

***TEMPERATURE EFFECT ON POLYMERIZATION  
KINETICS OF POLY METHYL METHACRYLATE  
(PMMA)***

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## ABSTRACT

Polymerization is a process which is chemically combined of small molecules to produce a very large chain or network molecule, called a polymer. By the way, the small molecules may be alike, or they may represent of two, three, or more different compounds with different molecular weight. This research proposes is to study the effect of temperature on polymerization kinetics of methyl methacrylate (MMA). Thermal study on methyl methacrylate is important to explain the heat and mass transfer phenomena during polymerization reaction. The objective of this study is to determine the temperature effect on polymerization kinetics of methyl methacrylate (MMA) with initiator. Mass of methyl methacrylate as monomer will be fixed at 3miligrams and also mass of initiator which is azo-bisisobutyronitrile (AIBN) will constant at 2miligrams. These two components will put on the pan by micropipette. The pan will tightly seal and be put into the differential scanning calorimetry (DSC). Each of samples will run until five hours in different temperatures (35°C, 45°C, 55°C, 65°C and 75° C). Then the polymerization kinetics and heat released are analyzed using this differential scanning calorimetry (DSC). From the (DSC) the curves or data of temperature, time and heat released are obtained. From these result obtained, increasing the temperature will decrease the time of reaction taken. High temperature will increase the amount of heat low or heat release. As increase the temperature, the rate of reaction increase due to the increasing of collision frequency and produce more energy to start the reaction.

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## LIST OF SYMBOLS

$W$	<i>Watt</i>
$g$	<i>Gramme</i>
$g^{-1}$	<i>Reciprocalgramme</i>
$^{\circ}C$	<i>Degree celcius</i>
	<i>pi</i>
	<i>sigma</i>
$k_d$	<i>decomposition constant</i>

## **LIST OF ABBREVIATIONS**

PMMA	Poly methacrylate
MMA	Methacrylate
DSC	Differential Scanning Calorimetry
AIBN	Azo-bisisobutyronitrile
PVC	Poly vinyl chloride
LCD	Liquid Crystal Displays

# 1 INTRODUCTION

## *1.1 Background of Proposed Study*

Since the creation of the earth over 4 billion years ago, polymer already appeared in natural form like wood, cotton, cellulose, starch and others. To improve the quality of life, human started to develop ways to fulfil their basic needs. Many experiments and a lot of research are done about polymerization. According to Gowariker.V.K, Viswanathan.N.V and Sreedhar J (1986) polymer is one thing that is complex and giant molecules with different molecular weight compounds. The individual small molecules from which the polymer is formed are known as monomers and the process by which the monomer molecules are linked to form a big polymer molecule is called polymerization. Kinetics of polymerization is defined the speed of a reaction under a given set of conditions. In this research, the effect of reaction temperature on the rate will be examined.

Global demand for methyl methacrylate (MMA) is about 2.4 million tonnes due to its application as flat panel displays that grows rapidly in Asian region (Nexant, 2009). The largest uses of poly methyl methacrylate (PMMA) are in the cast and transparent acrylic sheet. Acrylic sheet is used for glazing, lighting, signage, displays, sanitary ware, and miscellaneous other applications. Its largest markets are in skylights, architectural applications, security glazing, and displays. PRNewswire (2010) reported that (MMA) demand is growth 3-5% per year and 8-10% per year in Asia and China respectively. It also reported that world consumption is forecast to grow at an average annual rate of 3.3% during 2010-2013 due to the continuing demand growth in Asia for (PMMA) electronic applications and surface coatings in Central and Eastern Europe, Africa and Middle East.

As mentioned by (Nexant, 2009) an acrylic also have been used in Liquid Crystal Displays (LCD). In Asia, demand (LCD) growth about seven to eight percent in 2005 to 2008. Then, in Japan, South Korea and Taiwan are projected to be around 40% in the period 2001-2004 and is expected to increase by about half as much again over 2005-2008.



