EFFECT OF TEMPERATURE ON KINETICS OF BULK POLYMERIZATION OF METHYL ACRYLATE

FATIN AZUREEN BINTI ZULKURNAIN

BACHELOR OF CHEMICAL ENGINEERING
UNIVERSITI MALAYSIA PAHANG

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EFFECT OF TEMPERATURE ON KINETICS OF BULK POLYMERIZATION OF METHYL ACRYLATE

FATIN AZUREEN BINTI ZULKURNAIN

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

SUPERVISOR’S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :
Name of main supervisor : DR. OMAR EL-HADAD
Position : SENIOR LECTURER
Date : 08 JANUARY 2014

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is my own except for quotations and summaries which have been duly acknowledged. The thesis has not been accepted for any degree and is not concurrently submitted for award of other degree.

Signature :
Name : FATIN AZUREEN BINTI ZULKURNAIN
ID Number : KA10096
Date : 08 JANUARY 2014

Dedication

Special dedication to my supervisors, my family members,
my friends, my fellow colleagues and all faculty members
for all your care, support and believe in me

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First of all, all thanks to Allah for His blessing and make things get easier for me to accomplish with a great results for this research project. I would like to express the deepest appreciation to my supervisor, Dr. Omar El-Hadad, who has shown the attitude and the substance of a genius: he continually and persuasively conveyed a spirit of adventure in regard to my research, and an excitement in regard to teaching. Without his supervision and constant help this dissertation would not have been possible to be done within the period of time.

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ABSTRACT

This research objective is to determine the effect of temperature on the kinetics of bulk polymerization of methyl acrylate. Because of previous research has mentioned that free radical polymerization is poorly controlled and results in high molecular weight, this research will be run at certain temperature which can be considered high but it should be lower than the boiling point of the monomer itself. The method used in this research is by using Differential Scanning Calorimetry (DSC). The DSC will measure the heat flow associated with polymerization as a function of time in a controlled atmosphere. Therefore, the change in the kinetics of polymerization based on temperature can be determined by using this equipment. The graph for heat flow versus time is recorded by DSC software until the reaction is completed. By referring to the graph it can be seen that the reaction rate of polymerization increase with the increase of temperature. As a conclusion, from this research, it can be seen that changing the temperature can affect polymerization kinetics of methyl acrylate.

ABSTRAK

Dalam kajian ini, objektifnya adalah untuk menentukan kesan suhu ke atas kinetik pempolimeran pukal metil akrilat. Pempolimeran radikal bebas telah dipilih sebagai satu proses untuk menjalankan kajian ini. Walaubagaimanapun, penyelidikan sebelum ini telah menyebut bahawa pempolimeran radikal bebas, sukar untuk mengawal proses dan menyebabkan berat molekul meningkat, akan tetapi, kajian ini akan dijalankan pada suhu tertentu yang boleh dianggap lebih tinggi tetapi ia harus lebih rendah daripada takat didih monomer itu sendiri. Oleh yang demikian, proses pempolimeran boleh dikawal dan sekaligus dapat mengurangkan berat molekul. Kaedah yang digunakan dalam kajian ini adalah dengan menggunakan peralatan yang dikenali sebagai Kalorimeter Pengimbasan Perbezaan (DSC). DSC akan mengukur suhu dan aliran haba yang berkaitan dengan peralihan dalam bahan-bahan sebagai fungsi masa dan suhu dalam suasana yang terkawal. Oleh itu, perubahan dalam kinetik pempolimeran berdasarkan suhu boleh ditentukan dengan menggunakan peralatan ini. Graf bagi pengaliran haba berbanding masa direkodkan oleh perisian Calorimetry sehingga tindak balas pempolimeran selesai. Dengan merujuk kepada graf, dapat dilihat bahawa kadar tindak balas pempolimeran meningkat dengan peningkatan suhu. Kesimpulannya, kajian ini, ia boleh dilihat bahawa perubahan suhu boleh menjejaskan pempolimeran kinetik metil akrilat.

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LIST OF ABBREVIATIONS

DSC	Differential scanning calorimetry
FRP	Free Radical Polymerization
ARTP	Atomic Radical Transfer Polymerization
RAFT	Reversible Addition Fragmentation Chain Transfer
AIBN	Azobisisobutyronitrile

1 INTRODUCTION

1.1 Motivation and statement of problem

Polymers have existed in natural form since life began such as DNA, RNA, proteins and polysaccharides play a very important role in plant and animal life. From the earliest times, man has exploited naturally-occurring polymers like cotton, wool (cellulose) as materials for providing clothing, shelter, tools, writing materials and other tools. Since polymers are very useful, polymerization has been introduced. The term polymer stems from the Greek roots poly (many) and meros (part). Polymers contain thousands to millions of atoms in a molecule that is large and they are prepared by joining a large number of small molecules called monomers (Manas Chanda, 2006). Polymerization is the process in which monomer units are linked by chemical reaction to form long chains. These long chains set polymers apart from other chemical species and give them their unique characteristic properties (Dotson, 1996). The polymer chains can be linear, branched, or cross-linked. Polymerization can proceed according to two different mechanisms, referred to as chain growth and step-growth polymerization. In chain-growth polymerization (also called addition polymerization) reaction occurs by successive addition of monomer molecules to the reactive end (e.g. a radical end) of a growing polymer chain. Chain-growth polymerization can be classified (in order of commercial importance) as radical, coordination, anionic, or cationic polymerization, depending on the type of initiation. (Hans-Geong, 2005). In step polymerization, the polymer build-up proceeds through a reaction between functional groups of the monomers. The reaction takes place in a step-wise-manner (i.e., one after another), and the polymer build-up is, therefore, slow (unlike in chain polymerization where the chain growth is in rapid reaction). Even though many known reactions with organic functional groups can be made use in step polymerization, condensation, addition, ring-opening, amidation and ester-interchange reaction are widely practiced (Gowariker V.K., Viswanathan N.V. and Sreedhar J, 1986). However, for this research, the most concerning part is only for free radical polymerization methyl acrylate can be polymerized by FRP only.

Free radical polymerization (FRP) is the most widely practiced method of radical polymerization, and is used almost exclusively for preparation of polymers from monomers of general structure (Robert J. Young and Peter A. Lovell, 2011). Furthermore, free radical is the most versatile type of chain growth. Most of the monomers are available for this type of method. On top of that, FRP is the most robust method, which means that it is less sensitive to solvent, impurities and atmospheric conditions. Therefore, it is easier and efficient to run the process using this method. However, there must be limitations on using FRP method. For examples, it is lack of control over PDI and difficult to make well defined block copolymers. (Paula Hammond, 2006). The four most commonly used methods for performing free radical polymerization are bulk, solution, suspension and emulsion polymerization. In this research project, bulk polymerization has taken into consideration. To be specified, the aim of this research is to determine the effect of temperature on the kinetics of bulk polymerization of methyl acrylate. This means, only bulk polymerization takes place in this research. Theoretically, when the temperature is increased, the speed of reaction will be increased leading to an increase in the rate of reaction (George Odian, 2004). Hence, to find whether the theory is acceptable or not, this research is going to take place.

According to Kelly A. Davis et al. (1999) they stated that free radical polymerization is poorly controlled and therefore leads to the increase in molecular weight early in the polymerization. Hence, they came out with atomic transfer radical polymerization (ATRP). By using relevant reaction temperature is an alternative way to produce low molecular weight polymer. At elevated temperature, the reactions become significant (Ahmad et al. (1998); McCord et al. (1997); Plesis et al. (2000)). Producing low molecular weight polymers using suitable reaction temperatures can decrease the process cost while minimizing the impurities of the reaction system. However, in terms of relevant temperature means, the temperature should be high enough but must be lower than the boiling point of monomer itself.

1.2 Objectives

The following are the objectives of this research:

- To investigate the effect of temperature on the kinetics of bulk polymerization of methyl acrylate.

1.3 Scope of this research

The following are the scope of this research:

i. Examining kinetics of bulk polymerization of methyl acrylates by using Differential Scanning Calorimetry (DSC).

ii. Analyzing the temperature effect on polymerization kinetic of methyl acrylates.

1.4 Main contribution of this work

The following are the contributions, by modelling the kinetics of material reactions provides the scientist and engineer with valuable information for: process development and prediction of optimum reaction temperatures, process control by optimization of reaction advancement or conversion, and estimation of material lifetimes.

1.5 Organisation of this thesis

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

Chapter 2 provides a description of the monomer and initiator used. General descriptions on the process of polymerization, as well as the kinetics of polymerization by using differential scanning calorimetry (DSC) are discussed in this chapter. This chapter also provides a brief discussion of the advantage of using the selected initiator which is Azobisisobutyronitrile (AIBN). A brief discussion on inhibitor is also provided.

Chapter 3 gives a review of the DSC approach applied for kinetics of polymerization of methyl acrylate. General discussion on the advantages and its uses of using DSC and to analyse the kinetics is also presented. The materials used in this research project are described in this chapter. The procedure of preparing the sample and analyse the effect of temperature on the kinetics of bulk polymerization are also presented.

Chapter 4 provides the results obtained from the experiment by using five different temperatures, 35°C, 45°C, 55°C, 65°C and 75°C. The graph of heat flow versus temperature for every temperature is shown in this chapter. Also, the trend of isothermal graph from the literature is presented to compare with the trend of the graph obtained from the experiment. A detailed discussion of the results obtained is introduced in this chapter. Comparison with the theoretical statement is also provided to ensure the results obtained are standardized with theory.

Chapter 5 draws together a summary of the thesis and the conclusion of the thesis are made in this chapter.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the experimental studies of the effect of temperature on kinetics of bulk polymerization of methyl acrylate. Methyl acrylate has been chosen as a monomer while AIBN is chosen as the initiator. Five different temperatures are used in this experiment which is 35°C, 45°C, 55°C, 65°C and 75°C. Bulk polymerization is the method of polymerization process used with the used of equipment called DSC. The kinetics of polymerization is studied based on the heat flow obtained from the DSC at different temperatures. At high temperature, the heat flow obtained is higher compare to the used of low temperature.

2.2 Monomer

There are many types of polymer to be used in industry nowadays. Most of them are organic compounds which have many applications and their advantages in the industry. However, in this research project, methyl acrylate has been chosen as the monomer to be used. Methyl acrylate offers significant advantages as an additive in copolymer-based adhesives, fibers, non-acrylic polymers (food packaging), and plastics. It is also used as the starting block for anti-oxidants and amino esters. On top of that, there are several advantages listed; for example, its flexibility, weatherability, adhesion, internal plasticization, wide range of hardness, resistance to abrasion and oils or greases. Methyl acrylate is an organic compound with the formula CH2CHCO2CH3. It is mainly produced to make acrylate fibre, which is used to weave synthetic carpets. Furthermore, methyl acrylate is also used for polymer manufacturing and act as raw materials for syntheses, formulating paints and dispersions for paints, inks, and adhesives. In addition, it is also useful in making aqueous resins and dispersions for textiles and papers.

Previously, (Nasir M. Ahmad, Frank Heatley and Peter A. Lovell , 1998) have been investigating the effect of temperature on kinetics of n-butyl acrylate. They used n-butyl acrylate as a monomer instead of methyl acrylate. Different monomer gives different characteristic and properties. But, theoretically, the increase of temperature leads to increase in the kinetics of reaction, therefore making the reaction goes faster. The aim of the research is to study the kinetics of the reaction at different temperatures.

Monomer can be polymerized under the influence of heat, light, ionic or high energy mechanisms, but using a method of free radical initiation is the most commonly used method of polymerization to get the best results (Alfred Rudin, 1999).

