0,20,21);
d=0.165;
rhom=0.94; % density of mma g/cm^3
rhop=1.18; % density of PMMA g/cm^3
v0=60; % mL starting volume of solution in dilatometer 5
z=v0*rhom*((1/rhom)-(1/rhop)); %denominator of conversion
function
conversion=deltav(l,d,v0)./z; % conversion of MMA to PMMA

scatter(time,conversion,'LineWidth',3)
hold on

xlabel('Time (s)')
ylabel('Conversion of MMA, [deltaM]/[M]')
title('Conversion vs time 60C 60:40 MMA:Ethyl Benzene')

grid on
hold off

format short
h = lsline;
h;
mdl=fitlm(time,conversion);
h.LineWidth = 3;
p = polyfit(time,conversion,1);
String = sprintf('y = %1.2e x + %1.2e',p(1), p(2));
text(150, 15e-4, String, 'FontSize', 18)
```

```

%disp('60:40 EB 60');
%disp(p(1))
% -----Change these
V = 63.1; %mL
d = 0.164; %cm
mon = 60;
sol = 40;
aibn = 0.0849;
T = 60;
h=linspace(0,20,21);
%-----

mwmma = 100.12; %g/mol
mwaibn = 164.21; %g/mol
dt = [0 diff(time)];
rhomma = .949; %g/mL
rhopmma = 1.18; %g/mL
m = (mon/100)*V*rhomma/mwmma/(V)/1000;
ma = zeros(1,length(h));
dma = zeros(1,length(h));
for i = 1:length(h)

ma(i) = m;
dm = (pi*d^2*m)/(4*V*rhomma*(1/rhomma-1/rhopmma));
m = m - dm;
dma(i) = dm;
end
M = ma;
dM = dma;

rate = dM/dt

box on
set(gca, 'FontName', 'Arial');
set(gca, 'FontSize', 16);
set(gca, 'FontWeight', 'b');
set(gca, 'LineWidth', 2);
set(gcf, 'color', 'w');

```

Sample calculations

Percent Conversion

$$X = 1 - \frac{[M]}{[M_0]} \times 100$$

Initial monomer Concentration

$$[M_0] = \left(\frac{\text{Ratio of MMA}}{100} \times \text{volume of dilatometer} \right) \left(\frac{\text{density of MMA}}{\text{MW of MMA}} \right)$$

Monomer Concentration

$$[M] = [M_0] - \Delta[M]$$

Change in Monomer Concentration

$$\Delta[M] = \left(\frac{\pi \times (\text{diameter of dilatometer})^2 \times [M_0]}{4 \times (\text{volume of dilatometer}) \times (\text{density of MMA}) \left(\frac{1}{(\text{density of MMA})} - \left(\frac{1}{(\text{density of PMMA})} \right) \right)} \right) \times \text{height increment}$$

Volumetric rate of Expansion

$$r_v = \frac{\text{length of hollow section}}{\text{time to fill}} \times \text{cross sectional area}$$

Rate of Conversion

$$r = \frac{\Delta[M]}{\Delta t}$$

Rate Constant

$$k = \frac{r}{[M][I]^{1/2}}$$

Activation Energy

$$E_a = -\text{slope of arrhenius plot} \times R$$