## ***1.2 Problem statement***

Currently, human compete to create more advanced technology. With this advancement, polymer technology is also improving rapidly. Recently, the polymers have been modified to fulfil the suitability according to their applications. So, the physical and chemical properties of a polymer will be improved to obtain a high quality of that polymer. It is very important to understand the mechanism and kinetics of polymerization in order to achieve desired properties of polymer. Thus, by running the experiments and researches, this kind of polymerization data will get.

So, this research is about the temperature effect on polymerization kinetics of polymethylmethacrylate (PMMA). Polymerization reaction is best described in polymer science. Copolymerization of different monomers is an important tool to design polymers with specific properties according to desired applications.

Therefore, it is helpful to know the kinetics of a certain copolymerization to be able to generate a particular polymer for a desired application. Various applications but only few data in literature make it interesting for both academia and industry to investigate this polymerization in term of temperature effect. Therefore, temperature is the parameter to be studied. It is because, high temperature may cause high cost, and give bad impact of polymerization kinetics due to the rate of polymerization.

## ***1.3 Objectives***

Based on the problem statement described previously, the following are the objectives of this research:

- i) To determine the temperature effect on bulk polymerization kinetics of methyl methacrylate.
- ii) To analyse the heat released during the bulk polymerization of methylmethacrylate

#### ***1.4 Scope of the study***

In this research, there are several scopes of the study in order to achieve the above objective mentioned which are:

1. Examining the polymerization kinetics of methyl methacrylate by using Differential Scanning Chromatography (DSC).
2. Analyse the heat released from the polymerization reaction curve.

#### ***1.5 Significant of the study***

Bulk polymerization of (PMMA) is a batch that doesn't produce a toxic compound and zero pollution. This research is also producing some data for MMA polymerization that useful for academia and industry. In order to produce a desired property of polymer, the kinetics and mechanism of polymerization is very important thing to deeply understand.

#### ***1.6 Organisation of this thesis***

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the applications and general polymerization of addition polymerization. A general description on the polymerization technique also discuss in this chapter. This chapter also provides a brief discussion of the polymerization mechanism of addition polymerization.

Chapter 3 gives a review of the chemical used for determine the heat flow on MMA polymerization by using differential scanning calorimetry. The result from appear will analysis and compared data with various operating temperature.

Chapter 4 is devoted to analyse data by plot the graphs. The graph of all data will plot and combine in one graph to get the trend of data.

Chapter 5 draws together a summary of the thesis and recommendation which might be useful for the future work.

## **2 LITERATURE REVIEW**

### ***2.1 Overview***

This paper presents the experimental studies of temperature effect on MMA polymerization kinetics by using differential scanning calorimetry (DSC). First, deeply study of polymerization mechanism is very important to undergo this experiment. Then, polymerization technique is also discussed in this chapter.

### ***2.2 Introduction***

This chapter provides a literature review for the research of temperature effect on polymerization kinetics of poly methyl methacrylate (PMMA). Another topic about types and classes of polymerization and polymerization technique also has been discussed in this chapter. This chapter also contain the polymerization mechanism of PMMA.

### ***2.3 Poly methyl methacrylate***

In year 1877, the polymethylmethacrylate was synthesized for the first time. “The person who started the research and further development of (PMMA) was Otto Röhm GmbH by his thesis in 1901”. He took 30 years to build the cast (PMMA) sheet production (Philip. N, 2006). Poly methyl methacrylate (PMMA) is widely used as low cost thermoplastic with various applications to daily life. Poly methyl methacrylate is the commercial important of acrylic and its high transparency makes it an ideal replacement for glass.

#### ***2.3.1 Properties of methyl methacrylate***

Methyl methacrylate is an organic compound with the chemical formula  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$ . This chemical is in liquid form and colourless. Methyl methacrylate is also used as modifier for poly vinyl chloride (PVC).

