

**Reactivity ratio determination for the terpolymerization of
poly(2-EHA-MMA-St)**

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Abstract:

The physical, chemical and mechanical properties of polymers depend on the micro-structural characteristics of the macromolecular chains. The reactivity ratio gives a clear idea about the mean composition of the polymer, the sequence distribution of monomers, and rate of polymerization. The reactivity ratio is a kind of kinetic parameter and is defined as the ratio of the propagation rate constant for one monomer to that of another.

Traditionally, reactivity ratio estimation using linearization techniques were used instead of non-linear parameter estimation methods because of lack of computational power. The linear estimation of copolymerization reactivity ratio led to distorted error structure. Previously, only low conversion data could be used, along with the Error-in-Variables Method, which is a non-linear parameter estimation technique that considers the error present in all variables. To be able to handle medium or high conversion data in determination of reactivity ratio for terpolymerization, DNI-EVM approach has been used. The terpolymer DNI-EVM approach requires three compositions to be run to high conversion, each rich in one monomer.

After assembling the apparatus and performing the degassing process in order to release oxygen gases dissolved in the solution, the polymerization process was performed in the range of 0-25% conversion level. Examining the peaks resulting from $^1\text{H-NMR}$ spectroscopy became challenging due to the overlap between the peaks related to PEHA and PMMA with three residual monomers for the region of 1.70 - 1.95 and 3 - 4.35. It is suggested to carry out additional experiment such as the pure PMMA, PSt., PEHA runs to full conversion also, 33.3/33.3/33.3 composition fully converted polymer sample and the three 80mol% compositions to full conversion.

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INTRODUCTION

Polymer coatings are thin films of polymer that adhere to a substrate and impart various functional and decorative properties such as adhesion, water/solvent resistance, and color. Due to the various unique characteristics caused by the combination of different monomers, which are difficult to achieve from pure homopolymers, the synthesis of copolymers and terpolymers have been popular in different fields.

The use of 2-ethylhexyl acrylate (EHA-2 or EHA) and methyl methacrylate (MMA) is quite popular in the synthesis of adhesives, paints, and other coatings. EHA imparts a low glass transition temperature [T_g , which characterizes the temperature range through which the polymer changes from a glassy (hard) state into a liquid (rubbery) state], good film formation characteristics, and tack/peel, while MMA introduces rigidity, impact strength, and thermal stability. Monomers like styrene are added for additional rigidity, gloss, and shear strength. Styrene is famously used in styrene-butadiene (SBR) rubber and adhesives. Although copolymer systems of these monomers have been studied, the terpolymer system (including kinetics) has not. In order to effectively control the final composition of copolymer or terpolymer, parameters such as copolymer reactivity ratios (r_i) are needed. Reactivity ratios are a key kinetic parameter that inform us about the polymerization rate too. (El-Wahab, 2019) This work will study the reactivity ratios of the terpolymer system of 2-EHA, MMA, and Styrene, which has so far not been explored. Research groups like those of Dr. Dube at the University of Ottawa, and Dr. Scott at Dalhousie University, including engineers and chemists in the polymer industry, would make great use of accurate reactivity ratios for this system, which is an attractive one for many polymer applications.

Estimating the reactivity ratio involves a set of low-conversion (roughly > 10 wt%) experiments and a set of moderate to high level of conversion (roughly $10 - 40$ wt%) experiments over a range of monomer feed compositions. The first set of data from low level conversion is used to determine initial estimates of the reactivity ratios using the error-in-variables-model (EVM). And the second set of data from moderate to high level conversion is used to determine the reactivity ratios using the Direct Numerical Integration (DNI) coupled with the EVM method. Both approaches will calculate precise reactivity ratio and consider the error present in all variables. The precision of the reactivity ratios is judged using the joint confidence region (JCR), which is represented an ellipsoid region around a point which is an estimated solution; the smaller area of the JCR, the smaller the variability. Further, the reactivity ratios will be compared to real results from validation

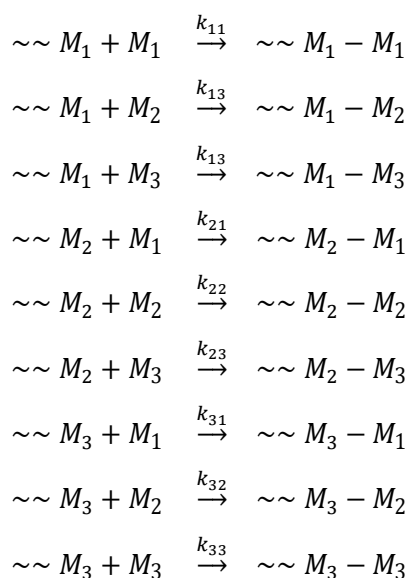
polymerizations that will be run to full conversion. These ratios are used to generate composition-conversion models, which will be validated with polymerizations at various compositions going to full conversion. To calculate the reactivity ratios of terpolymer systems, one needs to know the monomer feed and final terpolymer composition, as well as the monomer conversion.

The experiment was performed at 0 to 40 % conversions with three different compositions. The polymerization process was carried out with a constructed apparatus and ampoules and, through a freeze-thaw process under vacuum the dissolved oxygen in the solution was removed. At the final step, the ampoules were placed in a hot water bath as mini-reactors, and the polymerization reaction was performed. Conversion was calculated using gravimetry method and composition value (molar percentage) was determined through H-NMR Spectroscopy.

Free Radical Polymerization

The terpolymerization system is a topic of interest and growing among researchers. Because there are countless combinations of monomers to be discovered. However, due to the wide range of possibilities, terpolymerization systems are less studied than copolymerization systems.

The kinetics of terpolymerization systems were first described by Alfrey and Goldfinger. Since there are three different possibilities for the terminal monomer (on the growing polymer chain containing radical), and three different options for the addition of the monomer, there are nine different propagation steps according to the terminal model: (Scott A. G., 2019)



Reactivity Ratios

To control the mean composition of the polymer, the sequence distribution of monomers and rate of polymerization, and by extension, molecular weight and distribution of the final product, parameters such as the reactivity ratios are used. The reactivity ratio is a kind of kinetic parameter and is defined as the ratio of the propagation rate constant for one monomer to that of another.

Two general models used to estimate the reactivity ratio of copolymerization reactivities: instantaneous models and cumulative models. Monomer reactivity ratios are usually determined at low conversion copolymer composition data with the help of the instantaneous copolymer composition model. Indeed, for low conversion assuming a negligible composition drift in the monomer feed (and, hence, in the copolymer chains) it is referred to the Mayo-Lewis equation (a highly nonlinear equation). However, most copolymerization reactions inevitably undergo compositional drift as the degree of conversion increases (with the exception of special cases, which we do not often encounter). Also, the requirement to stop a reaction at a low conversion percentage often leads to experimental problems that can be considered as important sources of error in most cases. Therefore, it is reasonable to turn to cumulative copolymer composition models, that is, the integrated form of instantaneous copolymerization models. Furthermore, considering the calculation of the reactivity ratio using copolymers with high conversion percentages, it is a great advantage that a single copolymerization can provide multiple data points and, consequently, a great deal of information can be gathered. (Rudin, 2012)

Composition Drift

The monomer feed and copolymer composition must be known for the estimation of the reactivity ratios. The copolymer composition drifts during the polymerization process due to the difference between the reactivity ratios. To avoid this phenomenon and to form a uniform copolymer composition, various techniques have been proposed: the feed composition of a specific monomer can be continuously or periodically injected into the reactor to compensate for its lower reactivity. A common method to solve this problem is to pump the monomer into the reactor at suitable rates with conversions as high as about 90%. With this method, the burst of the polymer is always proportional to the last increase in the monomer feed. In the batch reaction, the composition of the copolymer,

which is dependent on the reactivity ratio and the initial composition of the monomer feed, changes in proportion to the change in the conversion percentage. But in a CSTR where the flow is segregated flow, we will not have any draft composition and the distribution of the product composition will be wide. (Rudin, 2012)

Cumulative VS Instantaneous Copolymer Composition Model Forms:

Mayo-Lewis Equation

The most widely used copolymerization model is the Mayo-Lewis model, which describes the instantaneous copolymer composition. Equation (1) relates the composition of instantaneous copolymers to the concentration of instantaneous monomers via the reactivity ratios of comonomers:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (1)$$

$[M_1]$ and $[M_2]$: The concentrations of monomer M_1 and M_2 in the polymerizing mixture

r_1 and r_2 : The ratios of individual propagation rate constants

The copolymerization equation can also be expressed in terms of monomer mole fractions (alternative form of the instantaneous copolymer composition equation). If f_1 is the mole fraction of the first unreacted monomer and F_1 is its mole fraction included in the copolymer, then equation (2) can be rewritten as follows:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (2)$$

Where;

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad \text{and} \quad f_1 = \frac{[M_1]}{[M_1] + [M_2]}$$

Meyer-Lowry Equation

The Meyer-Lowry model is the result of the analytical integration of the Mayo-Lewis equation. The Meyer-Lowry model can be used to estimate the reactivity ratios of the reaction at low to moderate levels of conversion (for example, up to 30-50% conversion, with a conversion range of 25-30% is safer). It should be noted that there are simplifying and limiting assumptions in the derivation of this model. For example, the polymerization must be isothermal. Therefore, no

variable temperature scenarios can be considered. This assumption can pose a slight problem, since the reactivity ratios are weak functions of temperature (for many but not all systems).

Another (relatively minor) assumption is that the volume of the polymerized mixture does not shrink significantly. This assumption is true for low to moderate conversion rates, but not for the entire reaction. The main assumption that must be satisfied to perform the integration and obtain the analytical solution is that the reactivity ratios must remain constant during the polymerization period, which means that the changes in the reactivity ratio values must be assumed to be independent of the conversion rates. However, it is well known that as long as the polymerization temperature is below the glass transition temperature of the polymerization mixture, at moderate to high conversion levels even diffusion reactions can be diffusion-controlled (and hence, functional are from conversion). Since these assumptions are likely to be violated during a typical copolymerization, the use of this model for kinetic studies (especially above the 25–40% conversion level, always dependent on the copolymer system) can be a source of error.

There are usually two well-known forms of the Meyer-Lowry model. A form of the logarithmic model. This form is obtained from Meyer-Lowry model with equation (3).

$$\log \left(\frac{[M_2]}{[M_{2,0}]} \right) = \log \left(\frac{[M_{2,0}][M_1]}{[M_{1,0}][M_2]} \right) - \frac{1-r_1r_2}{(1-r_1)(1-r_2)} \log \left(\frac{(r_1-1)\frac{[M_1]}{[M_2]}-r_2+1}{(r_1-1)\frac{[M_{1,0}]}{[M_{2,0}]}-r_2+1} \right) \quad (3)$$

$[M_1]$ and $[M_2]$: The monomer concentrations at some time t corresponding to a certain conversion level X_n .

$[M_{1,0}]$ and $[M_{2,0}]$: The initial monomer (feed) concentrations.