2.3 Properties of methyl acrylate

Table 1: Physical and chemical properties of methyl acrylate

PHYSICAL AND CHEMICAL PROPERTIES	
Physical State	clear liquid
Melting Point	-74 C
Boiling Point	79 – 81 C
Specific Gravity	0.953 – 0.958
Solubility In Water	slightly soluble (52 g/l)
Solvent Solubility	Soluble in ether and alcohol
Molecular weight	86.09

Sources from http://www.chemicalland21.com

2.4 Formula of methyl acrylate

CH2=CHCOOCH3

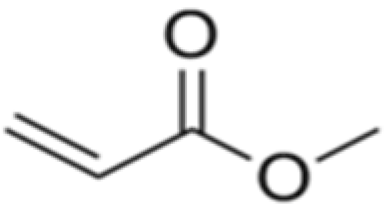

Figure 1:Chemical compound of methyl acrylate
Adapted from http://www.wikipedia.com

2.5 Free radical polymerization

Radical polymerization is a chain reaction and involves three fundamental steps: initiation, propagation and termination. Additionally, chain transfer is involved. The reactions of monomers can occur by the absorption of heat or light, but usually an initiator is added. The initiator is a weak organic compound which can be decomposed thermally or by the irradiation to produce free radicals, which are molecules atoms with unpaired electrons (Tatjana Haramina, 2004).

The four most commonly used methods for performing free-radical poymerization are bulk, solution, suspension and emulsion polymerization (Robert J.Young and Peter A. Lovell, 2011). As mention above, bulk polymerization is the method to be used in this research. The most common type of addition polymerization is free radical polymerization. A free radical is simply a molecule with an unpaired electron. The tendency of this free radical to gain an additional electron in order to form a pair makes it highly reactive leading to break the bond on another molecule by stealing an electron, leaving that molecule with an unpaired electron (which is another free radical). Free radicals are often created by the division of a molecule (known as an initiator) into two fragments along a single bond.

The stability of a radical refers to the molecule's tendency to react with other compounds. An unstable radical will readily combine with many different molecules. However a stable radical will not easily interact with other chemical substances. The stability of free radicals can vary widely depending on the properties of the molecule. The active center is the location of the unpaired electron on the radical because this is where the reaction takes place. In free radical polymerization, the radical attacks one monomer, and the electron migrates to another part of the molecule. This newly formed radical attacks another monomer and the process is repeated. Thus the active center moves down the chain as the polymerization occurs (Robert J.Young and Peter A. Lovell, 2011). There are three steps involve in FRP which are initiation step, propagation step, termination step. These three steps are very important in order for the process to run smoothly.

Initiation (Figure 2) is the first step to start free radical polymerization process. This step begins when an initiator decomposes into free radicals in the presence of monomers. This free radical is represented by dots. The instability of carbon-carbon double bonds in the monomer makes them susceptible to reaction with the unpaired electrons in the radical. In this reaction, the active centre of the radical "grabs" one of the electrons from the double bond of the monomer, leaving an unpaired electron to appear as a new active center at the end of the chain. Addition can occur at either end of the monomer (George Odian, 2004). The most common method, however, involves the use of thermomobile compound, called initiator which decomposes to yield free radicals when heated (Manas Chanda, 2006). The dissociation of an initiator forms a pair of radicals R•. Initiation involves a reaction between the initiator and the monomer itself. Only a few initiators suitable for polymerization in aqueous system have been fully investigating (Alfred Rudin, 1999). Based on previous researched, the best initiator for organic phase such as methyl acrylate is known as azoisobutyronitrile (AIBN) (S. Sivaram, 1991).

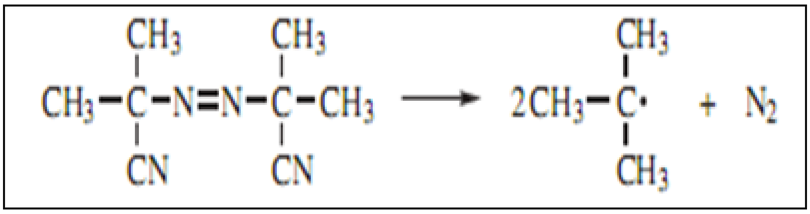

Figure 2: Initiation of AIBN. Source from (George Odian, 2004)

After the initiation step has occurred, it is then followed by propagation, (Figure 3) in which the chain starts to grow longer, taking place by successive addition of a large number of monomer molecules. The monomer addition takes place in the process, thus the size of chain is increased by one monomer unit, while the radical centre is transferred to the end of monomer unit (Manas Chanda, 2006).

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. In free radical polymerization, the entire propagation reaction usually takes place within a fraction of a second. Thousands of monomers are added to the chain within this time. The entire process stops when the termination reaction occurs (Figure 4 and 5), (George Odian, 2004). The step is shown below on how the monomer reacts with the initiator (AIBN). Symbol of M represent the monomer which is methyl acrylate and the dot represents the free radical.

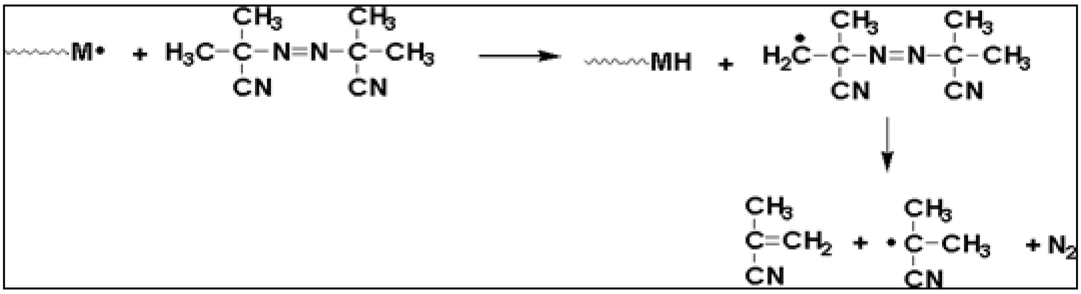

Figure 3: Propagation of methyl acrylate with AIBN. Retrieve from http://polychem.xicp.net/polymerworld/gfzwf203/Chapter3/pic

Theoretically, the propagation reaction could continue until the supply of monomers is exhausted. However, this outcome is very unlikely. Most often the growth of a polymer chain is halted by the termination reaction. Termination typically occurs in two ways: combination and disproportionation. First, two propagating chains are terminated when the two radicals are combined to form an electron-pair bond. Only one polymer chain is obtained without double bond (Carraher, 2008). Figure 4, depicts combination, with the symbol (R) representing the rest of the chain and X representing the alkyl group.

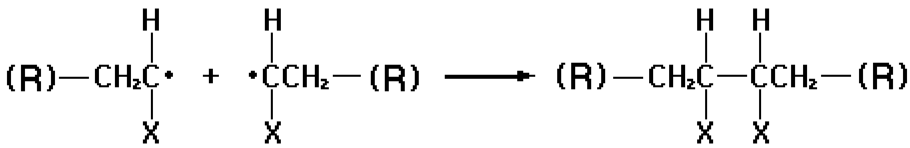

Figure 4:Termination step by combination Retrieved from http://plc.cwru.edu/tutorial/enhanced/files/polymers/synth/synth.htm

Second method of termination is by disproportionation. Disproportionation halts the propagation reaction when a free radical strips a hydrogen atom from an active chain. A carbon-carbon double bond takes the place of the missing hydrogen. Two polymer chains are obtained; one with double bond and the other one with single bond. Termination by disproportionation is shown in Figure 5.

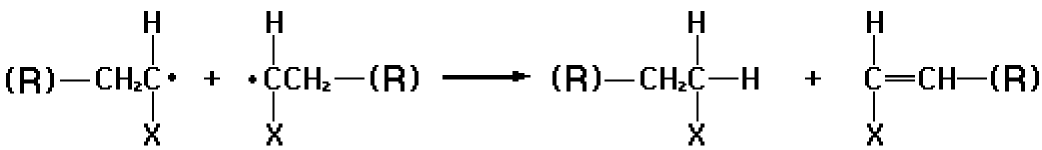

Figure 5:Termination step by disproportionation. Retrieved from http://plc.cwru.edu/tutorial/enhanced/files/polymers/synth/synth.htm

2.6 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 other monomers into a polymeric compound. In a free radical addition polymerization, the choice of polymerization initiator depends mainly on two factors: a) its solubility and b) its decomposition temperature. If the polymerization is performed in an organic solvent such alcohol and toluene, then the initiator should be soluble in that solvent and the decomposition temperature of the initiator must be at or below the boiling point of the solvent. Commonly, Azobisisobutyronitrile (AIBN) and Benzoyl peroxide suit these requirements.

In this research, AIBN (Figure 6) has been chosen as an initiator because it is safer to use than benzoyl peroxide because the risk of explosion is far less (Alfred Rudin, 1999). However, it is still considered as an explosive compound when decomposing above 65°C. A respirator dust mask, protective gloves and safety glasses are recommended while dealing with this chemical 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 initiator accelerating influence of polymerization rate not exactly catalysts since they are changed chemically in the polymerization. Azo compound is any organic chemical 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.

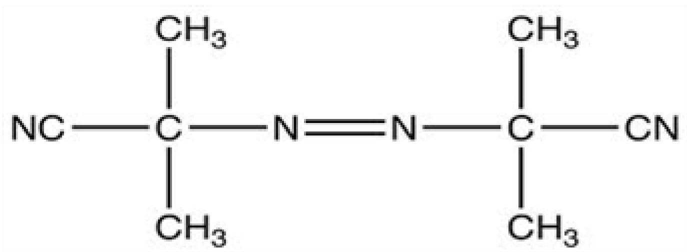

Figure 6:Chemical compound of azobisisobutyronitrile (AIBN). Adapted from http://science.uvu.edu/ochem

Azobisisobutyronitrile (AIBN) is an organic compound with the formula $[(CH_3)_2C(CN)]_2N_2)$. It is a white powder that soluble in alcohols and organic solvent but insoluble in water. It is often used as a foamer in plastics and rubber process. In its most characteristic reaction, AIBN decomposes 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. 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 depending on their rates of decomposition. Thus, AIBN is commonly used in 30-70℃, acuity peroxide at 70-90℃, benzoyl peroxide at 80-95℃ and dicumyl or di-t-butyl peroxide at 120-140℃.

2.7 Inhibitor

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

When inhibitors are 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 (Alfred Rudin, 1999). Therefore, the inhibitor should be removed from the monomer to get the best results. To remove inhibitor, aluminium oxide is used so that fresh monomer is obtained and the process can be preceded to the next stage.

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 (Paula Hammond, 2006). 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.

2.8 DSC as a tool to measure reaction rate

Kinetic has a bearing on the speed of a reaction under a given set of condition such as polymer molecular weight, chemical composition and extent of polymer conversion on how condition affected the kinetics of polymerization (Gowariker, 2009). In this research, kinetics of bulk polymerization is studied using DSC. DSC is used to measure heat flow into or out of a sample as it is exposed to a controlled thermal profile. DSC provides both qualitative and quantitative information about material transitions such as the glass transition, crystallization, curing, melting, and decomposition. For some of these transitions, DSC can provide not only the temperature at which the transition (reaction) occurs and how much heat total is involved, but DSC can also provide valuable information about the rate (kinetics) of reaction (Keenan, 1987). Furthermore, with the advent of easy-to-use computer based data analysis programs, the ability to obtain such kinetic information has become more practical (Borchardt and Daniels, 1956).