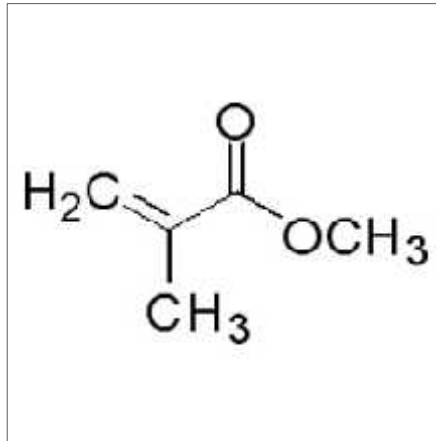


Figure 2-1: Chemical compound of methyl methacrylate (MMA) (<http://www.indiamart.com>)

Table 2-1 shows the properties of poly methyl methacrylate. ([www.matbase.com](http://www.matbase.com))

Molecular formula	$(C_5O_2H_8)_n$
Density	1.18 g/cm <sup>3</sup>
Melting point	160 °C (320 °F)
Young's modulus	1800 - 3100 MPa
Shear modulus	1700 - 1700 MPa
Tensile strength	48 - 76 MPa
Thermal expansion	50 - 90 e-6/K
Thermal conductivity	0.167 - 0.25 W/m.K
Specific heat	1466 - 1466 J/kg.K
Glass temperature	105 - 105°C

Poly methyl methacrylate also has greater scratch resistance when compared with other polymers like polycarbonate. However its scratch resistance still cannot compete with glass.

### ***2.3.2 Application of poly methyl methacrylate***

Most polymethylmethacrylate (PMMA) is used in various low cost products that require transparency and weather resistance in its applications. There are examples of these applications such as headlights and taillights on automobiles, illuminated signs and street lamp housings. The polymer also has been used commonly in aircraft windows as a glass replacement because of its low density and high toughness. It is still used as a glass substitute on a wide range of sub-sonic aircraft today and has expanded to other weight sensitive applications such as race car body, and motorcycles. (Alfredo. C, 2007)

## ***2.4 Polymerization***

Polymerization is the process where the relatively small molecules which are monomers combine chemically to produce a very large chain-like or network molecule. This network molecule is called a polymer. By the way, the monomer molecules may be alike, or they may represent two, three, or more different compounds with different molecular weights.

Two classes of polymerization are usually distinguished. There are condensation and addition polymerization. In condensation polymerization each step of the process is accompanied by the formation of a molecule of some simple compound like water. In addition polymerization, monomers will react to form a polymer without the formation of by-products. Usually, addition polymerization is carried out in the presence of a catalyst, which in certain cases exerts control over structural details that have important effects on the properties of the polymer.

One of the addition polymerizations is free-radical polymerization. This free-radical polymerization can occur in many states which are in the gas phase, bulk, solution, emulsion, suspension and even in solid state (Hans-Georg. E, 2005). This study is more focused on bulk polymerization technique. As mentioned by (Hans-Georg. E, 2005) in bulk polymerization, only monomers, polymer and initiators are present. Thus, the product is highly purified. It is also agreed by (Gowariker. V. K,

Viswanathan. N. V and Sreedhar J, 1986) that the product will have high purity since the initiator and the chain transfer agent do not add other contaminants.

To understand the underlying kinetics of radical polymerization, three steps of polymerization reaction are considered which are initiation, propagation and termination. Initiation step involves an active site of the monomer and it occurs spontaneously by absorbing heat, light like ultraviolet or high-energy irradiation (Robert, O.E, 2000).

In the propagation process, the initiated monomer adds other monomers in rapid succession by the active center which will continuously relocate at the end of the growing polymer chain until deactivated by termination. The process of termination thus results in the deactivation of the growing chain. These three processes will be more discussed in the next sub topic in this study. In initiation step of bulk polymerization, initiator is dominant in this process to produce free radical. And inhibitor is used to avoid polymerization.

### ***2.4.1 Initiator***

The initiator is a source of any chemical species that reacts with a monomer (single molecule that can form chemical bonds) to form an intermediate compound capable of linking successively with a large number of monomers into a polymeric compound.