In this form of the Meyer-Lowry model, considering the left-hand side of equation (3) is based only on the conversion of monomer 2, this has led to misinterpretations regarding this equation [ie, it may only monitor the conversion of monomer 2]. Therefore, for cases where the difference between reactivity ratios is important, using this model may not be appropriate. Another form of this model uses overall monomer conversion as the response. This is the general form of Meyer-Lowry model and it is obtained by equation (4):

$$X_n = 1 - \left(\frac{f_1}{f_{1,0}} \right)^\alpha \left(\frac{f_2}{f_{2,0}} \right)^\beta \left(\frac{f_{1,0} - \delta}{f_1 - \delta} \right)^\gamma \quad (4)$$

Where

$$\alpha = \frac{r_2}{(1-r_2)}; \beta = \frac{r_1}{(1-r_1)}; \gamma = \frac{1-r_1r_2}{(1-r_1)(1-r_2)}; \delta = \frac{(1-r_2)}{(2-r_1-r_2)}$$

f_1 and f_2 : The free (unreacted, unbound) monomer mole fractions at time, t .

$f_{1,0}$ and $f_{2,0}$: The initial monomer (feed) mole fractions.

X_n : Molar conversion, defined by Equation (5), assuming that the polymerizing mixture has a constant volume.

$$X_n = 1 - \frac{[M_1] + [M_2]}{[M_{1,0}] + [M_{2,0}]} \quad (5)$$

One must note that typical measurements in an experiment are the initial monomer mole fractions and final monomer mole fractions. Therefore, the molar conversion as described in equation (5) cannot be obtained. To avoid this problem, and to use the cumulative mole fraction of monomer 1 confined in the copolymer in the X_n conversion, we should use equation (6), the molar conversion can be obtained with the help of the Skeist equation, as shown in Equation (7).

$$\bar{F}_1 = \frac{[M_{1,0}] - [M_1]}{[M_{1,0}] + [M_{2,0}] - [M_1] - [M_2]} \quad (6)$$

$$X_n = \frac{f_1 - f_{1,0}}{f_1 - \bar{F}_1} \quad (7)$$

Subsequently, the Meyer-Lowry model can be rewritten as Equation (8), which can easily be calculated by measuring all participant variables during a typical experiment.

$$g(f_1, f_{10}, \bar{F}_1) = \frac{f_1 - f_{10}}{f_1 - \bar{F}_1} - 1 + \left(\frac{f_1}{f_{1,0}} \right)^\alpha \left(\frac{f_2}{f_{2,0}} \right)^\beta \left(\frac{f_{1,0} - \delta}{f_1 - \delta} \right)^\gamma \quad (8)$$

Equation (8) is called as the molar transformation form of Meyer-Lowry model. An alternative equation can also establish a relationship between the mole fraction of the initial monomer (feed), f_{10} , the mole fraction of the final copolymer, $\bar{F}_1$, and the weight conversion X_w . This relationship is as follows:

$$g(X_n, f_{10}, \bar{F}_1) = X_n - 1 + \left(\frac{f_{10} - \bar{F}_1 X_n}{f_{10}(1 - X_n)} \right)^\alpha \left(\frac{1 - X_n - f_{10} - \bar{F}_1 X_n}{(1 - f_{10})(1 - X_n)} \right)^\beta \left(\frac{(\delta - f_{10})(1 - X_n)}{\delta - \delta X_n - f_{10} + \bar{F}_1 X_n} \right)^\gamma \quad (9)$$

The X_n component in equation (9) can be replaced by mass conversion using equation (10).

Equation (9) is commonly referred to as the mass conversion form of the Meyer-Lowry model, and this is the form that will be used in the rest of this paper for parameter estimation purposes.

$$X_n = X_w \frac{Mw_1 f_{10} + (1 - f_{10}) Mw_2}{Mw_1 \bar{F}_1 + (1 - \bar{F}_1) Mw_2} \quad (10)$$

Mw_1 and Mw_2 : the molecular weights of monomer 1 and 2.

More specifically, since the value of δ in the last quotient of Equation (9) is equal to the azeotropic composition of a copolymerization system, this situation might arise for copolymerization systems with an azeotrope. This also means that this situation can only arise theoretically for those binary systems with both values of reactivity ratios less or greater than 1.

Direct Numerical Integration

The numerical integration model is based on this, which relates the cumulative copolymer composition $\bar{F}_1$ to the mole fraction of unreacted monomer f_1 in the polymerization mixture and molar conversion, X_n . As mentioned earlier, this relationship (or Skeist equation) is obtained by equation (7), which is expressed as follows:

$$\bar{F}_1 = \frac{f_{1,0} - f_1(1 - X_n)}{X_n} \quad (11)$$

As the reaction proceeds with time, X_n changes and f_1 , the mole fraction of unreacted monomer in the polymerization mixture, is evaluated by numerically solving the equation of the differential composition of the copolymer, given by equation (12):

$$\frac{df_1}{dX_n} = \frac{f_1 - F_1}{1 - X_n} \quad (12)$$

F_1 : Is given by the Mayo–Lewis equation

& The assumption is that, the initial condition $f_1 = f_{10}$ when $X_n = 0$.

Using direct numerical integration of the differential copolymer composition equation is a convenient alternative method for estimating reactivity ratios. Indeed, to estimate reactivity ratio, direct numerical integration of the differential copolymer composition equation is a powerful method, compared with the analytical form of the Meyer-Lowry model. This method may be computationally complex, but it avoids distort error structure and other restrictive assumptions for medium or high conversion data. For example, at low conversions, the measurable cumulative copolymer composition is approximately equal to its instantaneous value. However, this restrictive assumption introduces additional sources of error, including significant experimental difficulties. (Kazemi N. D., Reactivity ratio estimation from cumulative copolymer composition data, 2011)

Backbiting Reactions

Polymerization consists of three main stages: initiation, propagation and termination. In the initiation stage of the reaction, at a temperature above 60°C, an initiator such as a thermal initiator starts to form free radicals. The polymerization process may be started immediately (without the need of a known initiator) by a monomer, usually at a high temperature of 140-350°C.

In propagation reaction, free radicals grow in size through reaction with monomers. In the termination stage, the grown macroradicals react with each other to form dead polymer chains.

In addition to the main reactions of the polymerization process, free radical polymerization may also include other reactions called secondary reactions. The extent of participation of these types of reactions in free radical polymerization depends on the type of monomers, polymerization temperature, and type of polymerization environment.

A common type of secondary reaction at high temperature for acrylate free radical polymerization is backbiting. Backbiting reactions lead to a decrease in the effective value of the propagation rate coefficient. Backbiting reactions (intramolecular chain transfer-to-polymer) produce tertiary radicals that are still able to propagate and create short chain branches. In a high-temperature backbiting reaction, the secondary radical is converted into a tertiary radical by separating a hydrogen from the backbone. Tertiary radicals are also formed through intermolecular chain-transfer-to-polymer reactions, which are subsequently able to propagate and create long chain branches. And if there are such reactions in free radical polymerization, we need a final and comprehensive model for reliable description of the characteristics of polymers.

Backbiting and the formation of tertiary radicals have been reported mainly in the polymerization of several acrylates such as MA, EHA, and BA. According to the published reports about MMA monomer, no warning about backbiting has been reported for this monomer. For EHA monomer, the backbiting reaction also occurs at temperature in the range of 100 to 140°C, and since our study experiment takes place at a temperature of 60°C, we can ignore the backbiting reaction for EHA monomer. (Riazi, 2019)

Monomer Feed Composition

the location of the optimal feed compositions based on the EVM design criterion practical heuristics that can guide experimenters and researchers to the location of optimal feed compositions without having to implement the whole complex design procedure every time.

A terpolymerization system which reactivity ratio is equal to one is called an "ideal" system. First, we examine such a system in order to evaluate the results of the EVM design criterion for a system

with equal reactivity ratios and to visualize the behavior. Our goal of additive versus multiplicative error structures is to find its effect on designed experiments.

At first, according to the EVM design criterion equation mentioned below and with the help of two types of error structure, we will calculate the optimal compositions. The results are shown in Figure (1). Figure (1) is a triangular plot used to visualize the composition of a terpolymerization system. The sides of the triangle represent the mole fraction of the monomer, and the corners of the triangle represent the concentration of 100% of each monomer. The optimal compositions for an ideal terpolymerization system within the triangle are marked by points.

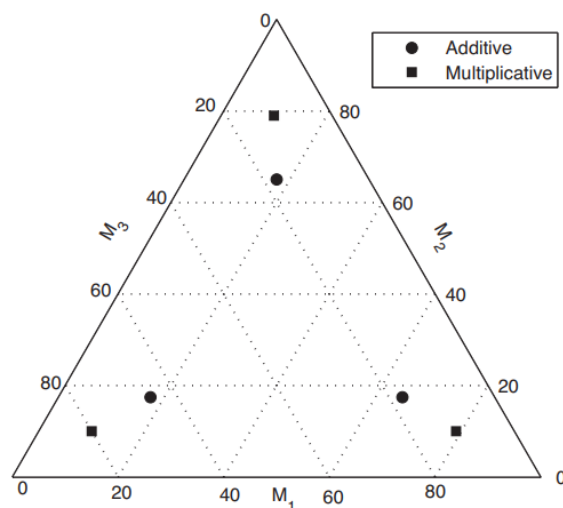


Figure 1. Optimal feed compositions (ideal terpolymerization system, $r_{ij} = 1$); error structure effect. From “Design of optimal experiments for terpolymerization reactivity ratio estimation” by Kazemi, N., Duever, T. A., & Penlidis, A. (2015). *Macromolecular Reaction Engineering*, 9(3), 228-244, p.8.

The optimal feed compositions calculated for the ideal terpolymerization system, as shown in Figure (1), have a very interesting observation. In this way, each of the three optimal feed compositions is rich in one of the monomers and the other two monomers have equal amounts of the composition. The additive optimal compositions tend more toward the center of the triangle, while multiplicative optimal points tend toward the corners of the triangular design. This difference can be explained based on the fact that the multiplicative error structure, as it is clear in the equation, has $\ln(f_i)$ and therefore in the vicinity of $f_1 = 0$, $\ln(f_i)$ goes to negative infinite which causes the maximum of EVM design criterion. Due to this fact, it is very important to set the feasible region based on practical considerations. According to equation (13), the lower and upper limits of the

possible region for mole fractions of monomers in the feed are 0.1 and 0.9, respectively.

$$\ln \ln (x) = \ln \ln (x^*) + k\varepsilon \quad (13)$$

The purpose of sequential design scheme is to find the optimal feed composition for subsequent experiments. However, as is clear in Figure (2), there is more than one option for sequentially optimal experiments. For additive error, we can have six suggestions for the next optimal experiments according to the "o" points marked in the left triangle. These points are very close to the optimum points of the initial design, are symmetric in terms of mole fraction values for the three monomers, and have the same amount of information. For the multiplicative error, according to the "o" points marked in the right triangle, we can have three suggestions. These points also have the same amount of information because they exactly match the optimal points of the initial design.