With DSC, the kinetics of a polymerization can be determined by three different approaches; single dynamic heating experiment, multiple dynamic heating experiments (three or more different heating rates), and isothermal studies at three or more different temperatures. However, this research is going to use isothermal studies for five difference temperatures. The isothermal approach provides the highest degree of accuracy of the kinetics of a polymer material (Pope and Judd, 1977). This is because the maintenance of isothermal conditions eliminates potential problems such as the occurrence of thermal gradients. Performing proper isothermal studies requires a DSC instrument with a very fast response time. This ensures the sample and instrument can equilibrate quickly once the isothermal target temperature is obtained (Sichina, 1987). The advantage of using DSC for kinetics study is it tends to be faster and more straightforward than other methods. On top of that, the isothermal method offers the advantages of easier data interpretation and broader applicability (Gabbott, 2007). Although the isothermal experiments may be more time consuming, they often generate more reliable kinetic parameters. This is because; isothermal method introduces fewer experimental variables into a single measurement so that the scope for ambiguity in the interpretation of data is reduced (Waters & Paddy, 1988).

The kinetics of reaction provide the scientist and engineer with valuable information for process development and prediction of optimum reaction temperatures, process control by optimization of reaction advancement or conversion, and estimation of material lifetimes (Prime, 1973). Based on DSC reading, an increase in temperature leads to increase in the flow of heat. The heat flow can determine how fast the reaction goes. As the reaction is keep running, at certain time, the heat flow will become constant and independent to time. It shows that the reaction is completed and thus, the next temperature can be run and analyze the reaction kinetics.

3 MATERIALS AND METHODS

3.1 *Chemicals*

Chemicals were obtained from Sigma-Aldich. Three chemicals were used in this research. First, methyl acrylate (M27301-1L) is used as a liquid monomer (99% purity). The monomer should be kept in the fridge since it cannot expose to the temperature above 4°C. Second, Azobisisobutyrylnitrile (AIBN) is in liquid form (98% purity), used as an initiator to react with the monomer to form a polymer. Last, aluminium oxide is used to purify the stabilized monomer by removing the inhibitor.

3.2 *Equipment*

Differential Scanning Calorimetry (DSC)
Source/ supplier: Research Instrument
Model No. : DSC Q100
Series No. : Q1000-0567

Differential Scanning Calorimetry, or DSC, is thermal analysis techniques which determine how material's heat capacity (Cp) is changed with temperature. A sample of known mass is heated or cooled and the changes in its heat capacity are tracked as changes in the heat flow. This allows the detection of kinetics, transitions like melts, glass transitions, phase changes, and curing. Because of this flexibility, DSC is used in many industries including pharmaceuticals, polymers, food, paper, printing, manufacturing, agriculture, semiconductors, and electronics as most materials exhibit some sort of transitions (Gabbott, 2007).

The biggest advantage of DSC is the ease and speed by which it can be used to see transitions in materials. DSC is the most common thermal analysis technique and is found in many analytical, process control, quality assurance and R&D laboratories. DSC is a primary technique for measuring the thermal properties of materials to establish a connection between temperature and specific physical properties of substances and is the only method for direct determination of the enthalpy associated with the process of interest (Hohne, 1996 and Privalov, 1986).

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity. By using DSC, it can determine reaction kinetics, melting and boiling points, heats of fusion and reactions, specific heat, oxidative/thermal stability, rate and degree of cure and purity of certain materials (Lauren, 2010).

Figure 7:Differential Scanning Calorimetry (DSC)
Source from (Leuven, 2010)

3.3 Sample preparation

Column chromatography method is a method used for preparing methyl acrylate without inhibitor (Viciosa et al.,2007). By using this method, the inhibitor in methyl acrylate was removed by using aluminium oxide. Firstly, aluminium oxide was poured into the column and then the methyl acrylate will flow down to the column. After that, the aluminium oxide will absorb the inhibitor from methyl acrylate. The removal of inhibitor was needed so that fresh monomer can be obtained. Inhibitor was used in the preservation of monomer. If the inhibitor was not removed from the monomer, the radical site end was not active enough to attack the fresh monomer. Therefore, propagation step cannot take place and the desired product cannot produce (Lewis, 2010). Finally, the fresh methyl acrylate (without the inhibitor) was ready for the polymerization reaction. Then, approximately 5.0mg sample of the methyl acrylate (without inhibitor) and azobisisobutyronitrile (AIBN) solution were put into the pan using micropipette. To make sure the weight of methyl acrylate and AIBN solution were below 5mg, this method was done on the analytical balance. The weight must not exceed 5mg because the pan of DSC provides only 5mg of each sample to run in the DSC and to avoid any leakage while running the process in the DSC.

3.4 Method description

For the methodology part, free radical polymerization (bulk polymerization) is used to conduct this research project by using DSC under constant temperature (isothermal). This is one of the simplest methods where the monomer is injected with initiator to form a polymer (Robert J. Young and Peter A. Lovell, 2011). For this case, methyl acrylate as a monomer was poured into an aluminium pan of DSC, and the initiator which is the AIBN was injected into it. Once the monomer and AIBN were mixed together in the pan of DSC, the process of polymerization starts to occur. By using this method, it can reduce the time while minimizing the cost as it is the simplest method rather than using an advance method such as ARTP and RAFT (Mohammad Ali Semsarzadeh and Mohammad Reza Rostami Daronkola, 2006).

3.5 Effect of temperature on kinetics of bulk polymerization analysis

Firstly, aluminium pan with the sample solution and initiator was covered with the lid. Then, the weight of this pan with lid and its sample solution was measured by analytical balance to get the sample weight. The weights of sample size must not more than 5mg because the DSC can only process a sample of less than 5 mg to avoid any leakage which might affect the results and also might damage the DSC itself. The next step, both of the reference lid and sample lid were put into the heater. Then, all the measurements were recorded in the differential scanning calorimetry software. The temperature of the polymerization of methyl acrylate was firstly set at 35˚C and the DSC was ready to be run. Once completed, the graph for heat flow versus time was recorded by DSC software. The experiment was repeated using different temperatures but with nearly constant mass of sample solution. This experiment was run for 20 minutes on every sample.

3.6 Flow diagram of analysis

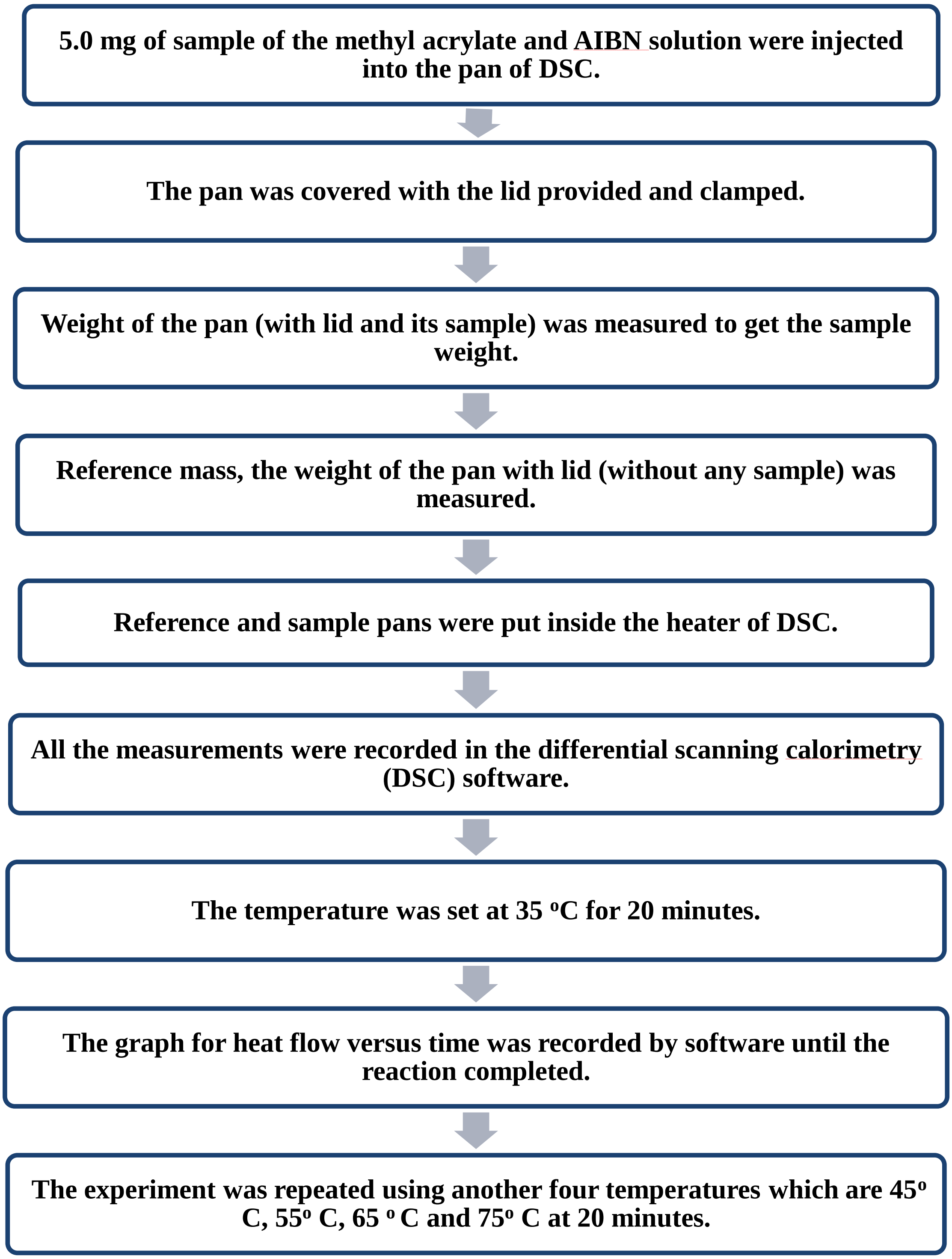

Figure 8:Flow diagram of experiment

4 KINETICS OF BULK POLYMERIZATION OF METHYL ACRYLATE

4.1 *Introduction*

The purpose of this research study is to determine the effect of kinetics on bulk polymerization of methyl acrylate. The experiment was run at different temperatures, 35°C, 45°C, 55°C, 65°C and 75°C while keeping the mass of initiator constant, 0.9mg. The mass of sample should not exceed 5mg to avoid any leakage which might affect the results of experiments. Each of temperature was run for two times to get the best results and to ensure the results obtained have no significant difference. The samples were run in DSC under isothermal condition. DSC can give value of heat flow which indicates the kinetics of the reaction polymerization at different temperatures. Therefore, the results obtained can analyse the temperature effect on kinetics of polymerization, whether the kinetics increase with increase in temperature or vice versa. After prepared and run the samples, the results obtained for all temperatures and samples were drawn in a graph as shown below.

4.2 *Results and discussion*

Table 2: Mass of monomer at every temperature for each sample

Temperature (°C)	Mass of monomer (mg)	
	1st Sample	2nd Sample
35	2.3	2.4
45	3.0	3.2
55	2.4	2.3
65	3.0	2.7
75	4.1	3.8

Heat flow is measured as the amount of energy transferred per unit of time. In SI units this would be measured in Joules per second per gram of monomer (Gavin Sullivan and Campbell Edmondson, 2008). The results obtained from DSC software were given in Watt per gram of sample, W/g. Therefore, to get the value of heat flow in W/g of monomer, the heat flow need to times with the mass of sample and divided by mass of monomer for each sample used.