The functionality of initiators depends on the presence of functional end groups such as hydroxyl and carbonyl, or azo and perester bonds which undergo dissociation to alkyl, alkoxy or acyloxy radicals under the influence of temperature or irradiation (Pabin-Szafko, 2009). According to Gowariker. V. K, Viswanathan. N. V and Sreedhar J (1986) in free radical polymerization, the initiator concentration is very low and the growing chain interaction with the initiator may be very small. The accelerating influence of polymerization rate is not exactly that of catalysts since they are changed chemically in the polymerization.

Benzoyl peroxide, Azobisisobutyronitrile (AIBN) and di-t-butyl peroxide are commonly used in free-radical initiator. Azo compound is any organic chemical compound in which the azo group ( $-N=N-$ ) is part of the molecular structure. The atomic groups attached to the nitrogen atoms may be of any organic class.

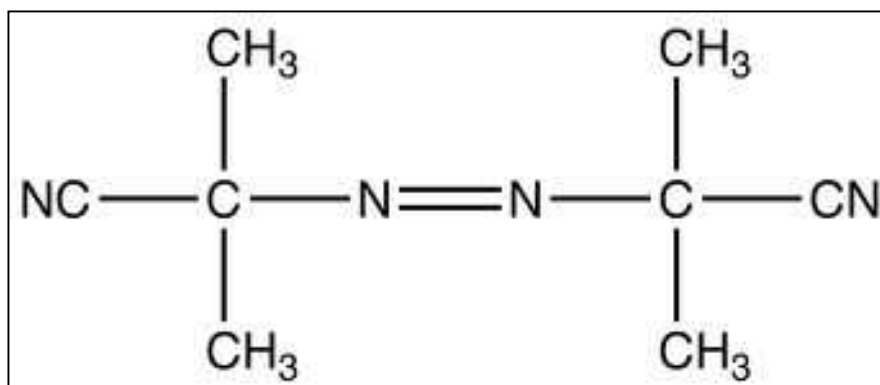


Figure 2-2: Chemical compound of azobisisobutyronitrile. (<http://science.uvu.edu/ochem>)

Azobisisobutyronitrile (AIBN) is an organic compound with the formula  $[(CH_3)_2C(CN)]_2N_2$ . Usually, the AIBN is a white powder that soluble in alcohols and organic solvent but insoluble in water but in this research the liquid form of AIBN will used. Commonly, this AIBN was used as a foamer in plastics and rubber process.

The (AIBN) will decompose by eliminating a molecule of nitrogen gas to form two 2-cyanoprop-2-yl radicals. These radicals can initiate the free radical polymerization and other radical-induced reactions.

In safety fact, (AIBN) is safer to use than benzoyl peroxide because the risk of explosion is far less. However, it is still considered as an explosive compound when decomposing above  $65^\circ C$ . Thus, a respirator dust mask, protective gloves and safety glasses are recommended while conducting this chemical compound.

The dissociation of azo compound is not due to the presence of a weak bond as in the case of the peroxy compound. As discuss in (George. O, 2004) the C-N bond

dissociation energy is high about 290 KJ/Mol-1 but the driving force for homolysis is the formation of the highly stable nitrogen molecule. The initiators are used at different temperatures depend on their rates of decomposition. Thus, (AIBN) commonly used in 50-70 °C, acuity peroxide at 70-90 °C, benzoyl peroxide at 80-95 °C and dicumyl or di-t-butyl peroxide at 120-140 °C.

The value  $k_d$  varies in the range  $10^{-4}$  to  $10^{-9}$  s<sup>-1</sup> depend on the initiator and temperature (Eastmond, 1976a. b. c) as mention in (George. O, 2004). Most initiators are used at temperatures where  $k_d$  is usually in the range  $10^{-4}$  to  $10^{-6}$  s<sup>-1</sup>. The rate of decompositions is different depending on the structure of the initiator and the radical produced.

#### **2.4.2 Inhibitor**

Inhibitor is a chemical substance that capable to inhibit or kill the chain growth by combining with the active free- radicals and forming either stable products or inactive free-radicals. Hydroquinone, nitrobenzene, dinitrobenzene and benzothiazine are some of the inhibitors commonly used in the polymer industry (Gowariker. V. K, Viswanathan. N. VandSreedhar J, 1986).