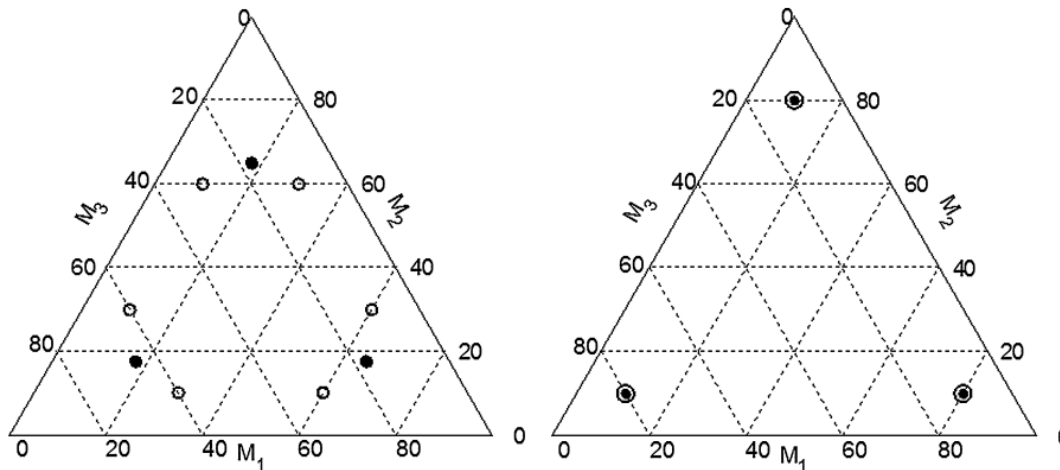


Figure 2. Sequential optimal feed compositions for: (left) additive error, and (right) multiplicative error, with “•” as the initial and “o” as the sequential design points. From “Design of optimal experiments for terpolymerization reactivity ratio estimation” by Kazemi, N., Duever, T. A., & Penlidis, A. (2015). *Macromolecular Reaction Engineering*, 9(3), 228-244, p.9.

In order to further investigate these findings, the objective function level for sequential design criterion can be drawn, which is a function of f_1 and f_2 . The minimum points of this level represent the optimal points of the sequential design criterion. Figures (3) and (4) show the surface of the sequential design function along with the optimal points for two types of multiplicative and additive error, respectively. As you can see in figure (3), for multiplicative error, the surface has a "parachute" shape and the corners have the lowest level, which represent the optimal points shown in figure (2). For additive error, as shown in figure (4), the level of design criterion has six points

with the minimum value and with the same information, indicated by "•" in this figure, which are also drawn in figure (2). The results from figures 2-4 clearly show that the sequential design scheme for the ternary system experiments leads to very similar points as the original design. Therefore, it is reasonable to suggest that conducting experiments in these feed compositions or repeating the initial optimum points could lead to the same level of improvement in the accuracy of the triplet reactivity ratio. (Kazemi N. D., Design of optimal experiments for terpolymerization reactivity ratio estimation. , 2015)

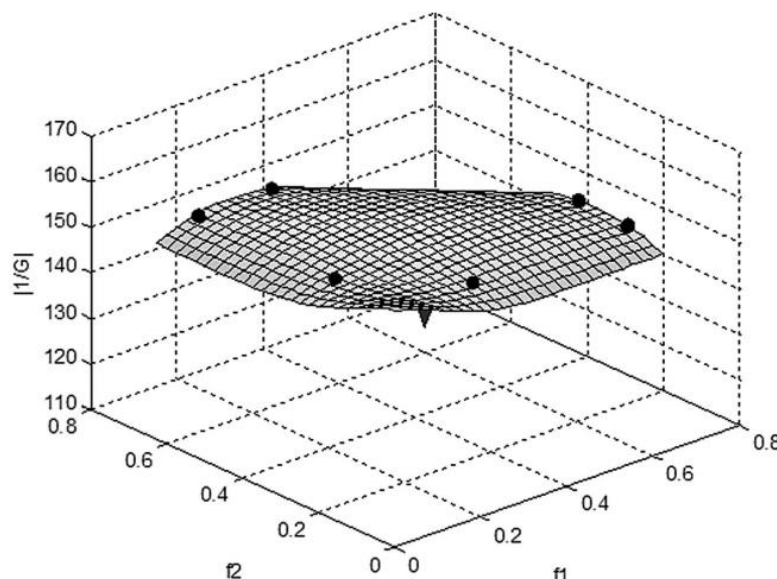


Figure 3. The objective function surface for the sequential design criterion with additive error (ideal terpolymerization system, with "•" as the optima). From "Design of optimal experiments for terpolymerization reactivity ratio estimation" by Kazemi, N., Duever, T. A., & Penlidis, A. (2015). *Macromolecular Reaction Engineering*, 9(3), 228-244, p.9.

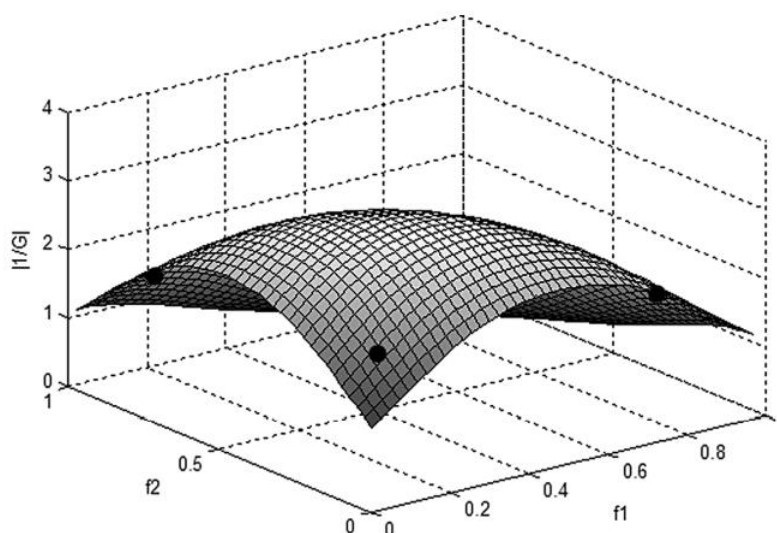


Figure "4". The objective function surface for the sequential design criterion with multiplicative error (ideal terpolymerization system, with "•" as the optima). From "Design of optimal experiments for terpolymerization reactivity ratio estimation" by Kazemi, N., Duever, T. A., & Penlidis, A. (2015). *Macromolecular Reaction Engineering*, 9(3), 228-244, p.9.

EXPERIMENTAL

Materials

Styrene ($\geq 99\%$ purity), Methyl methacrylate ($\geq 99\%$ purity) and 2-Ethylhexyl acrylate ($\geq 99\%$ purity) were supplied from Merck Company. Azobisisobutyronitrile (AIBN) from Merck Company was used as initiator. The inhibitor remover has been supplied by Sigma-Aldrich Company. Monomers were purified of hydroquinone and monomethyl ether hydroquinone inhibitor by passing through inhibitor removal column (Sigma- Aldrich).

Equipment

Glass Ampoules:

Polymerizations will be conducted inside ampoules, which through a freeze-thaw process under vacuum, will be devoid of oxygen and used as mini-reactors in a heating bath.

(The schematic for the ampoules is attached in appendix A)



Glass Ampoule

Vacuum Pump:

In case of less pressure than atmospheric pressure, vacuum pump, which will be a quick and efficient solution.

This process is possible by an electric motor installed in the central part of the vacuum pump. With the onset of electric motor activity and rotational or rotary motion, vacuum is created and the air in the cycle is completely drained.



Vacuum Pump

Temperature Controlled Water Bath:

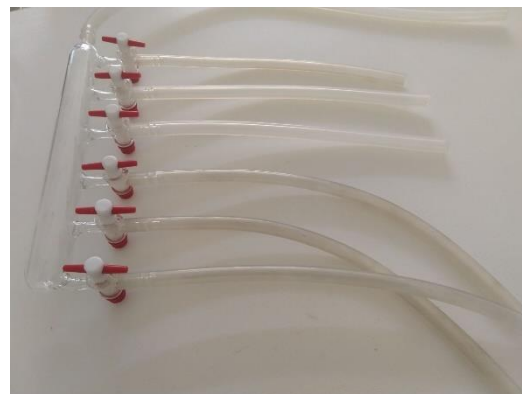
Bain-marie or water bath is actually a method to heat or keep at a certain temperature and in some cases to melt materials. There are many applications of Ben-Marie in laboratories. This device is used in laboratories for gradually heating samples which are sensitive to direct and high temperature, flammable, preventing some reactions at high temperature, etc.



Temperature Controlled Water Bath

Glass Vacuum Manifold:

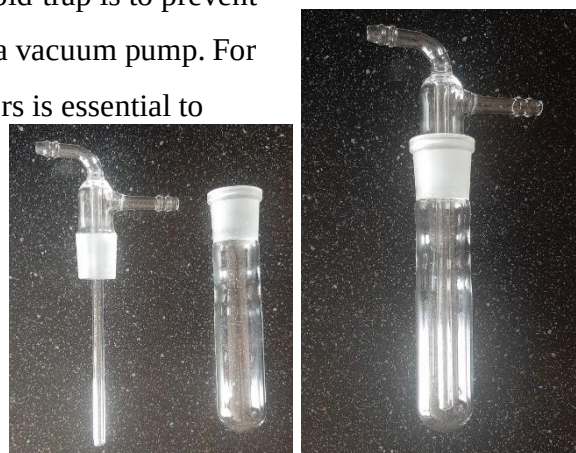
Manifold is a practical equipment in the industry, which is made by combining several valves in one body with several connections. This tool is generally used as a helper along with pressure tools. This equipment is generally used to measure and calculate pressures, etc.



Glass Vacuum Manifold

Cold Trap:

During laboratory evaporation, the main function of the cold trap is to prevent vapors being evacuated from an experiment from entering a vacuum pump. For a vacuum pump that requires oil, collection of solvent vapors is essential to prevent them from collecting in the vacuum pump's oil.



Cold Trap

Torch:

Some kind to melt the ampoule neck and seal it.



Torch from <https://pyrexfan-shop.com/lavazem-shishe-gari/237072>

Small Handheld Empty Liquid Nitrogen Dewar:

The storage and transportation tank of liquid nitrogen is double-walled and its body is made of high-grade aluminum. For this reason, liquid nitrogen has the ability to withstand the temperature shock of -196 degrees Celsius, and to prevent the exchange of liquid gas temperature with the ambient temperature, the internal space between the two walls of the flask is a vacuum. In this way, the evaporation of liquid nitrogen and its transformation into nitrogen gas are prevented.