Heat Flow (W/g) of monomer = Heat Flow (W/g of sample) x mass of sample (g) ÷ mass of monomer (g)

Mass of monomer (g) = mass of sample (g) – mass of initiator (g)

Table 3:Heat flow of polymerization of methyl acrylate at starting point for each temperature

Temperature (°C)	(-ve) Heat Flow (W)	
	1st Sample	2nd Sample
35	0.05147	0.03259
45	0.06298	0.06580
55	0.09626	0.09928
65	0.14482	0.16626
75	0.24402	0.25578

4.3 Comparison between results obtained and literature study

Based on literature, the trend of the graph of isothermal reaction should be from higher value to lower value regardless the temperature used, since the polymerization reaction reacts fast at starting point. After sometimes, the heat flow keeps decreasing and gives constant value since the monomer is completely polymerized. The negative sign indicate the polymerization is exothermic reaction because monomer will lose heat to surrounding while polymerizing. From the results obtained in this research study, the trend of heat flow follows the literature, which the heat flow decreases over the time. The graphs of heat flow from literature and from research study were shown below.

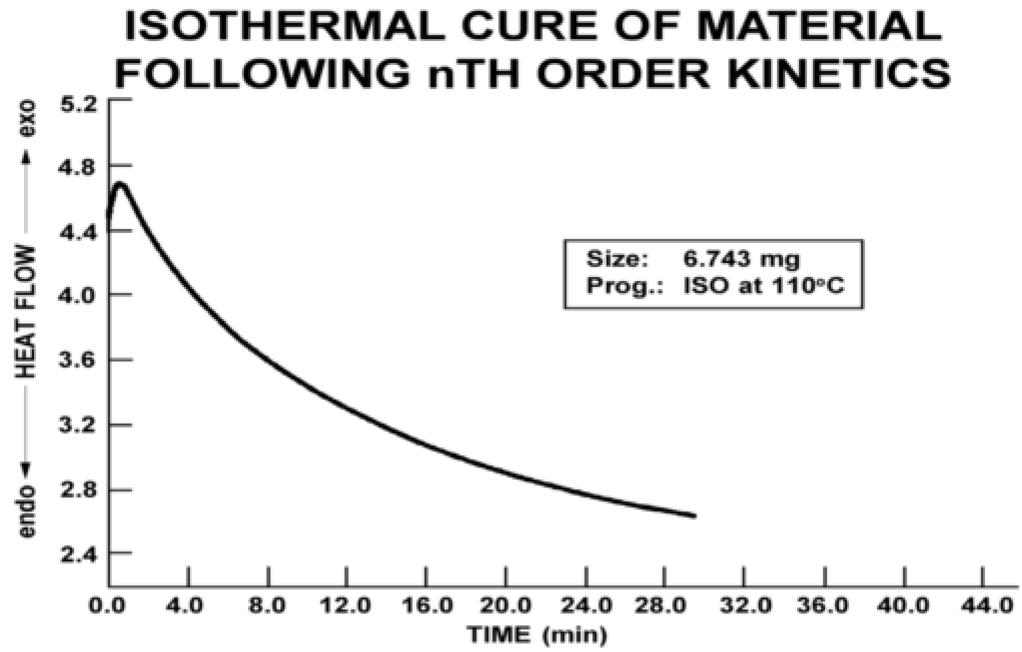

Figure 9: Graph of isothermal heat flow versus time (Source from Keenan, 1987)

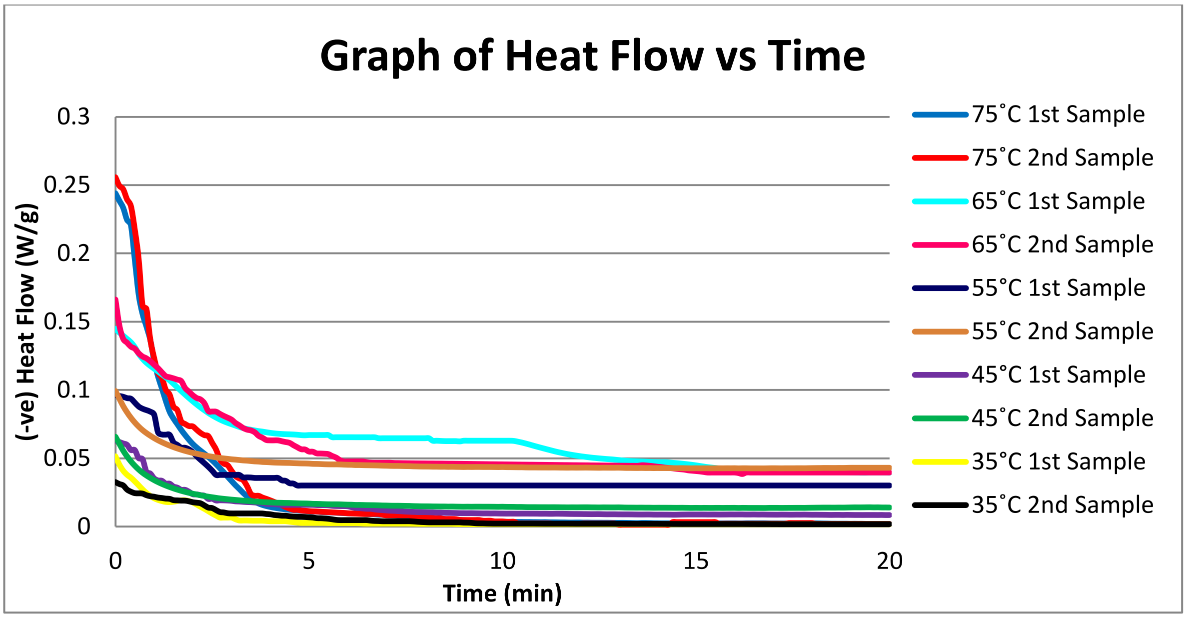

Figure 10: Graph of heat flow versus time for all samples at different temperatures (Isothermal)

4.4 Graph of heat flow of polymerization of methyl acrylate versus time at every temperature

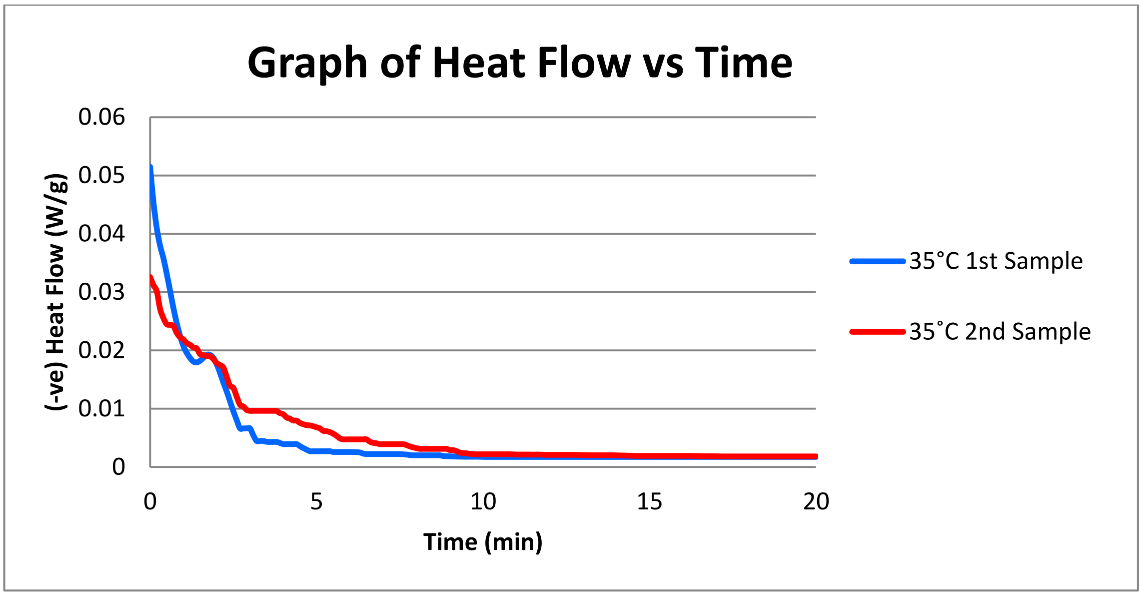

Figure 11:Graph of heat flow versus time at temperature 35°C for first and second sample

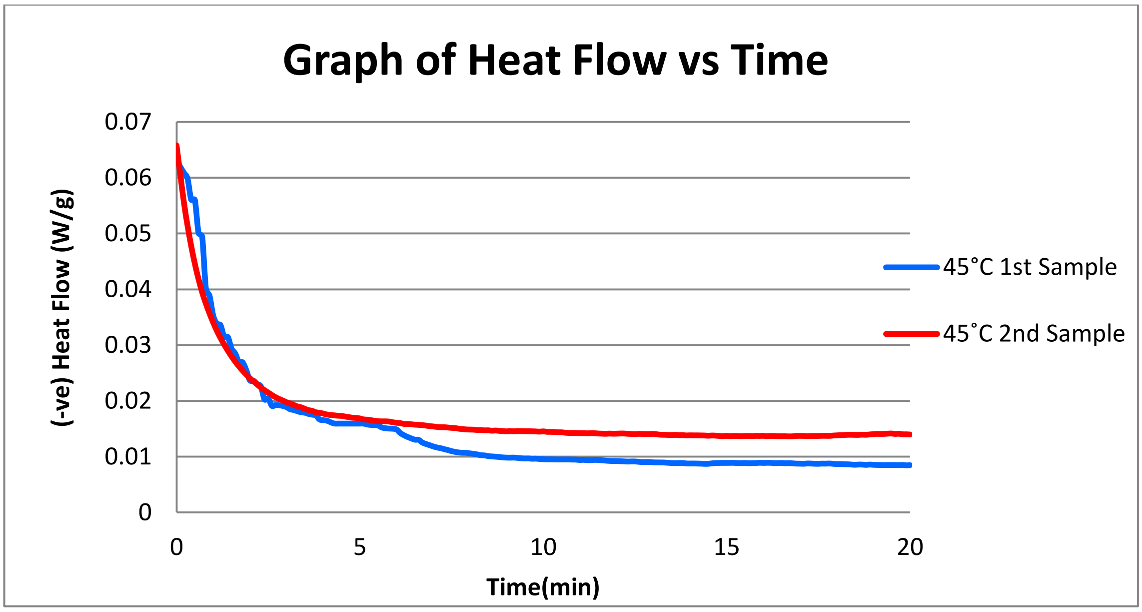

Figure 12: Graph of heat flow versus time at temperature 45°C for the first and second sample

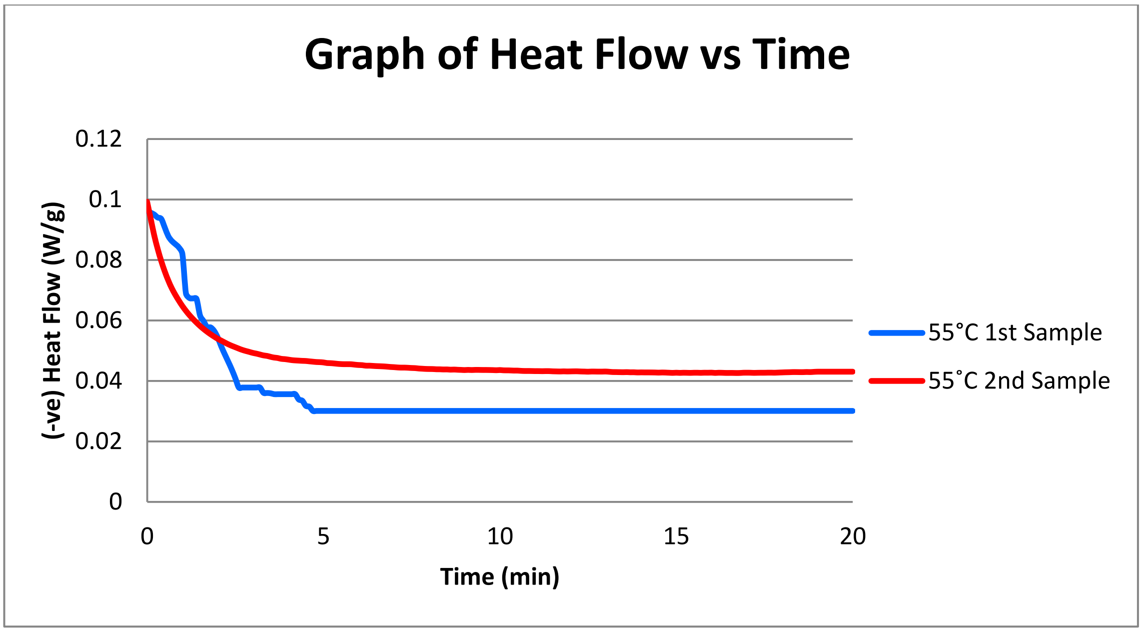

Figure 13: Graph of heat flow versus time at temperature of 55°C for first and second sample