When inhibitors added to the growing chain of polymer, it will form the polymer chain with an inhibitor end group carrying radical site. So, this resonance-stabilized free radical end is not active enough to attack a fresh monomer molecule and add it on to the chain. No further propagation can take place. However, this free radical powerful enough to recombine with another radical growing chain and terminate the growth.

A major use of inhibitors is in the preservation of monomers during production and storage. Without inhibitors the monomers cannot be transported from one place to another and also cannot be stored before actual use. Inhibitors are also used in the polymer industry for the purpose of arresting the polymerization beyond a certain conversion as to achieve a uniform product and avoid cross-linking.



### **2.4.3 Polymerization Techniques**

Bulk polymerization is an exothermic reaction of mixture containing only monomer and initiator. The main advantages of this technique lie in the optical clarity of the product and free from contaminations.

Other polymerization technique is solution polymerization. In this technique, a monomer and a catalyst will dissolve in a non-reactive solvent. During this process, the solvent liquid absorbs the heat generated by the chemical reaction. This reaction will control the reaction rate. This process is only suitable to create wet polymer types.

Suspension polymerization counteracts the heat problem by suspending droplets of water insoluble monomer in an aqueous phase. The initiator is monomer soluble. The monomer is suspended in water in form of fine droplets which are stabilized and prevented from coalescing by using suitable water-soluble protective colloids, surface active agents and by stirring.

Emulsion polymerization is an important technology process that widely used to prepare acrylic polymer and a large number of copolymers. This technique differs from suspension method in the particles is much smaller and the initiator is soluble in the aqueous phase rather than in the monomer droplets. The emulsion is stabilized by surface active agents, protective colloids and also by certain buffers. The process offers the unique opportunity of being able to increase the polymer chain length without altering the reaction rate.

### ***2.5 Free Radical Polymerization of Poly Methylmethacrylate (PMMA) Mechanism.***

Free-radical polymerization is a synthesis route for obtaining a variety of polymer and composite materials. The successive addition of free radical by polymerization process can form polymer which is grow by polymer chain. There are three steps in free-radical polymerization which are initiation, propagation and termination step.

### 2.5.1 Initiation

The initiator is thermal unstable compound. Energy is supplied to this compound. Then, the molecule will split into two molecules which are called free radicals. Each of these components carries one of the unpaired (lone) electrons with it. This free radical is represented by dots. The rate of decomposition of these initiators depends on the reaction temperature and the solvents used.

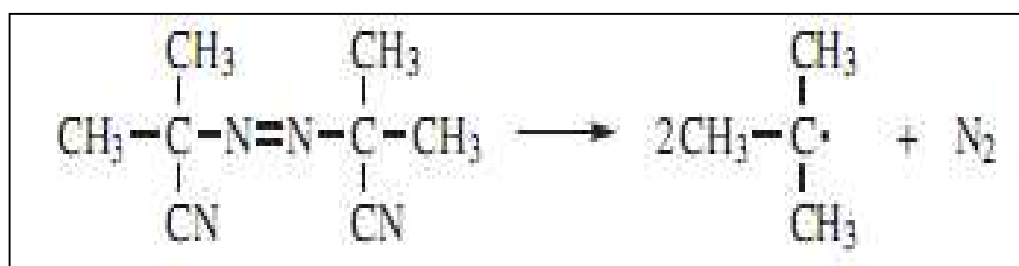


Figure 2-3: Initiation of Azobisisobutyronitrile. (George, O. ,2004."Principles of Polymerization".4<sup>th</sup> Ed).

At initiation step, a free radical is always looking for another lone electron to couple with and get stabilized. Therefore, the free radical will attack the double bond in the monomer molecule due to the highly reactive of free radical. In a double bond, one pair of electron exists as sigma ( ) electrons while the other exists as pi ( ) electrons that not close to the nucleus. Hence, the electrons are stronger than electrons.