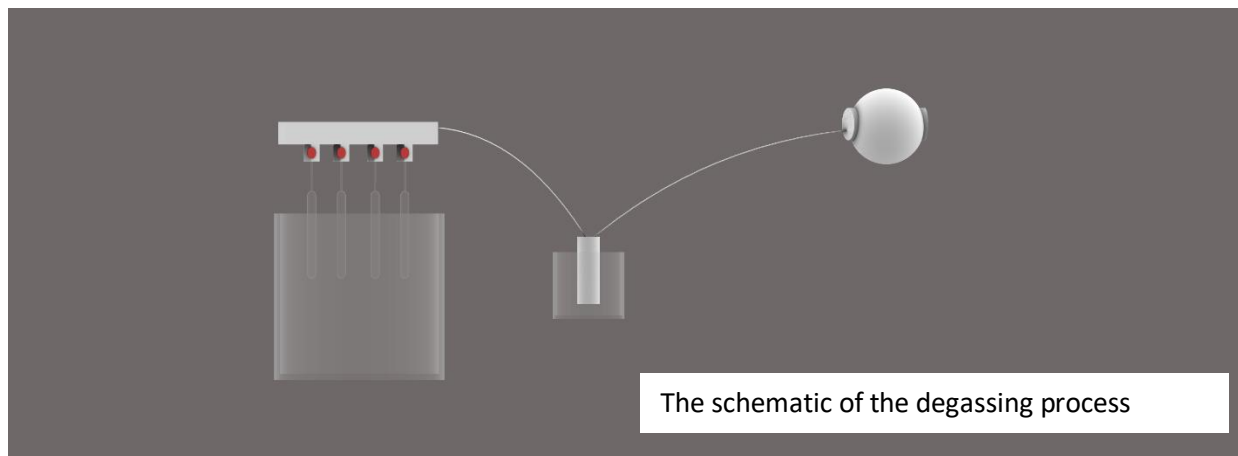
Small handheld empty liquid nitrogen dewar from <https://www.alibaba.com/pr>

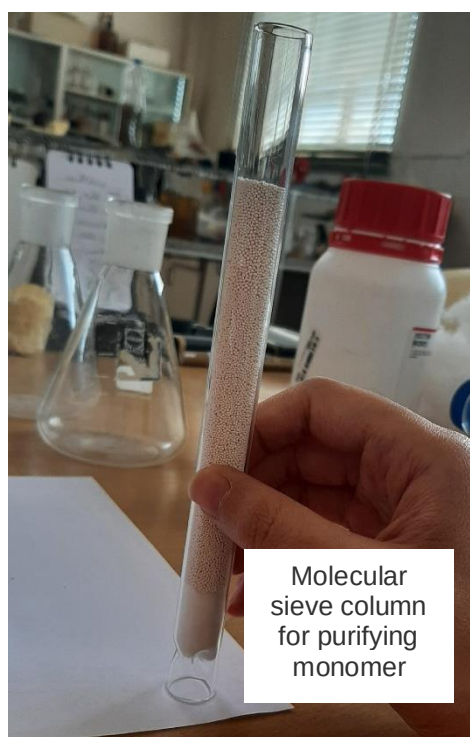
Diamond Tip Glass Cutter:

A tool to break the top of the ampoules (laser blade to make a cut around the neck of the ampoule to weakened it.)



Diamond Tip Glass Cutter







Procedure

The terpolymerization experiment of EHA/MMA/St. ran at 60°C in three sets of experiments at 80/10/10 mol% composition of monomer (each monomer taking turns to be at 80 mol%), to calculate the reactivity ratio in ampoules (mini-reactors) in bulk free radical polymerization (Experimental monomer feed compositions for this system are detailed in Table 1).

A certain composition of each purified monomer was mixed together and 0.08 wt.% of initiator was added to each solution. Then, each prepared solution was distributed between 6 ampoules (160–180 mm in length, 5 mm in tube inner diameter, and roughly 3.35 mL in volume (The schematic for the ampoules is attached in Appendix A) by pipette, and then the ampoules were connected to the degassing apparatus. The contents of the ampoules were degassed (to remove oxygen from the ampoules) in three steps by the freeze-pump-thaw process. After three cycles of the freeze-thaw procedure, the ampoules were sealed. The sealed ampoules were placed directly in the cold bath. the day after that they submerged into the hot bath as required by the operation manual at 60°C. After the time needed to perform the polymerization process, the ampoules were removed from the hot water bath and to quench the reaction, they directly entered into the cold-water bath. After the ampoules were cooled, the weight of the labeled aluminum pans was measured and the ampoules' heads were cut with a diamond tip glass cutter pen. Then the contents of the ampoules were poured into aluminum pans and their weight was measured again. Then the polymer samples were placed inside the fume hood so that the unreacted monomers evaporate over time and the sample dries. After 7 days because of the liquid state of the samples, we put them into the oven for 390 min at 38°C to reduce the monomer presence. The weight of the samples was measured and the conversion of the samples were calculated. They were weighed again 4 days later, and the weight of all samples

was constant and had not changed compared to the previous series. The method for determining monomer conversion is gravimetry, while terpolymer composition is determined by H-NMR spectroscopy. The terpolymer compositions were measured using a Avance 800 MHz NMR spectrometer in Central Laboratory of University of Isfahan. Samples were dissolved in deuterated chloro-form (CDCl_3). A typical ^1H -NMR spectrum along with peak assignments for a St./MMA/EHA terpolymer is shown in figure (5). (Central Lab of University of Isfahan, 2022)

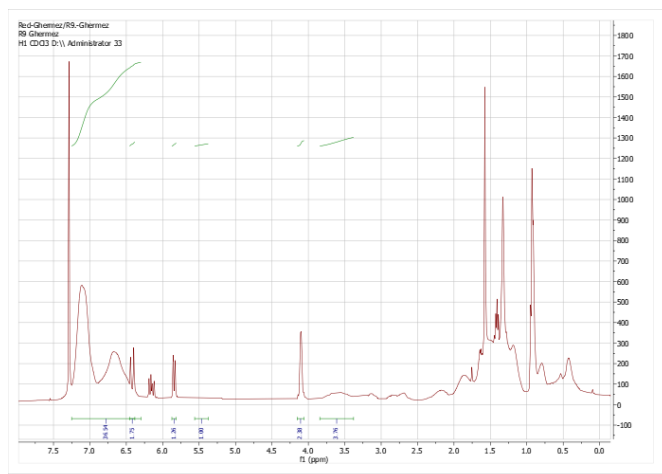


Figure 5. ^1H -NMR spectrum along with peak assignments for a St./MMA/EHA copolymer

Freeze-Pump-Thaw Process

First, the desired solution was prepared according to the feed composition of the monomer and kept in the freezer until the components of the degassing apparatus were assembled. Then the appropriate amount of solution was distributed among all 6 ampoules. The ampoules were connected to the manifold. Then the vacuum pump was turned on and all the ampoules entered the container containing liquid nitrogen, at this time the manifold valves were closed. After freezing the contents inside the ampoules, the valves were kept open for 15 minutes. Then the valves were carefully closed and the ampoules were removed from the liquid nitrogen and placed in another container and the contents were melted by pouring ethanol from top to bottom on the ampoules. This process was repeated 4 times. After the last cycle of freezing and thawing the ampoules, with the help of a blue flame of a torch connected to oxygen and gas, the narrowest part of the ampoules was heated and rotated to seal. And at the end, the sealed ampoules were directly entered into the cold-water bath, and the polymerization process was carried out the next day.

Experimental conditions for the bulk terpolymerization of Sty, EHA and MMA at 60 °C.						
Monomer Feed (mol % EHA)	Monomer Feed (mol % MMA)	Monomer Feed (mol % Sty)	EHA (mLit)	MMA (mLit)	Sty (mLit)	AIBN (gr)
80 mol%	10 mol%	10 mol%	166.5808	10.6511	11.4576	0.1283
10 mol%	80 mol%	10 mol%	20.8226	85.2085	11.4576	0.0798
10 mol%	10 mol%	80 mol%	20.8226	85.2085	91.6612	0.0837

Table1. Experimental conditions for the bulk terpolymerization of Sty, EHA and MMA at 60 °C

RESULTS AND DISCUSSION

Conversion

Bulk Sty./MMA/EHA terpolymerizations from 0-25 wt.% conversion was conducted at 60°C to determine the reactivity ratios. The monomer conversion versus time data for the low and high conversion Sty./MMA/EHA terpolymerizations are shown in figure (6) and Table 2 for the three monomer feed compositions used (Table 1). The Sty. rich composition (80 / 10 / 10) showed the lowest overall reaction rate.

All three samples have an interval at 90 min. The thing that is obvious in figure (6) is that at 90 min the EHA rich composition (10 / 10 / 80) had the highest conversion and the Sty. rich composition (80 / 10 / 10) had the lowest conversion. Thus, the reactivity ratio of the three monomers respectively would be like this: EHA, MMA, Sty. . Also compared to other plots from the other literature it seemed to be logical.

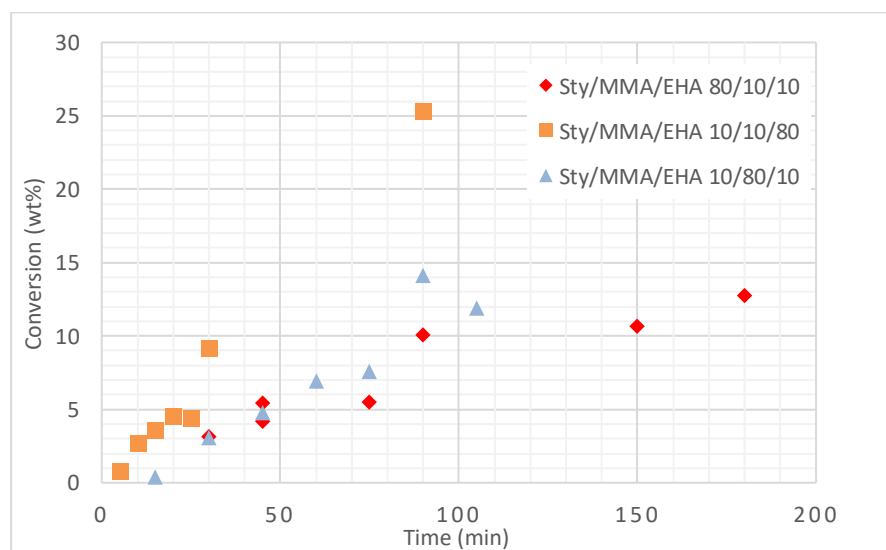


Figure 6. Conversion versus time for bulk MMA/EHA/Sty terpolymerization at 60 °C and 0.08 wt% [AIBN].

Table 2. Conversion Data

Initial composition (mol %)	Time (min)	Conversion (wt%)
Sty/MMA/EHA 80/10/10	30	3.1358
	45	4.1958
	45	5.4545
	75	5.5016
	90	10.0529
	150	10.6617
	180	12.734
Sty/MMA/EHA 10/10/80	5	0.8
	10	2.7118
	15	3.6184
	20	4.5643
	25	4.3796
	30	9.1575
	90	25.3164
Sty/MMA/EHA 10/80/10	15	0.4032
	30	3.0928
	45	4.797
	60	6.9231
	75	7.5757
	90	14.1243
	105	11.9231

Estimation and Experimental Design

To calculate the reactivity ratios of terpolymer systems, one needs to know the monomer feed and final copolymer composition, the monomer conversion, and initial reactivity ratio estimates. The experiment ran at three different compositions, each running from 0 - 25.31% conversion.

Estimation of the reactivity ratio includes an experiment set with certain composition of monomers with a range of conversions (low, < 10 wt.% and high, > 10 wt.%) and the data obtained from these experiments will be sent to Dr. Scott and Dr. Dube in Canada for the DNI/EVM approach, which will generate final reactivity ratio estimates. These ratios will be used to generate composition-conversion models, which can be validated with polymerizations at various compositions going to full conversion.

Traditionally, reactivity ratio estimation used linearization techniques were used instead of non-linear parameter estimation method because of lack of computational power. The linear estimation of copolymerization reactivity ratio led to distorted error structure. Error-in-Variables Method which is a non-linear parameter estimation technique considers the error present in all variables. The

nonlinear least squares (NLLS) method is not appropriate for reactivity ratio determination with the cumulative copolymer composition models because of its distort error.