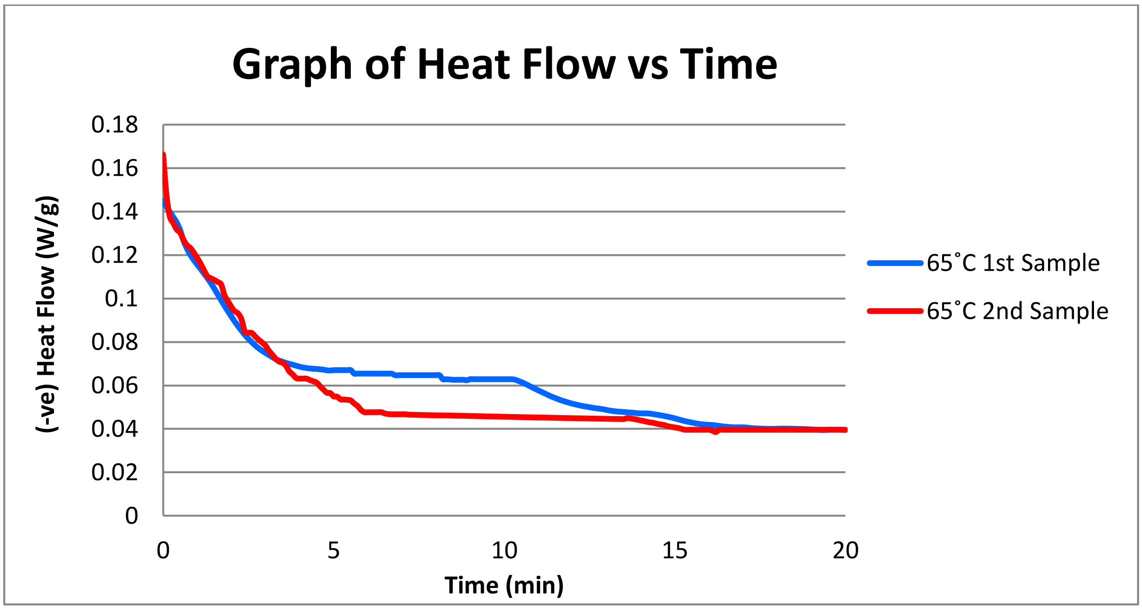

Figure 14: Graph of heat flow versus time at temperature 65°C for the first and second sample

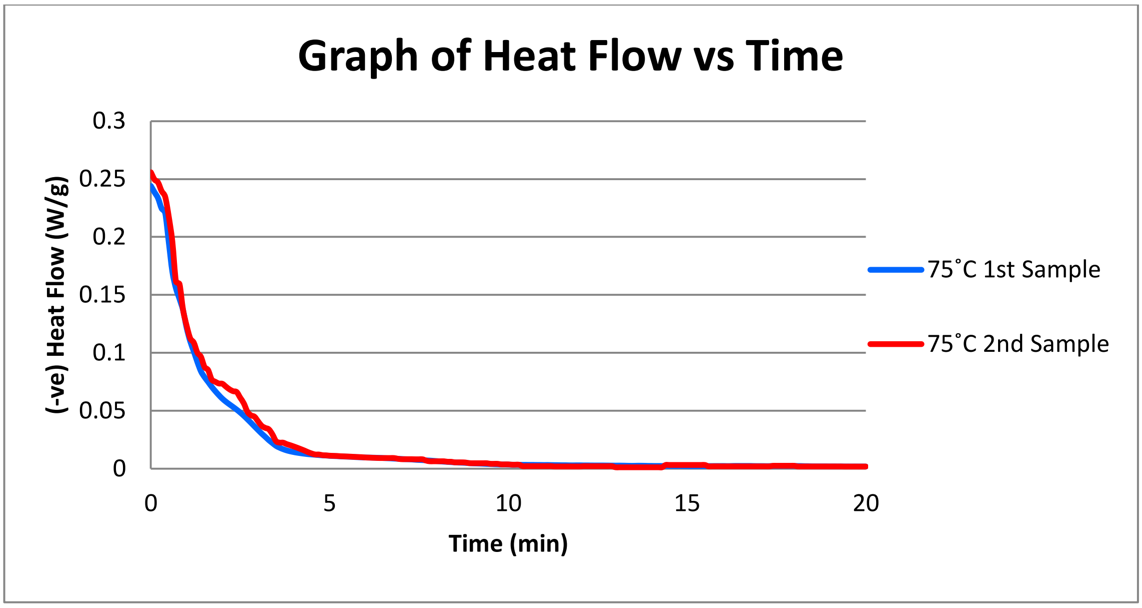

Figure 15: Graph of heat flow versus time at temperature 75°C for first and second sample

4.5 *Discussions*

Firstly, the kinetics of polymerization was studied using DSC under a constant temperature of 35°C for the first sample. The DSC will show the graph of heat flow at constant temperature (isothermal) over the time. The curve obtained represents the heat flow versus time. The graphs shown above were for temperature of 35°C, 45°C, 55°C, 65°C and 75°C. Every temperature was repeated two times to get better results for 20 minutes. At certain time, the curve starts to give constant value. This is where the kinetics of polymerization has been constantly achieved throughout the remaining time. This is because; the polymerization takes place within 15 minutes of the reaction. The values of heat flow were in negative sign as the reactions occur in exothermic reaction, since the monomer loses heat to surrounding while polymerizing. Thus, comparing the heat flow with the temperatures used will analyse the kinetics of reaction, whether increasing temperature leads to an increase in kinetics of reaction or not. The kinetic theory of matter posits that the atoms and molecules that make up matter are constantly in motion. It relates to heat transfer because as atoms and molecules gain kinetic energy and move faster, more heat is produced (Homer, 1957).

Table 4:Heat flow of polymerization of methyl acrylate at starting point for each temperature

Temperature (°C)	(-ve) Heat Flow (W)	
	1st Sample	2nd Sample
35	0.05147	0.03259
45	0.06298	0.06580
55	0.09626	0.09928
65	0.14482	0.16626
75	0.24402	0.25578

The value of heat flows for first and second sample of every temperature gave a slight difference, since the same temperature was used for first and second sample, and the mass of sample used also nearly the same. From the graph, it can be concluded that the heat flow increased as the temperature increased.

The relationship between temperature and heat flow were studied since both parameters relate with kinetics of polymerization. Temperature represents the amount of thermal energy available, whereas heat flow represents the movement of thermal energy from place to place (Gavin Sullivan and Campbell Edmondson, 2008). Heat flow of energy is in the form of kinetics energy because heat is related to the motion of particles. In order to understand the nature of heat and temperature, it is necessary to appreciate the fact that matter consists of moving particles which can interact more or less strongly with one another (Delpierre and Sewell, 2005). Heat flow is the amount of heat involved in a chemical reaction (added or removed). All polymerization reactions (production of polymers) are exothermic, they involve liberation of heat (John Vlachopoulos and David Strutt, 2002).

The motion of the particles is increased by raising the temperature. Conversely, the motion of the particles is reduced by lowering the temperature, until, at the absolute zero (0 K), the motion of the particles ceases altogether. Because the particles are in motion, they will have kinetic energy. The particles will not all have the same energy, and the energy of the particles is constantly changing as they undergo changes in speed (Gavin Sullivan and Campbell Edmondson, 2008). An increase in heat flows indicate that the kinetics of reaction increase. Thus, this research study has proven that in theoretical; increase in temperature will increase the kinetics of polymerization (George Odian, 2004).

5 CONCLUSION

5.1 Conclusion

The experimental results showed the kinetics of polymerization of methyl acrylate at five different temperatures. By referring to the graphs, it has proven from the objective that the experiment conducted at higher temperature had higher kinetics of polymerization compared to the experiment which conducted at lower temperature. Modelling the kinetics of material reactions provides the scientist and engineer with valuable information for: process development and prediction of optimum reaction temperatures, process control by optimization of reaction advancement or conversion, and estimation of material lifetimes. Several DSC approaches are available for obtaining this kinetic information (Widdman, 1975).

5.2 Recommendation

There are some recommendation can be apply for this research which are :

1. In order to get more accurate result, the newest version of differential scanning calorimetry Q2000 can be used instead of using differential scanning calorimetry version Q1000. This is because, performance of this Q2000 had been increased by 65% than Q1000 version. (TA instrument,2009)
2. Make sure to put the pan (with sample and initiator) and lid immediately into the heater after calculated the mass of sample, so that methyl acrylate and AIBN solution does not polymerize outside the heater of differential scanning calorimetry and consequently affect the results obtained from experiment.

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APPENDICES

Heat Flow at temperature 35°C for first and second samples

	35°C 1st Sample	35˚C 2nd Sample
TIME (min)	(-ve) HEAT FLOW (W/g)	(-ve) HEAT FLOW (W/g)
0	0.051478261	0.0325875
0.1	0.045467826	0.031185
0.2	0.040973913	0.0301675
0.3	0.037954783	0.027115
0.4	0.035812174	0.02553375
0.5	0.033126957	0.02448875
0.6	0.030233043	0.02437875
0.7	0.027255652	0.02418625
0.8	0.024667826	0.02300375
0.9	0.022525217	0.02226125
1	0.020758261	0.02189
1.1	0.019575652	0.02127125
1.2	0.018713043	0.020955
1.3	0.018086957	0.020515
1.4	0.017947826	0.02033625
1.5	0.018212174	0.01937375
1.6	0.018726957	0.0192225
1.7	0.019241739	0.01901625
1.8	0.019227826	0.0190025
1.9	0.018726957	0.0185075
2	0.017627826	0.0178475
2.1	0.016153043	0.01749
2.2	0.014483478	0.01706375
2.3	0.012976696	0.01549625

2.4	0.011287652	0.01392875
2.5	0.009576348	0.013585
2.6	0.008065391	0.012095875
2.7	0.006630957	0.01067825
2.8	0.006630957	0.010396375
2.9	0.006630957	0.00979825
3	0.006630957	0.0096415
3.1	0.005441391	0.0096415
3.2	0.004474435	0.0096415
3.3	0.004474435	0.0096415
3.4	0.004474435	0.0096415
3.5	0.00433113	0.0096415
3.6	0.00430887	0.0096415
3.7	0.00430887	0.0096415
3.8	0.00430887	0.009607125
3.9	0.004134957	0.009246875
4	0.003937391	0.009051625
4.1	0.003937391	0.008501625
4.2	0.003937391	0.008292625
4.3	0.003937391	0.00798875
4.4	0.003937391	0.0079475
4.5	0.003589565	0.007579
4.6	0.003264	0.00735075
4.7	0.002989913	0.007176125
4.8	0.002717217	0.007140375
4.9	0.002717217	0.007005625
5	0.002717217	0.006810375
5.1	0.002717217	0.006642625