### 2.5.2 Propagation

The propagation process occurs after initiation process. In the propagation step, the radical site at the first monomer attacks the double bond in the fresh monomer molecule. This process will continue until the free-radical site being killed by some impurities or termination process. This process produces a large number of repeating units of the monomer.

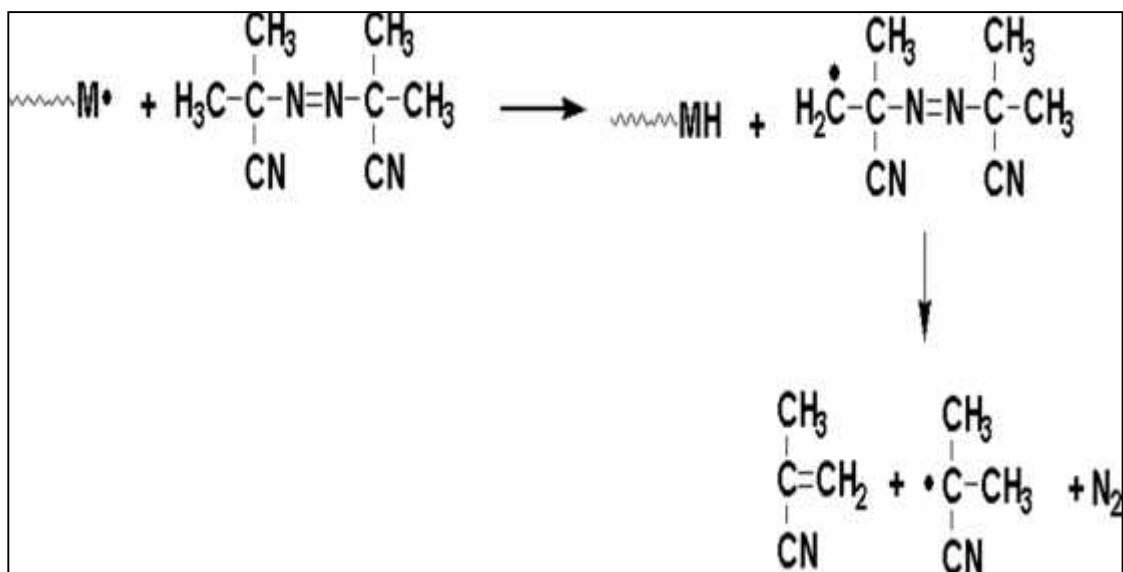


Figure 2-4: Propagation of methyl methacrylate.  
 (<http://polychem.xicp.net/polymerworld/gfzwf203/Chapter3/pic>)

### 2.5.3 Termination

There are two types of termination process which is terminated by coupling and termination by dis-proportionating. In the coupling termination, the two growing chains unite by the coupling of the lone electron present in each chain to form an electron pair. By dis-proportional termination, the polymer molecule obtained is shorter chain length than by coupling termination.