The EVM procedure consists of two statements. First, the vector of measurements, x_i , is equated to the vector of true (yet unknown) values of these measurements, ξ_i , plus an error term ε_i .

$$x_i = \xi_i + \varepsilon_i \quad \text{where } i = 1, 2, \dots, n$$

The second statement relates the true (yet unknown) values of the parameters, u , with the true values of variables, j_i , via a model represented by

$$g(\xi_i, \theta^*) = 0 \quad \text{where } i = 1, 2, \dots, n$$

The vector function g may be linear or non-linear.

The standard equations of Alfrey and Goldfinger (AG) in terpolymerization system use the instantaneous mole fraction ratio. However, according to the measurements resulting from experimental works, they are usually single mole fractions and not ratios. Therefore, the evaluation of the ratios (F_i/F_j) leads to the loss of information and distortion of the error structure. Thus, the AG model was re-derived from basic terpolymerization kinetics for this study, so that each terpolymer mole fraction is presented as a single response (Equations (13) - (15)). This formulation is an improvement over the original A-G model, as it promotes symmetric estimation and avoids distorting error structures.

$$F_1 - \frac{f_1 \left(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right) \left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right)}{f_1 \left(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right) \left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right) + f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right) + f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right)} = 0 \quad (13)$$

$$F_2 - \frac{f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right)}{f_1 \left(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right) \left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right) + f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right) + f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right)} = 0 \quad (14)$$

$$F_3 - \frac{f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right)}{f_1 \left(\frac{f_1}{r_{21}r_{31}} + \frac{f_2}{r_{21}r_{32}} + \frac{f_3}{r_{31}r_{23}} \right) \left(f_1 + \frac{f_2}{r_{12}} + \frac{f_3}{r_{13}} \right) + f_2 \left(\frac{f_1}{r_{12}r_{31}} + \frac{f_2}{r_{12}r_{32}} + \frac{f_3}{r_{13}r_{32}} \right) \left(f_2 + \frac{f_1}{r_{21}} + \frac{f_3}{r_{23}} \right) + f_3 \left(\frac{f_1}{r_{13}r_{21}} + \frac{f_2}{r_{23}r_{12}} + \frac{f_3}{r_{13}r_{23}} \right) \left(f_3 + \frac{f_1}{r_{31}} + \frac{f_2}{r_{32}} \right)} = 0 \quad (15)$$

The newly derived equations are only valid for the instantaneous type. When using low conversion data, it is possible to assume that terpolymer drift is negligible. (In such a way that, at a low conversion rate, the value of cumulative copolymer composition is almost equal to the value of instantaneous copolymer composition.) Although such a limiting assumption causes other sources of error, including significant experimental problems.

As another method, the cumulative ternary composition model can be introduced, which is used to estimate the reactivity ratios due to full conversion. As it is clear in the relevant equation, it relates the

cumulative terpolymer composition for each comonomer (F_i) to the mole fraction of monomer in the initial feed ($f_{i,0}$), the mole fraction of unreacted monomer in the polymerizing mixture (f_i), and the overall molar conversion (X_n).

$$\overline{F}_1 = \frac{f_{1,0} - f_1(1 - X_n)}{X_n} \quad (16)$$

$$\overline{F}_2 = \frac{f_{2,0} - f_2(1 - X_n)}{X_n} \quad (17)$$

$$\overline{F}_3 = \frac{f_{3,0} - f_3(1 - X_n)}{X_n} \quad (18)$$

If we cannot assume constant composition (that is, if composition drift is no longer negligible), f_i must be evaluated over conversion X_n , as shown in Equations (7)–(9).

$$\frac{df_1}{dX_n} = \frac{f_1 - F_1}{1 - X_n} \quad (19)$$

$$\frac{df_2}{dX_n} = \frac{f_2 - F_2}{1 - X_n} \quad (20)$$

$$\frac{df_3}{dX_n} = \frac{f_3 - F_3}{1 - X_n} \quad (21)$$

the initial condition $f_1 = f_{10}$ when $X_n = 0$.

The models used to introduce the terpolymerization process, although they are a little complicated, but it can be said that they are the result of the extension of the copolymer models. Also, it is important not to consider the unique ternary systems similar to combining three copolymer systems. When the third monomer is added to the polymerization formula, it is able to alter the characteristics of the polymer and the degree of incorporation of all three comonomers. Therefore, the kinetics of terpolymerization systems should be measured and checked according to its own steps. (Scott A. G., 2019)

Experimental challenges

1. Since there wasn't any supplier for the inhibitor remover packing in Iran, we were trying to try other techniques for purification of monomer such as trying to find directly the code of the inhibitor remover packing in Iran or passing the liquid monomer through a column filled with silica or alumina gels or washing the monomers with a concentrated solution of NaOH (4N), followed by drying (dehydrating agent) and sometimes distilled under reduced pressure. But because the lab's rotary evaporator was infected and they washed it with acid but it had some oil fraction's dopant still in it, I wasn't able to use it for removing the inhibitor. Finally, we had to get it shipped from Canada from Dr. Dube.
2. The small volume of the nitrogen flask (5 Lit) and the existence of a distance of 58 km between the liquid nitrogen supply and the place of the laboratory.
3. The difficulty of performing the seal process and trying to coordinate the presence of the glass blower at the same time as the end of the last round of the freeze- thaw process. In order to use his torch to melt the ampoule neck and his definite presence during the freeze- thaw process according to the owner of the factory's request.
4. It was difficult to cut the heads of the ampoules with the help of a blade and a hammer in the first and second round of the experiment.
5. The accurate scale was not level and takes some times. This issue postponed the experiment to another day.
6. The other challenges were like building a new apparatus, ampoule or finding a lab in Isfahan and having a budget appropriate for this (I eventually received funding assistance from Dr. Cummings and BIHE).



NMR Challenges

^1H -NMR spectroscopy is commonly used to determine the composition of polymer samples. There are generally an abundance of well documented peaks relating to most types of protons one would find on a polymer sample. In order to determine composition, you first need to identify the region of the spectrum where the desired proton peak is located. For a terpolymer system, you require one proton from each different monomer unit in the polymer chain. Then you need to measure the area under the peak of each proton (for peaks that correspond to multiple of the same type of proton, you must calculate the area under only one proton by division), and finally determine the mol. % composition of one type of monomer by dividing the area under one proton of one type of monomer to the sum of the areas of one proton from each different monomer unit.

Examining the peaks resulting from ^1H -NMR spectroscopy became challenging due to the overlap between the peaks related to PEHA and PMMA with three monomers. If three monomers have similar structure (if they have the same protons) then it's going to overlap so, the EHA and MMA if they have the same H then it's going to be at the same spot in the spectrum. Thus, we need to have a non-overlapped peak for each component in the system, and the spectrum must be devoid of monomer. in the case where there is monomer, we have to have a unique monomer peak in order to subtract from the overlap. if we have overlapped polymer peaks, we need at least one unique peak to do polymer subtraction. if we have only overlapped peaks in the entire spectrum, we need to revisit approach

According to the Figure 7 and the spectrum result of our experiment it seems that EHA and MMA at the zone of 3-4.35 have similar structure (they have the same H) then, it's going to be at the same spot in the spectrum and it has overlap. For the zone of, the selected monomer peaks seem to be overlapped with both MMA and EHA monomer and their corresponding polymers.

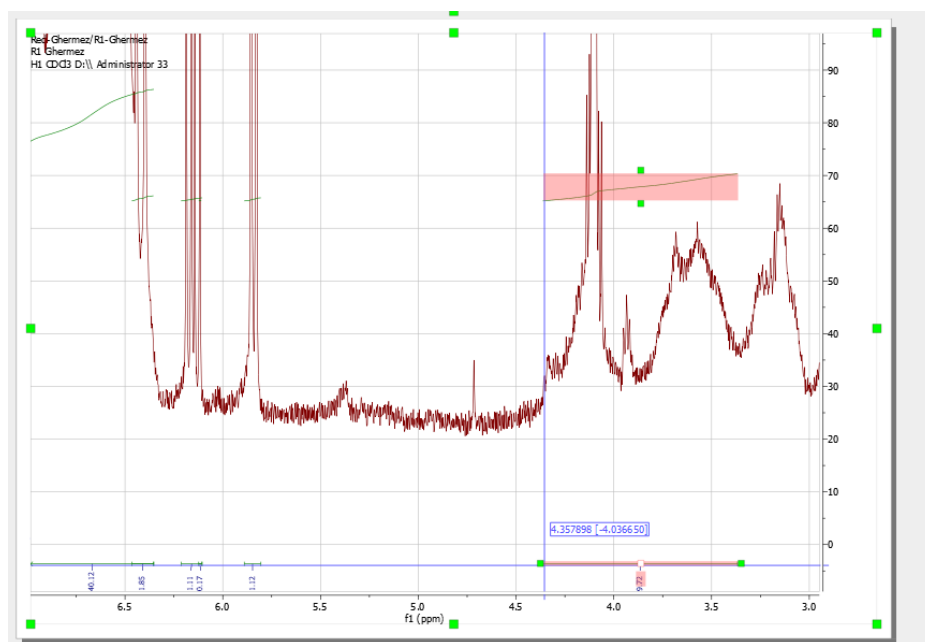


Figure 7. H-NMR spectrum of poly(Sty./MMA/2-EHA) with feed molar composition 80 / 10 / 10

It needs to find a peak that has no other peaks in the same region. So, the selected region won't work. Also, as mentioned before, after 7 days because of the liquid state of the samples, we put them into the oven for 390 min at 38°C to reduce the monomer presence.

Figure (8) (Koiry & Singha, 2014) shows the protons used to calculate the copolymer composition of Sty. and 2-EHA. The area under region of 6.4 - 7.3 represents the area of five Sty. protons.

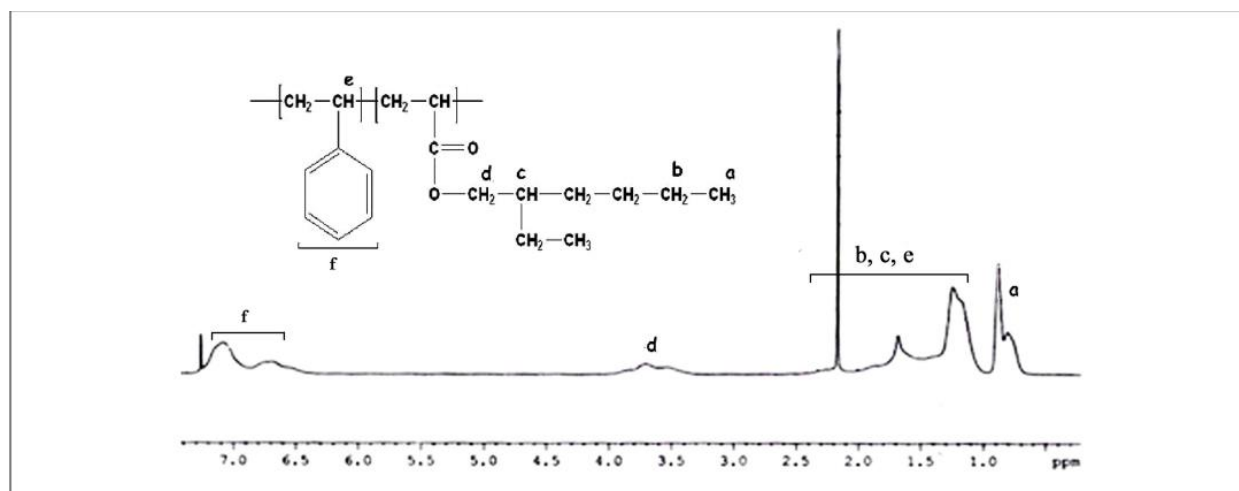


Figure 8. H-NMR spectrum of poly(sty. - co - 2-EHA) with feed molar composition 50 / 50. From Koiry, B. P., & Singha, N. K. (2014). Copper mediated controlled radical copolymerization of styrene and 2-ethylhexyl acrylate and determination of their reactivity ratios. *Frontiers in Chemistry*, 2, 91.