5.2	0.002717217	0.006205375
5.3	0.00270887	0.006149
5.4	0.002721391	0.0059895
5.5	0.002585043	0.00571725
5.6	0.002585043	0.00535975
5.7	0.002585043	0.0049225
5.8	0.002585043	0.0047465
5.9	0.002585043	0.0047465
6	0.002585043	0.0047465
6.1	0.002566957	0.0047465
6.2	0.002555826	0.0047465
6.3	0.002501565	0.0047465
6.4	0.002306783	0.0047465
6.5	0.002231652	0.0047465
6.6	0.002231652	0.0043505
6.7	0.002231652	0.004153875
6.8	0.002231652	0.0040755
6.9	0.002231652	0.003927
7	0.002231652	0.003927
7.1	0.002231652	0.003927
7.2	0.002231652	0.003927
7.3	0.002231652	0.003927
7.4	0.002231652	0.003927
7.5	0.002223304	0.003927
7.6	0.002184348	0.003927
7.7	0.002146783	0.003771625
7.8	0.002056348	0.00354475
7.9	0.002021565	0.003372875

8	0.002021565	0.003243625
8.1	0.002021565	0.003125375
8.2	0.002021565	0.003125375
8.3	0.002021565	0.003125375
8.4	0.002021565	0.003125375
8.5	0.002021565	0.003125375
8.6	0.002021565	0.003125375
8.7	0.002021565	0.003125375
8.8	0.001897739	0.003125375
8.9	0.001865739	0.003125375
9	0.001849043	0.002927375
9.1	0.001822609	0.002902625
9.2	0.001800348	0.00274175
9.3	0.001785043	0.0024915
9.4	0.001772522	0.0023815
9.5	0.001772522	0.00236225
9.6	0.001772522	0.002267375
9.7	0.001772522	0.002223375
9.8	0.001772522	0.00219175
9.9	0.001764174	0.00219175
10	0.001747478	0.00219175
10.1	0.001734957	0.00219175
10.2	0.001734957	0.00219175
10.3	0.001734957	0.00219175
10.4	0.001734957	0.00219175
10.5	0.001734957	0.00219175
10.6	0.001734957	0.00219175
10.7	0.001734957	0.00219175

10.8	0.001734957	0.00219175
10.9	0.001734957	0.002173875
11	0.001734957	0.002149125
11.1	0.001734957	0.002143625
11.2	0.001734957	0.002143625
11.3	0.001734957	0.002143625
11.4	0.001734957	0.002140875
11.5	0.001734957	0.00212575
11.6	0.001734957	0.002143625
11.7	0.001734957	0.002127125
11.8	0.001734957	0.002112
11.9	0.001734957	0.002091375
12	0.001734957	0.002091375
12.1	0.001734957	0.002091375
12.2	0.001734957	0.002091375
12.3	0.001734957	0.002091375
12.4	0.001734957	0.002091375
12.5	0.001734957	0.002091375
12.6	0.001734957	0.002091375
12.7	0.001734957	0.002091375
12.8	0.001734957	0.002091375
12.9	0.001734957	0.002068
13	0.001734957	0.002058375
13.1	0.001734957	0.002041875
13.2	0.001734957	0.002022625
13.3	0.001734957	0.002022625
13.4	0.001734957	0.002022625
13.5	0.001734957	0.002022625

13.6	0.001734957	0.002022625
13.7	0.001734957	0.002022625
13.8	0.001734957	0.002022625
13.9	0.001734957	0.002022625
14	0.001734957	0.00201025
14.1	0.001734957	0.001989625
14.2	0.001734957	0.001978625
14.3	0.001734957	0.001958
14.4	0.001734957	0.001948375
14.5	0.001734957	0.001936
14.6	0.001734957	0.001912625
14.7	0.001734957	0.001912625
14.8	0.001734957	0.001912625
14.9	0.001734957	0.001912625
15	0.001734957	0.001912625
15.1	0.001734957	0.001912625
15.2	0.001734957	0.001912625
15.3	0.001734957	0.001912625
15.4	0.001734957	0.001912625
15.5	0.001734957	0.001912625
15.6	0.001734957	0.001912625
15.7	0.001734957	0.001912625
15.8	0.001734957	0.001912625
15.9	0.001734957	0.001912625
16	0.001734957	0.001912625
16.1	0.001734957	0.001912625
16.2	0.001734957	0.001912625
16.3	0.001734957	0.00190575

16.4	0.001734957	0.00188925
16.5	0.001734957	0.001881
16.6	0.001734957	0.001865875
16.7	0.001734957	0.0018645
16.8	0.001734957	0.00185625
16.9	0.001734957	0.001852125
17	0.001734957	0.001843875
17.1	0.001734957	0.00183425
17.2	0.001734957	0.001824625
17.3	0.001734957	0.001824625
17.4	0.001734957	0.001824625
17.5	0.001734957	0.001824625
17.6	0.001734957	0.001824625
17.7	0.001734957	0.001824625
17.8	0.001734957	0.001824625
17.9	0.001734957	0.001824625
18	0.001734957	0.001824625
18.1	0.001734957	0.001824625
18.2	0.001734957	0.001824625
18.3	0.001734957	0.001824625
18.4	0.001734957	0.001824625
18.5	0.001734957	0.001824625
18.6	0.001734957	0.001824625
18.7	0.001734957	0.001824625
18.8	0.001734957	0.001824625
18.9	0.001734957	0.001824625
19	0.001734957	0.001824625
19.1	0.001734957	0.001824625

19.2	0.001734957	0.001824625
19.3	0.001734957	0.001824625
19.4	0.001734957	0.001824625
19.5	0.001734957	0.001824625
19.6	0.001734957	0.001824625
19.7	0.001734957	0.001824625
19.8	0.001734957	0.001824625
19.9	0.001734957	0.001824625
20	0.001734957	0.001824625

Heat Flow at temperature 45°C for first and second samples

	45°C 1st Sample	**45˚C 2nd Sample**
TIME (min)	**(-ve) HEAT FLOW (W/g)**	**(-ve) HEAT FLOW (W/g)**
0	0.062985	0.065805
0.1	0.061958	0.06073125
0.2	0.060892	0.055631875
0.3	0.059865	0.051442188
0.4	0.056056	0.047765
0.5	0.05603	0.0445875
0.6	0.050102	0.041832813
0.7	0.0494	0.039449688
0.8	0.04017	0.037450938
0.9	0.03887	0.035682813
1	0.035295	0.034042813
1.1	0.033813	0.032582188
1.2	0.033566	0.031275313
1.3	0.031473	0.030096563
1.4	0.031447	0.028994688
1.5	0.029354	0.0279825
1.6	0.028509	0.02706
1.7	0.026975	0.026214375
1.8	0.026923	0.025445625
1.9	0.025545	0.024740938
2	0.023686	0.024074688
2.1	0.023621	0.023510938
2.2	0.023023	0.022947188
2.3	0.022607	0.02239625
2.4	0.020267	0.021922188

2.5	0.020449	0.021499375
2.6	0.019123	0.02106375
2.7	0.019266	0.020666563
2.8	0.019214	0.02034625
2.9	0.019097	0.020064375
3	0.018889	0.019756875
3.1	0.018499	0.019539063
3.2	0.018369	0.01927
3.3	0.018148	0.019000938
3.4	0.017966	0.018847188
3.5	0.017888	0.018578125
3.6	0.017667	0.0183475
3.7	0.017537	0.018219375
3.8	0.017394	0.017963125
3.9	0.016679	0.017873438
4	0.016549	0.0177325
4.1	0.016458	0.017565938
4.2	0.016185	0.01747625
4.3	0.015951	0.017412188
4.4	0.015938	0.017348125
4.5	0.015938	0.017309688
4.6	0.015938	0.017194375
4.7	0.015938	0.017091875
4.8	0.015938	0.016989375
4.9	0.015938	0.016950938
5	0.015938	0.01686125
5.1	0.015938	0.016681875
5.2	0.015782	0.016643438

5.3	0.015691	0.01655375
5.4	0.015691	0.016438438
5.5	0.015574	0.016361563
5.6	0.015236	0.016335938
5.7	0.015106	0.016335938
5.8	0.015041	0.0162975
5.9	0.015015	0.016169375
6	0.014885	0.016079688
6.1	0.014248	0.016028438
6.2	0.013858	0.015874688
6.3	0.013546	0.015874688
6.4	0.013286	0.015810625
6.5	0.013052	0.015746563
6.6	0.013026	0.015708125
6.7	0.0125567	0.015656875
6.8	0.012285	0.01558
6.9	0.0120783	0.0154775
7	0.0118443	0.01542625
7.1	0.0116584	0.015336563
7.2	0.0115349	0.015285313
7.3	0.0113542	0.015285313
7.4	0.0111969	0.015234063
7.5	0.0110058	0.01517
7.6	0.0108628	0.015131563
7.7	0.0107562	0.01501625
7.8	0.0107029	0.014952188
7.9	0.0106925	0.014888125
8	0.0106015	0.0148625

8.1	0.0105131	0.014849688
8.2	0.0104117	0.014785625
8.3	0.0102674	0.014772813
8.4	0.0102362	0.014721563
8.5	0.0101101	0.014734375
8.6	0.010049	0.0146575
8.7	0.0100074	0.014695938
8.8	0.0099424	0.014631875
8.9	0.0098722	0.014593438
9	0.0098384	0.014542188
9.1	0.009828	0.014593438
9.2	0.009841	0.014555
9.3	0.009789	0.014593438
9.4	0.0097214	0.014593438
9.5	0.0096798	0.014567813
9.6	0.0096876	0.014567813
9.7	0.0096369	0.014555
9.8	0.0096525	0.014529375
9.9	0.0095914	0.014490938
10	0.0095498	0.014542188
10.1	0.0095212	0.014465313
10.2	0.009529	0.0144525
10.3	0.0095134	0.014426875
10.4	0.0095004	0.014375625
10.5	0.0095056	0.014375625
10.6	0.0095082	0.01429875
10.7	0.0095017	0.014260313
10.8	0.0094861	0.014260313

10.9	0.0094744	0.0142475
11	0.0094068	0.014221875
11.1	0.0094432	0.014221875
11.2	0.0093769	0.01419625
11.3	0.0093782	0.014221875
11.4	0.0094341	0.014209063
11.5	0.0094016	0.014157813
11.6	0.0093561	0.014132188
11.7	0.0093002	0.014106563
11.8	0.0092534	0.014145
11.9	0.0092313	0.014119375
12	0.0092274	0.014132188
12.1	0.009191	0.014157813
12.2	0.009165	0.014157813
12.3	0.0091299	0.014106563
12.4	0.0091507	0.014080938
12.5	0.0091481	0.0140425
12.6	0.0090922	0.01409375
12.7	0.0090337	0.014080938
12.8	0.0090454	0.014068125
12.9	0.0090415	0.014068125
13	0.0089921	0.01409375
13.1	0.0089752	0.014016875
13.2	0.0089687	0.01394
13.3	0.0089557	0.013927188
13.4	0.0089089	0.013901563
13.5	0.0088738	0.01388875
13.6	0.0088491	0.013914375

13.7	0.0088751	0.013863125
13.8	0.0088738	0.013875938
13.9	0.0087971	0.013811875
14	0.0087802	0.0138375
14.1	0.0087867	0.013824688
14.2	0.0087711	0.013824688
14.3	0.0087555	0.013811875
14.4	0.0087204	0.013799063
14.5	0.0087321	0.013760625
14.6	0.0088114	0.013799063
14.7	0.0088595	0.013773438
14.8	0.0088816	0.013722188
14.9	0.0088894	0.01368375
15	0.0088894	0.013735
15.1	0.0088972	0.01368375
15.2	0.0088972	0.013722188
15.3	0.0088582	0.013709375
15.4	0.0088634	0.01368375
15.5	0.0088777	0.013722188
15.6	0.0088348	0.013722188
15.7	0.0088582	0.013696563
15.8	0.0088634	0.013735
15.9	0.0089115	0.013722188
16	0.0088855	0.013747813
16.1	0.0089037	0.013670938
16.2	0.008905	0.013722188
16.3	0.0088517	0.013709375
16.4	0.0088595	0.013670938