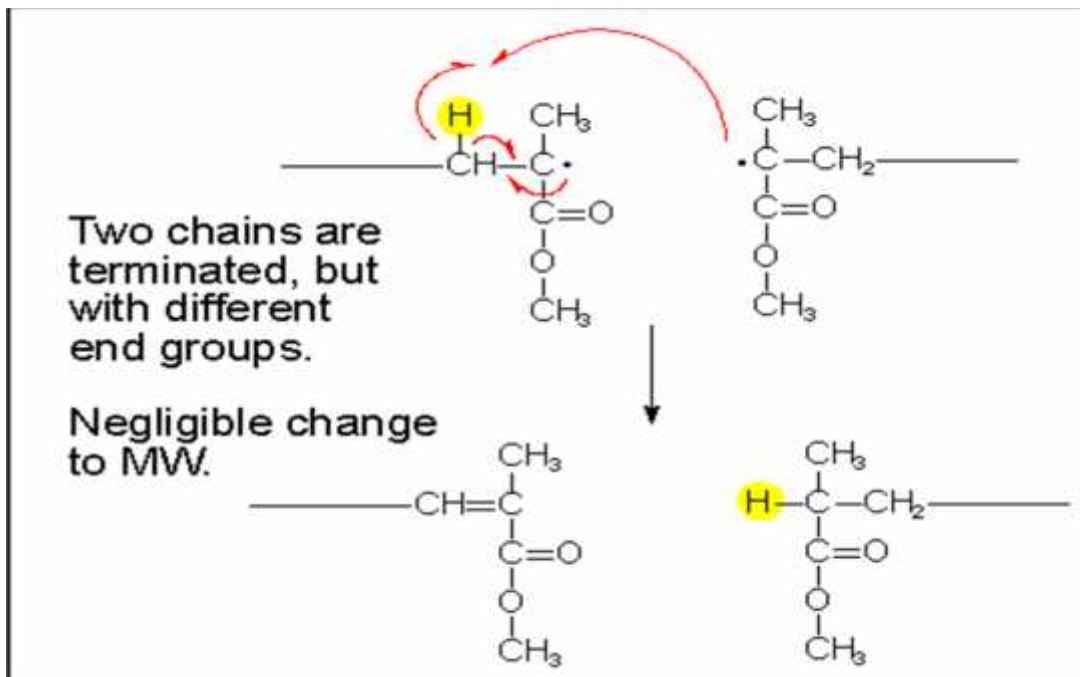


Figure 2-5: Termination. (<http://chem.chem.rochester.edu/~chem421/disprop.gif>)

## 2.6 Differential scanning calorimetry (DSC)

The term of differential scanning calorimetry refers to both of the technique measure calorimetric data while scan the temperature changed. A sample of known mass is heated or cooled while the changes in the heat capacity are tracked as changes in the heat flow.

DSC can detect any change of heat flow in and out of a sample. It include more than glass transition and melting temperature. Furthermore DSC also used in many industries such as including pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors and electronics (Perkin.E, 2013).

### 2.6.1 How are kinetics study done with DSC?

Kinetics studies on the DSC are done by using scanning methods. Where, the sample is heated through a temperature ramp in an isothermal on a set of temperature. The data from this method will be exported to Excell for analysis. One of the advantages

of DSC for kinetics study is it tend to be faster and more straight forward than other method.

## **2.8 Summary**

This paper presents polymerization kinetics of MMA study of differential scanning calorimetry (DSC) for 5mg of sample.

## 3 MATERIALS AND METHODS

### 3.1 Overview

This paper presents an experimental of the polymerization kinetics. This polymerization kinetics was performed using DSC to analyze the heat flow. The operating temperature is considered the effect of the polymerization kinetics. The data obtained from experimental had analyzed.

### 3.2 Introduction

This research will divide into two parts. Firstly, preparation of MMA sample. Lastly, to analyse the reaction temperature effect on bulk polymerization kinetics of MMA by using DSC.

### 3.3 Chemicals

This paper presents an experimental of MMA polymerization kinetics.

1. Methyl methacrylate
2. Basic aluminium oxide
3. Azo-bisisobutyronitrile

Methyl methacrylate was purchased purely from common industry. This methyl methacrylate purity is 99% in toluene solution. So, to get the more pure methyl methacrylate, a method to purify is exposed.

Basic aluminium oxide was used to remove inhibitor in the methyl methacrylate solution. The methyl methacrylate was passed through the column that filled with basic aluminium oxide in vacuum condition. This is to make sure that all the inhibitor and impurities were removed.

This equipment's also used to complete the experiment.

1. Differential Scanning Calorimetry ( to analyse the heat flows)
2. Micro pipette ( to measure the monomer and initiator)

3. Analytical balance ( to weight the monomer and initiator)
4. Crucible ( to hold the samples)
5. Sealing press ( to seal the crucible tightly)



Figure 3-1: Micro pipette



Figure 3-2: Differential Scanning Calorimetry



Figure 3-3: Analytical balance



Figure 3-4: Crucible