Figure (9) (Gabriel, 2019) shows the protons used to calculate the copolymer composition of MMA and 2-EHA. The area under region of 3.2 - 4.2 represents the area of 2 protons of 2-EHA and 3 MMA protons. To obtain the area of protons that just relate to MMA, at first, we need to obtain the 2-EHA's proton area from the region of 1.2 - 0.9 and then subtract twice the area of 2-EHA protons.

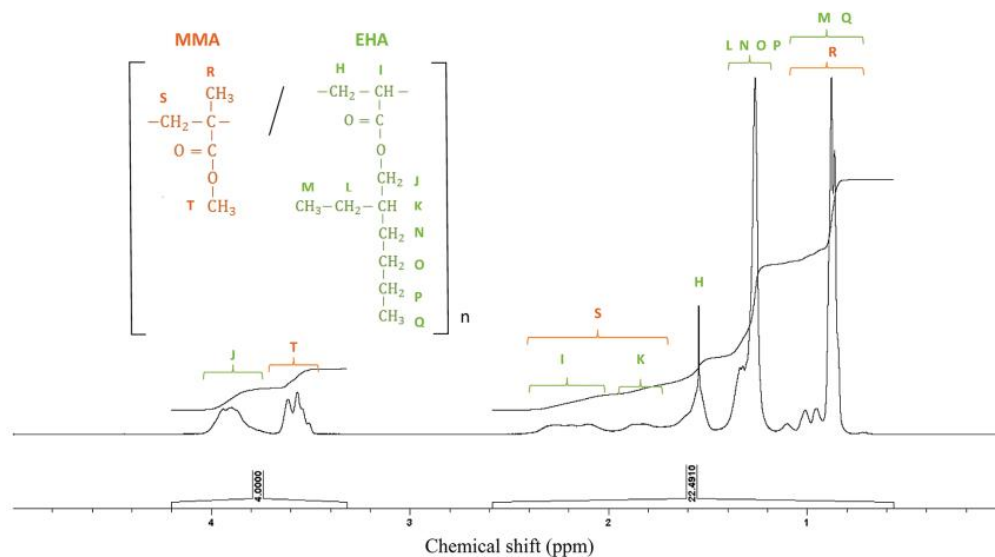


Figure 9. H-NMR spectrum of a MMA/2-EHA copolymer at 3.3 wt% conversion. From "Gabriel, V. A., & Dubé, M. A. (2019). Bulk Free-Radical Co- and Terpolymerization of n-Butyl Acrylate/2-Ethylhexyl Acrylate/Methyl Methacrylate. *Macromolecular Reaction Engineering*, 13(2), 1800057."

For the zone of 1.70 - 1.95 in Figure 10, the selected monomer peaks seem to be overlapped with both MMA and EHA monomer and their corresponding polymers. It needs to find a monomer peak that has no other peaks in the same region. So, the selected region won't work.

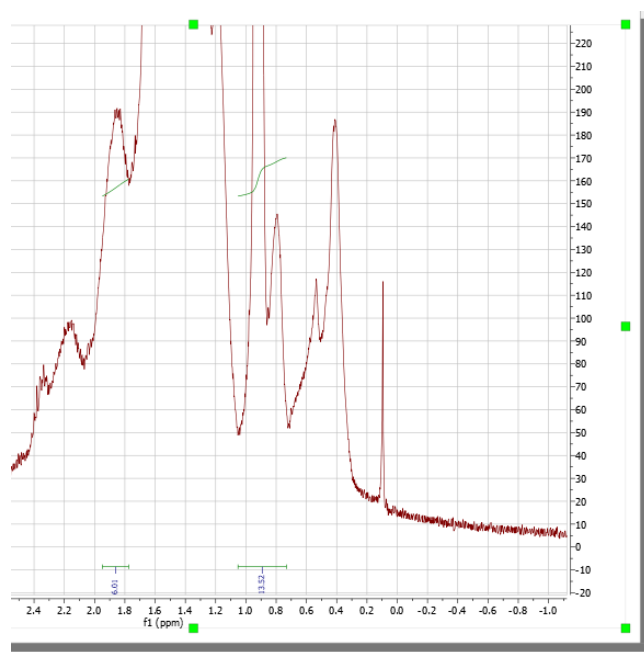


Figure 10. H-NMR spectrum of poly(Sty./MMA/2-EHA) with feed molar composition 80/0/0

Also, around the region of 5.80 - 6 all the monomer peaks overlap. And we cannot determine the area of each monomer separately. The zone of 0.5-1.7 has unique peaks for EHA but, it seems to overlap the polymer peaks too.

Basically, to not rely on online literature and to reach enough data to analyze the terpolymer samples, the composition calculations need the pure PMMA, PSt., PEHA runs to full conversion also, to run each of the three 80mol% compositions to full conversion as well as at 33.3/33.3/33.3 to full conversion to see a more fully developed terpolymer spectrum, in order to assist to identify the overlap peaks.

CONCLUSION AND RECOMMENDATIONS

An important parameter for estimating the copolymer composition is the reactivity ratio. Their importance cannot be underestimated because the copolymer composition directly affects the polymerization rate, molecular weight, and finally the final performance properties of the manufactured sample. In the past, to predict the copolymer composition related to the high-level conversion, using integrated Mayo - Lewis equation. And the reactivity ratios related to the copolymer system were used to predict the terpolymer composition of the terpolymer systems. Now, although the method of predicting the final composition related to the terpolymer system is similar to the method related to the copolymer system, these two methods should not be used interchangeably.

Both EVM and DNI/EVM methods are able to correctly account for the error in all the variables involved. Both sets of reactivity ratios from EVM and DNI/EVM methods yielded statistically identical cumulative and instantaneous copolymer composition predictions.

In my studies terpolymerization conducted in ampoules (mini reactors) in bulk polymerization. As shown in figure (6), conversion ranged from 0-25 wt.%, with the highest reactivity belongs to 2-EHA monomer and, Sty has the lowest reactivity ratio. The major challenges with reactivity ratio determination were related to analysis of ^1H -NMR peaks and calculation of composition. Due to overlapping peaks, accurate composition was not successfully determined with the spectra available. Residual monomer from insufficient drying was also present in many samples, making composition calculation difficult. Ultimately, reactivity ratios were not able to be determined.

In order to improve the experiment, the operated temperature of the polymerization or the amount of used initiator in the solution mixture or the duration of the polymerization process can be increased. As well as the duration of the prepared polymer evaporation can be increased to confirm that the most of the remain monomers have evaporated from the samples.

The MMA and EHA monomer and polymer peaks overlap. This issue with monomers is because they didn't dry properly. So, this study needs to take more time to do this as well as get the NMR of a 33.3/33.3/33.3 composition fully converted polymer sample and the three 80mol% compositions to full conversion, so that we can hopefully see more clearly defined and separate polymer peaks. Also, a spectrum of pure polymer for each EHA, MMA, and Styrene using the same laboratory that

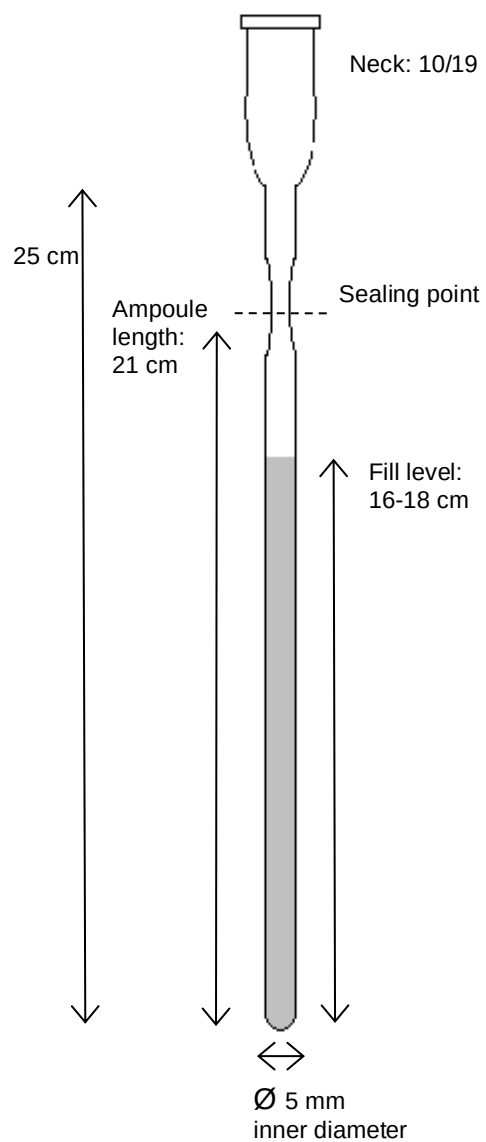
analyzed the other samples.