16.5	0.0088868	0.013670938
16.6	0.0088231	0.013670938
16.7	0.0088569	0.013645313
16.8	0.008814	0.013658125
16.9	0.0087672	0.013722188
17	0.0087581	0.013735
17.1	0.0087334	0.013722188
17.2	0.0087867	0.01368375
17.3	0.0087737	0.013709375
17.4	0.0087399	0.013722188
17.5	0.0087269	0.013722188
17.6	0.0087685	0.013747813
17.7	0.0087568	0.013747813
17.8	0.0087828	0.013735
17.9	0.0087347	0.01378625
18	0.0086801	0.013824688
18.1	0.0086905	0.013863125
18.2	0.0086554	0.01388875
18.3	0.0086398	0.013927188
18.4	0.0085969	0.013927188
18.5	0.0085553	0.013914375
18.6	0.0085943	0.013914375
18.7	0.0085891	0.013952813
18.8	0.0085358	0.013927188
18.9	0.008593	0.01399125
19	0.0085501	0.0140425
19.1	0.008528	0.01409375
19.2	0.0085163	0.014080938

19.3	0.0085046	0.01409375
19.4	0.0085137	0.014132188
19.5	0.0085163	0.014157813
19.6	0.008515	0.014080938
19.7	0.0084916	0.014119375
19.8	0.0085293	0.014016875
19.9	0.0084539	0.014016875
20	0.008489	0.013978438

Heat Flow at temperature 55°C for first and second samples

	55°C 1st Sample	55˚C 2nd Sample
TIME (min)	**(-ve) HEAT FLOW (W/g)**	**(-ve) HEAT FLOW (W/g)**
0	0.09626375	0.099283478
0.1	0.09565875	0.093773913
0.2	0.0950675	0.088236522
0.3	0.09406375	0.083686957
0.4	0.09362375	0.079693913
0.5	0.0907775	0.076243478
0.6	0.0879175	0.073252174
0.7	0.08630875	0.070664348
0.8	0.0852775	0.068493913
0.9	0.08416375	0.066573913
1	0.08201875	0.064793043
1.1	0.0689975	0.063206957
1.2	0.06744375	0.061787826
1.3	0.06730625	0.060507826
1.4	0.0671825	0.059311304
1.5	0.0616825	0.058212174
1.6	0.05982625	0.057210435
1.7	0.05781875	0.056292174
1.8	0.05773625	0.055457391
1.9	0.0565675	0.054692174
2	0.0544225	0.053968696
2.1	0.05149375	0.053356522
2.2	0.04888125	0.052744348
2.3	0.0463925	0.052146087
2.4	0.04379375	0.051631304

2.5	0.04093375	0.051172174
2.6	0.03784	0.05069913
2.7	0.03784	0.050267826
2.8	0.03784	0.04992
2.9	0.03784	0.049613913
3	0.03784	0.04928
3.1	0.03784	0.049043478
3.2	0.03784	0.048751304
3.3	0.03608	0.04845913
3.4	0.03603875	0.048292174
3.5	0.0359425	0.048
3.6	0.03564	0.047749565
3.7	0.03564	0.047610435
3.8	0.03564	0.047332174
3.9	0.03564	0.047234783
4	0.03564	0.047081739
4.1	0.03564	0.04690087
4.2	0.03564	0.046803478
4.3	0.03388	0.046733913
4.4	0.03348125	0.046664348
4.5	0.03177625	0.046622609
4.6	0.03150125	0.046497391
4.7	0.03009875	0.046386087
4.8	0.03009875	0.046274783
4.9	0.03009875	0.046233043
5	0.03009875	0.046135652
5.1	0.03009875	0.04594087
5.2	0.03009875	0.04589913

5.3	0.03009875	0.045801739
5.4	0.03009875	0.045676522
5.5	0.03009875	0.045593043
5.6	0.03009875	0.045565217
5.7	0.03009875	0.045565217
5.8	0.03009875	0.045523478
5.9	0.03009875	0.045384348
6	0.03009875	0.045286957
6.1	0.03009875	0.045231304
6.2	0.03009875	0.045064348
6.3	0.03009875	0.045064348
6.4	0.03009875	0.044994783
6.5	0.03009875	0.044925217
6.6	0.03009875	0.044883478
6.7	0.03009875	0.044827826
6.8	0.03009875	0.044744348
6.9	0.03009875	0.044633043
7	0.03009875	0.044577391
7.1	0.03009875	0.04448
7.2	0.03009875	0.044424348
7.3	0.03009875	0.044424348
7.4	0.03009875	0.044368696
7.5	0.03009875	0.04429913
7.6	0.03009875	0.044257391
7.7	0.03009875	0.044132174
7.8	0.03009875	0.044062609
7.9	0.03009875	0.043993043
8	0.03009875	0.043965217

8.1	0.03009875	0.043951304
8.2	0.03009875	0.043881739
8.3	0.03009875	0.043867826
8.4	0.03009875	0.043812174
8.5	0.03009875	0.043826087
8.6	0.03009875	0.043742609
8.7	0.03009875	0.043784348
8.8	0.03009875	0.043714783
8.9	0.03009875	0.043673043
9	0.03009875	0.043617391
9.1	0.03009875	0.043673043
9.2	0.03009875	0.043631304
9.3	0.03009875	0.043673043
9.4	0.03009875	0.043673043
9.5	0.03009875	0.043645217
9.6	0.03009875	0.043645217
9.7	0.03009875	0.043631304
9.8	0.03009875	0.043603478
9.9	0.03009875	0.043561739
10	0.03009875	0.043617391
10.1	0.03009875	0.043533913
10.2	0.03009875	0.04352
10.3	0.03009875	0.043492174
10.4	0.03009875	0.043436522
10.5	0.03009875	0.043436522
10.6	0.03009875	0.043353043
10.7	0.03009875	0.043311304
10.8	0.03009875	0.043311304

10.9	0.03009875	0.043297391
11	0.03009875	0.043269565
11.1	0.03009875	0.043269565
11.2	0.03009875	0.043241739
11.3	0.03009875	0.043269565
11.4	0.03009875	0.043255652
11.5	0.03009875	0.0432
11.6	0.03009875	0.043172174
11.7	0.03009875	0.043144348
11.8	0.03009875	0.043186087
11.9	0.03009875	0.043158261
12	0.03009875	0.043172174
12.1	0.03009875	0.0432
12.2	0.03009875	0.0432
12.3	0.03009875	0.043144348
12.4	0.03009875	0.043116522
12.5	0.03009875	0.043074783
12.6	0.03009875	0.043130435
12.7	0.03009875	0.043116522
12.8	0.03009875	0.043102609
12.9	0.03009875	0.043102609
13	0.03009875	0.043130435
13.1	0.03009875	0.043046957
13.2	0.03009875	0.042963478
13.3	0.03009875	0.042949565
13.4	0.03009875	0.042921739
13.5	0.03009875	0.042907826
13.6	0.03009875	0.042935652

13.7	0.03009875	0.04288
13.8	0.03009875	0.042893913
13.9	0.03009875	0.042824348
14	0.03009875	0.042852174
14.1	0.03009875	0.042838261
14.2	0.03009875	0.042838261
14.3	0.03009875	0.042824348
14.4	0.03009875	0.042810435
14.5	0.03009875	0.042768696
14.6	0.03009875	0.042810435
14.7	0.03009875	0.042782609
14.8	0.03009875	0.042726957
14.9	0.03009875	0.042685217
15	0.03009875	0.04274087
15.1	0.03009875	0.042685217
15.2	0.03009875	0.042726957
15.3	0.03009875	0.042713043
15.4	0.03009875	0.042685217
15.5	0.03009875	0.042726957
15.6	0.03009875	0.042726957
15.7	0.03009875	0.04269913
15.8	0.03009875	0.04274087
15.9	0.03009875	0.042726957
16	0.03009875	0.042754783
16.1	0.03009875	0.042671304
16.2	0.03009875	0.042726957
16.3	0.03009875	0.042713043
16.4	0.03009875	0.042671304

16.5	0.03009875	0.042671304
16.6	0.03009875	0.042671304
16.7	0.03009875	0.042643478
16.8	0.03009875	0.042657391
16.9	0.03009875	0.042726957
17	0.03009875	0.04274087
17.1	0.03009875	0.042726957
17.2	0.03009875	0.042685217
17.3	0.03009875	0.042713043
17.4	0.03009875	0.042726957
17.5	0.03009875	0.042726957
17.6	0.03009875	0.042754783
17.7	0.03009875	0.042754783
17.8	0.03009875	0.04274087
17.9	0.03009875	0.042796522
18	0.03009875	0.042838261
18.1	0.03009875	0.04288
18.2	0.03009875	0.042907826
18.3	0.03009875	0.042949565
18.4	0.03009875	0.042949565
18.5	0.03009875	0.042935652
18.6	0.03009875	0.042935652
18.7	0.03009875	0.042977391
18.8	0.03009875	0.042949565
18.9	0.03009875	0.04301913
19	0.03009875	0.043074783
19.1	0.03009875	0.043074783
19.2	0.03009875	0.043074783

19.3	0.03009875	0.043074783
19.4	0.03009875	0.043074783
19.5	0.03009875	0.043074783
19.6	0.03009875	0.043074783
19.7	0.03009875	0.043074783
19.8	0.03009875	0.043074783
19.9	0.03009875	0.043074783
20	0.03009875	0.043074783

Heat Flow at temperature 65°C for first and second samples

	65˚C 1st Sample	**65˚C 2nd Sample**
TIME (min)	**(-ve) HEAT FLOW (W/g)**	**(-ve) HEAT FLOW (W/g)**
0	0.14482	0.166266667
0.1	0.14209	0.147466667
0.2	0.13975	0.137466667
0.3	0.13741	0.134666667
0.4	0.13494	0.131733333
0.5	0.13143	0.130266667
0.6	0.126555	0.126933333
0.7	0.122902	0.124533333
0.8	0.120003	0.1232
0.9	0.117715	0.121066667
1	0.115596	0.118533333
1.1	0.113568	0.116
1.2	0.111488	0.112933333
1.3	0.109356	0.110133333
1.4	0.107081	0.109333333
1.5	0.104559	0.108533333
1.6	0.101881	0.1076
1.7	0.099229	0.106533333
1.8	0.096655	0.101466667
1.9	0.094146	0.0988
2	0.091741	0.096133333
2.1	0.089414	0.094133333
2.2	0.08723	0.093066667
2.3	0.085163	0.090266667
2.4	0.083213	0.084533333

2.5	0.081458	0.084266667
2.6	0.079872	0.084133333
2.7	0.07839	0.08252
2.8	0.077103	0.081053333
2.9	0.075985	0.079746667
3	0.074971	0.078346667
3.1	0.073996	0.07592
3.2	0.073008	0.07416
3.3	0.072124	0.072226667
3.4	0.071461	0.071
3.5	0.070915	0.070413333
3.6	0.070382	0.069066667
3.7	0.069927	0.066453333
3.8	0.06955	0.065013333
3.9	0.069082	0.063386667
4	0.06864	0.063146667
4.1	0.068289	0.063146667
4.2	0.068029	0.063146667
4.3	0.067808	0.062493333
4.4	0.067678	0.061893333
4.5	0.067574	0.061306667
4.6	0.067431	0.0596
4.7	0.067249	0.058093333
4.8	0.066976	0.05664
4.9	0.066859	0.056466667
5	0.067041	0.054946667
5.1	0.067041	0.054826667
5.2	0.067041	0.053613333