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Appendix A

The schematic of the constructed ampoules



Appendix B

The Cost of Equipment and Services

Equipment and items	Date of purchased	vendor	Cost (Toman)	Site
Vacuum pump	10/17/2021 0:00	tahviah shop	1,400,000	https://tahviahshop.com/product/pump-vacuum-value-model-115/
Temperature controlled water bath	10/24/2021 0:00	royan iran	4,200,000	https://royaniran.com/product/%D8%A8%D9%86-%D9%85%D8%A7%D8%B1%DB%8C/
MMA	11/8/2021 0:00	ilya shop	1,750,000	https://30o2.com/
EHA	11/8/2021 0:00	ilya shop	3,850,000	https://30o2.com/
Sty	11/8/2021 0:00	ilya shop	2,150,000	https://30o2.com/
AIBN	11/10/2021 0:00	ilya shop	900,000	https://30o2.com/
Flexible tube	10/28/2021 0:00	accessory shop	240,000	
Glass vacuum manifold			1,650,000	
60 Ampoules			2,550,000	
Cold trap			220,000	
Inhibitor remover column				
NMR services (26 sample)			1,794,000	https://labsnet.ir/lab
Liquid N2 (25 Lit)			250,000	
3 Column for monomer purification			90,000	
The glass blower's wage for coming to the lab			2,975,000	
Shipping Cost for inhibitor remover			2,000,000	
Received financial assistance from Dr Cumings.: 11,850,000 T	Received financial assistance from BIHE Chemistry Executive: 6,900,000 T			The rest of the expenses (Raha): 8,900,000 T

Appendix C

Conversion Calculation

Time (min)	Mp	Mp+Mwp	Mp+Mdp	Conversion	Mp+Mdp2	Conversion3	Mp+Mdp4	Conversion5
30	0.9	3.77			1.25	12.19512195	0.99	3.135888502
45	0.9	3.76			1.31	14.33566434	1.02	4.195804196
60	0.9	3.65			1.31	14.90909091	1.05	5.454545455
75	0.9	3.99			1.45	17.79935275	1.07	5.501618123
150	0.9	3.62			1.47	20.95588235	1.19	10.66176471
180	0.9	3.57			1.53	23.59550562	1.24	12.7340824
90 (First try)	1.16	2.97	1.31	8.287292818				
90 (First try)	1.43	3.32	1.62	10.05291005				
90 (First try)	1.46	3.41	1.61	7.692307692				
15	0.9	3.38			1.04	5.64516129	0.91	0.403225806
30	0.9	3.81			1.03	4.467353952	0.99	3.092783505
45	0.9	3.61			1.37	17.34317343	1.03	4.79704797
60	0.9	3.5			1.34	16.92307692	1.08	6.923076923
75	0.9	3.54			1.36	17.42424242	1.1	7.575757576
105	0.9	3.5			1.4	19.23076923	1.21	11.92307692
90 (First try)	1.35	3.24	1.6	13.22751323				
90 (First try)	1.04	2.81	1.29	14.12429379				
5	0.9	2.15					0.91	0.8
10	0.9	3.85					0.98	2.711864407
15	0.9	3.94					1.01	3.618421053
20	0.9	3.31					1.01	4.564315353
25	0.9	3.64					1.02	4.379562044
30	0.9	3.63					1.15	9.157509158
90 (First try)	1.33	3.02	1.38	2.958579882				
90 (First try)	1.17	2.75	1.57	25.3164557				
90 (First try)	1.29	2.87	1.53	15.18987342				

Appendix D

Safety Data Sheets

Styrene (Styrene MSDS, n.d.)

Hazards identification

Hazard pictograms

:



Signal word

:

Danger

Hazard statements

:

PHYSICAL HAZARDS:
H226 Flammable liquid and vapour.

HEALTH HAZARDS:
H304 May be fatal if swallowed and enters airways.
H315 Causes skin irritation.
H319 Causes serious eye irritation.
H332 Harmful if inhaled.
H335 May cause respiratory irritation.
H372 Causes damage to organs (Auditory system) through prolonged or repeated exposure if inhaled.

ENVIRONMENTAL HAZARDS:
H401 Toxic to aquatic life.
H412 Harmful to aquatic life with long lasting effects.

Precautionary statements

:

Prevention:
P210 Keep away from heat/ sparks/ open flames/ hot surfaces.
No smoking.
P240 Ground/bond container and receiving equipment.
P241 Use explosion-proof electrical/ ventilating/ lighting equipment.
P242 Use only non-sparking tools.
P243 Take precautionary measures against static discharge.
P260 Do not breathe dust/ fume/ gas/ mist/ vapours/ spray.
P264 Wash hands thoroughly after handling.
P270 Do not eat, drink or smoke when using this product.
P271 Use only outdoors or in a well-ventilated area.
P280 Wear protective gloves/ protective clothing/ eye protection/ face protection.
P273 Avoid release to the environment.

Response:

P303 + P361 + P353 IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.

P370 + P378 In case of fire: Use appropriate media to extinguish.

P301 + P310 IF SWALLOWED: Immediately call a POISON CENTER/doctor.

P331 Do NOT induce vomiting.

P332 + P313 If skin irritation occurs: Get medical advice/attention.

P305 + P351 + P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P337 + P313 If eye irritation persists: Get medical advice/attention.

P304 + P340 IF INHALED: Remove person to fresh air and

keep comfortable for breathing.

P312 Call a POISON CENTER/ doctor if you feel unwell.

Storage:

P403 + P233 Store in a well-ventilated place. Keep container tightly closed.

P235 Keep cool.

P405 Store locked up.

Disposal:

P501 Dispose of contents/ container to an approved waste disposal plant.

Other hazards which do not result in classification

Vapours are heavier than air. Vapours may travel across the ground and reach remote ignition sources causing a flashback fire danger. Highly reactive. Maintain dissolved oxygen and inhibitor at proper levels to prevent runaway polymerisation. May form flammable/explosive vapour-air mixture. This material is a static accumulator. Even with proper grounding and bonding, this material can still accumulate an electrostatic charge. If sufficient charge is allowed to accumulate, electrostatic discharge and ignition of flammable air-vapour mixtures can occur.

First aid measures

General advice	: Not expected to be a health hazard when used under normal conditions.
If inhaled	: Call emergency number for your location / facility. Remove to fresh air. Do not attempt to rescue the victim unless proper respiratory protection is worn. If the victim has difficulty breathing or tightness of the chest, is dizzy, vomiting, or unresponsive, give 100% oxygen with rescue breathing or Cardio-Pulmonary Resuscitation as required and transport to the nearest medical facility.
In case of skin contact	: Remove contaminated clothing. Immediately flush skin with large amounts of water for at least 15 minutes, and follow by washing with soap and water if available. If redness, swelling, pain and/or blisters occur, transport to the nearest medical facility for additional treatment.
In case of eye contact	: Immediately flush eye(s) with plenty of water. Remove contact lenses, if present and easy to do. Continue rinsing. Transport to the nearest medical facility for additional treatment.
If swallowed	: Call emergency number for your location / facility. If swallowed, do not induce vomiting: transport to nearest medical facility for additional treatment. If vomiting occurs spontaneously, keep head below hips to prevent aspiration. If any of the following delayed signs and symptoms appear within the next 6 hours, transport to the nearest medical facility: fever greater than 101° F (38.3°C), shortness of breath, chest congestion or continued coughing or wheezing.

Most important symptoms and effects, both acute and delayed	: Respiratory irritation signs and symptoms may include a temporary burning sensation of the nose and throat, coughing, and/or difficulty breathing. Skin irritation signs and symptoms may include a burning sensation, redness, swelling, and/or blisters. Eye irritation signs and symptoms may include a burning sensation, redness, swelling, and/or blurred vision. If material enters lungs, signs and symptoms may include coughing, choking, wheezing, difficulty in breathing, chest congestion, shortness of breath, and/or fever. If any of the following delayed signs and symptoms appear within the next 6 hours, transport to the nearest medical facility: fever greater than 101° F (38.3°C), shortness of breath, chest congestion or continued coughing or wheezing. Defatting dermatitis signs and symptoms may include a burning sensation and/or a dried/cracked appearance. Auditory system effects may include temporary hearing loss and/or ringing in the ears. Visual system disturbances may be evidenced by decreases in the ability to discriminate between colours.
Protection of first-aiders	: When administering first aid, ensure that you are wearing the appropriate personal protective equipment according to the incident, injury and surroundings.
Notes to physician	: IMMEDIATE TREATMENT IS EXTREMELY IMPORTANT! Call a doctor or poison control center for guidance. Potential for chemical pneumonitis. Treat symptomatically.

Fire-fighting measures

- Suitable extinguishing media : Foam, water spray or fog. Dry chemical powder, carbon dioxide, sand or earth may be used for small fires only.
- Unsuitable extinguishing media : Do not use water in a jet.
- Specific hazards during firefighting : Flammable vapours may be present even at temperatures below the flash point.
Sustained fire attack on vessels may result in a Boiling Liquid Expanding Vapor Explosion (BLEVE).
The vapour is heavier than air, spreads along the ground and distant ignition is possible.
Will float and can be reignited on surface water.
Hazardous combustion products may include:
Carbon monoxide.
Formaldehyde
- Specific extinguishing methods : Standard procedure for chemical fires.
Clear fire area of all non-emergency personnel.
All storage areas should be provided with adequate fire fighting facilities.
Keep adjacent containers cool by spraying with water.
- Special protective equipment for firefighters : Proper protective equipment including chemical resistant gloves are to be worn; chemical resistant suit is indicated if large contact with spilled product is expected. Self-Contained Breathing Apparatus must be worn when approaching a fire in a confined space. Select fire fighter's clothing approved to relevant Standards (e.g. Europe: EN469).
- Hazchem Code : 3Y

Accidental release measures

- Personal precautions, protective equipment and emergency procedures : Observe all relevant local and international regulations.
Notify authorities if any exposure to the general public or the environment occurs or is likely to occur.
Local authorities should be advised if significant spillages cannot be contained.
- : Isolate hazard area and deny entry to unnecessary or unprotected personnel.
Avoid contact with skin, eyes and clothing.
Be ready for fire or possible exposure.
Do not operate electrical equipment.

Stay upwind and out of low areas.

- Environmental precautions** : Shut off leaks, if possible without personal risks. Remove all possible sources of ignition in the surrounding area. Use appropriate containment to avoid environmental contamination. Prevent from spreading or entering drains, ditches or rivers by using sand, earth, or other appropriate barriers. Attempt to disperse the vapour or to direct its flow to a safe location for example by using fog sprays. Take precautionary measures against static discharge. Ensure electrical continuity by bonding and grounding (earthing) all equipment.
Monitor area with combustible gas indicator.
- Methods and materials for containment and cleaning up** : For small liquid spills (< 1 drum), transfer by mechanical means to a labeled, sealable container for product recovery or safe disposal. Allow residues to evaporate or soak up with an appropriate absorbent material and dispose of safely. Remove contaminated soil and dispose of safely.
For large liquid spills (> 1 drum), transfer by mechanical means such as vacuum truck to a salvage tank for recovery or safe disposal. Do not flush away residues with water. Retain as contaminated waste. Allow residues to evaporate or soak up with an appropriate absorbent material and dispose of safely. Remove contaminated soil and dispose of safely.
- Additional advice** : For guidance on selection of personal protective equipment see Section 8 of this Safety Data Sheet.
For guidance on disposal of spilled material see Section 13 of this Safety Data Sheet.

Handling and storage

- General Precautions** : Avoid breathing of or direct contact with material. Only use in well ventilated areas. Wash thoroughly after handling. For guidance on selection of personal protective equipment see Section 8 of this Safety Data Sheet.
Use the information in this data sheet as input to a risk assessment of local circumstances to help determine appropriate controls for safe handling, storage and disposal of this material.
Ensure that all local regulations regarding handling and storage facilities are followed.
- Advice on safe handling** : Avoid inhaling vapour and/or mists.
Avoid contact with skin, eyes and clothing.
Extinguish any naked flames. Do not smoke. Remove ignition sources. Avoid sparks.
The vapour is heavier than air. Beware of accumulation in pits and confined spaces.
Use local exhaust ventilation if there is risk of inhalation of vapours, mists or aerosols.
Bulk storage tanks should be diked (bunded).
Properly dispose of any contaminated rags or cleaning

materials in order to prevent fires.
Even with proper grounding and bonding, this material can still accumulate an electrostatic charge.
If sufficient charge is allowed to accumulate, electrostatic discharge and ignition of flammable air-vapour mixtures can occur.
Be aware of handling operations that may give rise to additional hazards that result from the accumulation of static charges.
These include but are not limited to pumping (especially turbulent flow), mixing, filtering, splash filling, cleaning and filling of tanks and containers, sampling, switch loading, gauging, vacuum truck operations, and mechanical movements.
These activities may lead to static discharge e.g. spark formation.
Restrict line velocity during pumping in order to avoid generation of electrostatic discharge (≤ 1 m/s until fill pipe submerged to twice its diameter, then ≤ 7 m/s). Avoid splash filling.
Do NOT use compressed air for filling, discharging, or handling operations.
Inhibitor levels should be maintained.
Protect against light.

Avoidance of contact

: Strong oxidising agents.
Copper alloys.

Product Transfer

: If positive displacement pumps are used, these must be fitted with a non-integral pressure relief valve. Refer to guidance under Handling section.

Methyl Methacrylate (Methyl Methacrylate MSDS, n.d.)

Hazards identification

Classification

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Flammable liquids	Category 2
Skin Corrosion/Irritation	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Skin Sensitization	Category 1
Specific target organ toxicity (single exposure)	Category 3
Target Organs - Respiratory system.	

Label Elements

Signal Word

Danger

Hazard Statements

Highly flammable liquid and vapor
Causes skin irritation
Causes serious eye irritation
May cause an allergic skin reaction
May cause respiratory irritation



Precautionary Statements

Prevention

Wash face, hands and any exposed skin thoroughly after handling
Wear protective gloves/protective clothing/eye protection/face protection
Avoid breathing dust/fume/gas/mist/vapors/spray
Contaminated work clothing should not be allowed out of the workplace
Use only outdoors or in a well-ventilated area
Keep away from heat/sparks/open flames/hot surfaces. - No smoking
Keep container tightly closed
Ground/bond container and receiving equipment
Use explosion-proof electrical/ventilating/lighting equipment
Use only non-sparking tools
Take precautionary measures against static discharge
Keep cool

Inhalation

IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
Call a POISON CENTER or doctor/physician if you feel unwell

Skin

If skin irritation or rash occurs: Get medical advice/attention
IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower
Wash contaminated clothing before reuse

Eyes

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
If eye irritation persists: Get medical advice/attention

Fire

In case of fire: Use CO₂, dry chemical, or foam for extinction

Storage

Store in a well-ventilated place. Keep container tightly closed

Store locked up

Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

None identified

First aid measures

Eye Contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.
Skin Contact	Wash off immediately with soap and plenty of water while removing all contaminated clothes and shoes. In the case of skin irritation or allergic reactions see a physician.
Inhalation	Remove from exposure, lie down. Remove to fresh air. If not breathing, give artificial respiration. Get medical attention.
Ingestion	Do NOT induce vomiting. Clean mouth with water. Get medical attention.
Most important symptoms and effects	May cause allergic skin reaction. Difficulty in breathing. Symptoms of allergic reaction may include rash, itching, swelling, trouble breathing, tingling of the hands and feet, dizziness, lightheadedness, chest pain, muscle pain or flushing: Inhalation of high vapor concentrations may cause symptoms like headache, dizziness, tiredness, nausea and vomiting
Notes to Physician	Treat symptomatically

Fire-fighting measures

Suitable Extinguishing Media	Carbon dioxide (CO ₂). Foam. Dry chemical. Water mist may be used to cool closed containers. Water mist may be used to cool closed containers.
Unsuitable Extinguishing Media	No information available
Flash Point	8 °C / 46.4 °F
Method -	No information available
Autoignition Temperature	430 °C / 806 °F
Explosion Limits	
Upper	12.5%
Lower	2.1%
Sensitivity to Mechanical Impact	No information available
Sensitivity to Static Discharge	No information available
Specific Hazards Arising from the Chemical	
Flammable. Vapors may form explosive mixtures with air. Vapors may travel to source of ignition and flash back. Containers may explode when heated. Vapors may form explosive mixtures with air.	
Hazardous Combustion Products	
Carbon monoxide (CO). Carbon dioxide (CO ₂).	
Protective Equipment and Precautions for Firefighters	
As in any fire, wear self-contained breathing apparatus pressure-demand, MSHA/NIOSH (approved or equivalent) and full protective gear.	

NFPA

Health
2

Flammability
3

Instability
2

Physical hazards
N/A

Accidental release measures

Personal Precautions	Remove all sources of ignition. Take precautionary measures against static discharges.
Environmental Precautions	Do not flush into surface water or sanitary sewer system. See Section 12 for additional Ecological Information.
Methods for Containment and Clean Up	Soak up with inert absorbent material (e.g. sand, silica gel, acid binder, universal binder, sawdust). Keep in suitable, closed containers for disposal. Remove all sources of ignition. Use spark-proof tools and explosion-proof equipment. Do not let this chemical enter the environment.

Handling and storage

Handling	Avoid contact with skin and eyes. Do not breathe mist/vapors/spray. Handle product only in closed system or provide appropriate exhaust ventilation. Use spark-proof tools and explosion-proof equipment. Use only non-sparking tools. Keep away from open flames, hot surfaces and sources of ignition. To avoid ignition of vapors by static electricity discharge, all metal parts of the equipment must be grounded. Take precautionary measures against static discharges.
Storage.	Keep in a dry, cool and well-ventilated place. Keep container tightly closed. Keep away from heat, sparks and flame. Refrigerator/flammables. Incompatible Materials. Acids. Bases. Amines. Halogens. Peroxides. Reducing Agent.

2-Ethylhexyl Acrylate (2-Ethylhexyl Acrylate MSDS, n.d.)

Hazards identification

According to Hazardous Products Regulations (HPR) (SOR/2015-17)

Classification of the product

Flam. Liq.	4	Flammable liquids
Skin Corr./Irrit.	2	Skin corrosion/irritation
Skin Sens.	1B	Skin sensitization
STOT SE	3 (irritating to	Specific target organ toxicity — single exposure
	respiratory system)	
Aquatic Acute	2	Hazardous to the aquatic environment - acute
Aquatic Chronic	3	Hazardous to the aquatic environment - chronic

Label elements

Pictogram:



Signal Word:
Warning

Hazard Statement:

H227	Combustible liquid.
H315	Causes skin irritation.
H317	May cause an allergic skin reaction.
H335	May cause respiratory irritation.
H412	Harmful to aquatic life with long lasting effects.
H401	Toxic to aquatic life.

Precautionary Statements (Prevention):

P280	Wear protective gloves and eye protection or face protection.
P261	Avoid breathing mist or vapour or spray.
P271	Use only outdoors or in a well-ventilated area.
P273	Avoid release to the environment.
P210	Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P272	Contaminated work clothing should not be allowed out of the workplace.
P264	Wash contaminated body parts thoroughly after handling.

Precautionary Statements (Response):

P312	Call a POISON CENTER or physician if you feel unwell.
P304 + P340	IF INHALED: Remove person to fresh air and keep comfortable for breathing.
P302 + P352	IF ON SKIN: Wash with plenty of soap and water.
P333 + P313	If skin irritation or rash occurs: Get medical attention.
P332 + P313	If skin irritation occurs: Get medical attention.
P362 + P364	Take off contaminated clothing and wash it before reuse.
P370 + P378	In case of fire: Use water spray, dry powder, foam, carbon dioxide or dry sand for extinction.

Precautionary Statements (Storage):

P403 + P233	Store in a well-ventilated place. Keep container tightly closed.
P405	Store locked up.

Precautionary Statements (Disposal):

P501	Dispose of contents/container in accordance with local regulations.
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Hazards not otherwise classified

No applicable information available.

Labeling of special preparations (GHS):

Risk of hazardous polymerization under certain conditions (e.g. elevated temperatures, low inhibitor and oxygen concentration).

First aid measures**Description of first aid measures****General advice:**

First aid personnel should pay attention to their own safety. If the patient is likely to become unconscious, place and transport in stable sideways position (recovery position). Immediately remove contaminated clothing.

If inhaled:

Keep patient calm, remove to fresh air, seek medical attention.

If on skin:

Wash thoroughly with soap and water

If in eyes:

Wash affected eyes for at least 15 minutes under running water with eyelids held open, consult an eye specialist.

If swallowed:

Immediately rinse mouth and then drink 200-300 ml of water, seek medical attention.

Most important symptoms and effects, both acute and delayed

Symptoms: Overexposure may cause: convulsions, lethargy

Indication of any immediate medical attention and special treatment neededNote to physician

Treatment:

Treat according to symptoms (decontamination, vital functions), no known specific antidote.

Fire-fighting measures**Extinguishing media**

Suitable extinguishing media:

carbon dioxide, dry powder, water spray, foam

Unsuitable extinguishing media for safety reasons:

water jet

Special hazards arising from the substance or mixture

Hazards during fire-fighting:

Risk of violent self-polymerization if overheated in a container.

Advice for fire-fighters**Further information:**

In case of a fire in the vicinity a restabilization system should be used if the temperature in the bulk storage-tank reaches 45°C. Evacuate area of all unnecessary personnel. In case of a fire in the vicinity evacuate all personnel in a greater area if the temperature in the bulk storage-tank reaches 60°C.

Contaminated extinguishing water must be disposed of in accordance with official regulations.

Impact Sensitivity:

Remarks:

Based on the chemical structure there is no shock-sensitivity.

Accidental release measures**Personal precautions, protective equipment and emergency procedures**

Take appropriate protective measures.

Ensure adequate ventilation. Use personal protective clothing. Breathing protection required.

Environmental precautions

Do not discharge into waterways or sewer systems without proper authorization.

Methods and material for containment and cleaning up

Spills should be contained, solidified, and placed in suitable containers for disposal. Use spark-proof tools and explosion-proof equipment.

Handling and storage

Precautions for safe handling

Handle in accordance with good industrial hygiene and safety practice. The substance/ product may be handled only by appropriately trained personnel. Facility parts must be checked for polymer residues and cleaned on regular basis in order to avoid hazardous reactions.

Do not use any sparking tools. Avoid all sources of ignition: heat, sparks, open flame.

Protection against fire and explosion:

Substance/product can form explosive mixture with air. Ground all transfer equipment properly to prevent electrostatic discharge. Containers should be grounded against electrostatic charge. It is recommended that all conductive parts of the machinery are grounded. Explosion-proof equipment is not necessary when loading and processing of the product takes place at a minimum of 5 °C below the flash point.

Heated containers should be cooled to prevent polymerization. If exposed to fire, keep containers cool by spraying with water. Emergency cooling must be provided for the eventuality of a fire in the vicinity. Sealed containers should be protected against heat as this results in pressure build-up. Avoid influence of heat.

Vapours are heavier than air and may accumulate in low areas and travel a considerable distance up to the source of ignition.

Conditions for safe storage, including any incompatibilities

Further information on storage conditions: Risk of polymerization. Protect against heat. Protect from direct sunlight. Protect contents from the effects of light. Avoid UV-light and other radiation with high energy. Protect against contamination.

Storage stability:

Storage temperature: < 35 °C

Storage duration: 12 Months

The stated storage temperature should be noted.

Avoid prolonged storage.

Do not store with less than 10 % headspace above liquid.

Storage stability is based upon ambient temperatures and conditions described.

Storage temperature: 45 °C

A restabilization system should be used if the temperature in the bulk storage-tank reaches the indicated value.

Storage temperature: 60 °C

All personnel in a greater area should be evacuated if the temperature in the bulk storage-tank reaches the indicated value.