5.3	0.067041	0.053506667
5.4	0.067041	0.05336
5.5	0.067041	0.053093333
5.6	0.065468	0.05172
5.7	0.065455	0.050546667
5.8	0.065442	0.04872
5.9	0.065442	0.04768
6	0.065442	0.04768
6.1	0.065442	0.04768
6.2	0.065429	0.04768
6.3	0.065429	0.04768
6.4	0.065429	0.04768
6.5	0.065429	0.047093333
6.6	0.065416	0.046813333
6.7	0.065416	0.046746667
6.8	0.064714	0.046746667
6.9	0.064714	0.046746667
7	0.064714	0.046746667
7.1	0.064714	0.046746667
7.2	0.064714	0.04656
7.3	0.064714	0.04652
7.4	0.064714	0.046466667
7.5	0.064714	0.046426667
7.6	0.064714	0.046386667
7.7	0.064714	0.046346667
7.8	0.064714	0.046306667
7.9	0.064714	0.04628
8	0.064714	0.046253333

8.1	0.064714	0.046226667
8.2	0.062868	0.046213333
8.3	0.062868	0.046186667
8.4	0.062738	0.04616
8.5	0.062608	0.04612
8.6	0.062595	0.04608
8.7	0.062595	0.046053333
8.8	0.062595	0.046026667
8.9	0.0624	0.045986667
9	0.062868	0.045946667
9.1	0.062868	0.04592
9.2	0.062868	0.04588
9.3	0.062868	0.04584
9.4	0.062868	0.0458
9.5	0.062868	0.04576
9.6	0.062868	0.04572
9.7	0.062868	0.04568
9.8	0.062868	0.045653333
9.9	0.062868	0.045613333
10	0.062868	0.045586667
10.1	0.062868	0.045546667
10.2	0.062868	0.04552
10.3	0.062712	0.04548
10.4	0.062166	0.04544
10.5	0.061555	0.0454
10.6	0.06084	0.045373333
10.7	0.060073	0.045346667
10.8	0.059254	0.04532

10.9	0.058474	0.04528
11	0.057707	0.045253333
11.1	0.056966	0.045226667
11.2	0.056225	0.045186667
11.3	0.055484	0.04516
11.4	0.054782	0.04512
11.5	0.054158	0.045093333
11.6	0.053547	0.045053333
11.7	0.052988	0.045026667
11.8	0.052494	0.044986667
11.9	0.052039	0.04496
12	0.051597	0.044933333
12.1	0.051207	0.044906667
12.2	0.050856	0.04488
12.3	0.050505	0.04484
12.4	0.050232	0.044813333
12.5	0.049972	0.044786667
12.6	0.049712	0.044746667
12.7	0.049478	0.04472
12.8	0.049283	0.044693333
12.9	0.049023	0.044666667
13	0.048711	0.044626667
13.1	0.048425	0.0446
13.2	0.048191	0.044573333
13.3	0.048009	0.044546667
13.4	0.047892	0.044533333
13.5	0.047775	0.04452
13.6	0.047658	0.044933333

13.7	0.047528	0.0448
13.8	0.047398	0.044533333
13.9	0.047242	0.044266667
14	0.047164	0.043866667
14.1	0.047125	0.0436
14.2	0.047125	0.0432
14.3	0.046969	0.042933333
14.4	0.046709	0.042666667
14.5	0.046475	0.042266667
14.6	0.046215	0.042
14.7	0.045903	0.041733333
14.8	0.045591	0.0412
14.9	0.04524	0.040933333
15	0.04485	0.040666667
15.1	0.044408	0.0404
15.2	0.043966	0.04
15.3	0.043563	0.0396
15.4	0.043225	0.0396
15.5	0.042913	0.0396
15.6	0.042588	0.0396
15.7	0.042328	0.0396
15.8	0.04212	0.0396
15.9	0.041951	0.0396
16	0.041873	0.0396
16.1	0.041782	0.0392
16.2	0.0416	0.038533333
16.3	0.041379	0.0396
16.4	0.041171	0.0396

16.5	0.041015	0.0396
16.6	0.040872	0.0396
16.7	0.040781	0.0396
16.8	0.040729	0.0396
16.9	0.040755	0.0396
17	0.040742	0.0396
17.1	0.040625	0.0396
17.2	0.040469	0.0396
17.3	0.040326	0.0396
17.4	0.040209	0.0396
17.5	0.040157	0.0396
17.6	0.040092	0.0396
17.7	0.040053	0.0396
17.8	0.040027	0.0396
17.9	0.04004	0.0396
18	0.040079	0.0396
18.1	0.040131	0.0396
18.2	0.040131	0.0396
18.3	0.040118	0.0396
18.4	0.040092	0.0396
18.5	0.040053	0.0396
18.6	0.040014	0.0396
18.7	0.039975	0.0396
18.8	0.03991	0.0396
18.9	0.039845	0.0396
19	0.039754	0.0396
19.1	0.03965	0.0396
19.2	0.039533	0.0396

19.3	0.039481	0.0396
19.4	0.039481	0.0396
19.5	0.039559	0.0396
19.6	0.039598	0.0396
19.7	0.039585	0.0396
19.8	0.039572	0.0396
19.9	0.039546	0.0396
20	0.039481	0.0396

Heat Flow at temperature 75°C for first and second samples

	75˚C 1st Sample	75˚C 2nd Sample
TIME (min)	**(-ve) HEAT FLOW (W/g)**	**(-ve) HEAT FLOW (W/g)**
0	0.24402439	0.255778947
0.1	0.238658537	0.249594737
0.2	0.233414634	0.246997368
0.3	0.224512195	0.239576316
0.4	0.220609756	0.234628947
0.5	0.195365854	0.217436842
0.6	0.17	0.196039474
0.7	0.155731707	0.161778947
0.8	0.146585366	0.159428947
0.9	0.136707317	0.137042105
1	0.12152439	0.123436842
1.1	0.10997561	0.112577368
1.2	0.101280488	0.108866842
1.3	0.092134146	0.100208947
1.4	0.084097561	0.096634474
1.5	0.079097561	0.087840526
1.6	0.075	0.085230789
1.7	0.070792683	0.077067632
1.8	0.067060976	0.075125789
1.9	0.063585366	0.073616842
2	0.060463415	0.073344737
2.1	0.057865854	0.070871053

2.2	0.05554878	0.068533421
2.3	0.053341463	0.066950263
2.4	0.051036585	0.066245263
2.5	0.0485	0.061297895
2.6	0.045756098	0.056437105
2.7	0.042743902	0.049238684
2.8	0.039695122	0.046146579
2.9	0.036512195	0.044909737
3	0.033414634	0.04089
3.1	0.030353659	0.037043421
3.2	0.027585366	0.035287105
3.3	0.024682927	0.034050263
3.4	0.022195122	0.029696579
3.5	0.019804878	0.023883421
3.6	0.018195122	0.022597105
3.7	0.016914634	0.022547632
3.8	0.015865854	0.021286053
3.9	0.015060976	0.020321316
4	0.014402439	0.019245263
4.1	0.013853659	0.018107368
4.2	0.013390244	0.016907632
4.3	0.01297561	0.015670789
4.4	0.012621951	0.014310263
4.5	0.012329268	0.013197105
4.6	0.012085366	0.012331316

4.7	0.011817073	0.012331316
4.8	0.011589024	0.011753711
4.9	0.011430488	0.011592921
5	0.011164634	0.011323289
5.1	0.011018293	0.011174868
5.2	0.010908537	0.011063553
5.3	0.010719512	0.010871842
5.4	0.010581707	0.010732079
5.5	0.010456098	0.010604684
5.6	0.010326829	0.010473579
5.7	0.010140244	0.010284342
5.8	0.010007317	0.010149526
5.9	0.009882927	0.010023368
6	0.009754878	0.009772289
6.1	0.009687805	0.009657263
6.2	0.009645122	0.009533579
6.3	0.009543902	0.009409895
6.4	0.009462195	0.009302289
6.5	0.009284146	0.009302289
6.6	0.009135366	0.009302289
6.7	0.008989024	0.009302289
6.8	0.008789024	0.009302289
6.9	0.00864878	0.008722211
7	0.008502439	0.008297974
7.1	0.008302439	0.008297974

7.2	0.008221951	0.008297974
7.3	0.008042683	0.008297974
7.4	0.007787805	0.008207684
7.5	0.007619512	0.008207684
7.6	0.007476829	0.008207808
7.7	0.007295122	0.007082158
7.8	0.007110976	0.006479816
7.9	0.006884146	0.006479816
8	0.006639024	0.006479816
8.1	0.00637439	0.006479816
8.2	0.006143902	0.006479816
8.3	0.00595122	0.006075368
8.4	0.005739024	0.006071658
8.5	0.00555122	0.005574571
8.6	0.00535122	0.005574571
8.7	0.005264634	0.005574571
8.8	0.005104878	0.005429613
8.9	0.004876829	0.004905316
9	0.004708537	0.004816263
9.1	0.004569512	0.004816263
9.2	0.004479268	0.004807605
9.3	0.004337805	0.004806368
9.4	0.004187805	0.004803153
9.5	0.00409878	0.004305324
9.6	0.003962195	0.004305324

9.7	0.003832927	0.004305324
9.8	0.00374878	0.003810587
9.9	0.003717073	0.003810587
10	0.003623171	0.003810587
10.1	0.003540244	0.003533658
10.2	0.003506098	0.003533658
10.3	0.003453659	0.003533658
10.4	0.003431707	0.002298053
10.5	0.003414634	0.002298053
10.6	0.003380488	0.002298053
10.7	0.00337439	0.002298053
10.8	0.003329268	0.002298053
10.9	0.003313415	0.002298053
11	0.003269512	0.002298053
11.1	0.00329878	0.002298053
11.2	0.003212195	0.002298053
11.3	0.003181707	0.002032132
11.4	0.003147561	0.002032132
11.5	0.003087805	0.002032132
11.6	0.003068293	0.002032132
11.7	0.002997561	0.002032132
11.8	0.002968293	0.002032132
11.9	0.003012195	0.002032132
12	0.003008537	0.002032132
12.1	0.002942683	0.002259711

12.2	0.002946341	0.002259711
12.3	0.00290122	0.002259711
12.4	0.002879268	0.002259711
12.5	0.002873171	0.002259711
12.6	0.002863415	0.002259711
12.7	0.002852439	0.002259711
12.8	0.002818293	0.002259711
12.9	0.002779268	0.002259711
13	0.002765854	0.001309816
13.1	0.002770732	0.001309816
13.2	0.002741463	0.001309816
13.3	0.002671951	0.001309816
13.4	0.00260122	0.001309816
13.5	0.002563415	0.001309816
13.6	0.002671951	0.001309816
13.7	0.002671951	0.001309816
13.8	0.00262561	0.001309816
13.9	0.002532927	0.001309816
14	0.002497561	0.001309816
14.1	0.00244878	0.001309816
14.2	0.002446341	0.001309816
14.3	0.002443902	0.001309816
14.4	0.002478049	0.003301132
14.5	0.002489024	0.003301132
14.6	0.002457317	0.003301132

14.7	0.002408537	0.003301132
14.8	0.002446341	0.003301132
14.9	0.002369512	0.003301132
15	0.002332927	0.003301132
15.1	0.002293902	0.003301132
15.2	0.002295122	0.003301132
15.3	0.002319512	0.003301132
15.4	0.002345122	0.003301132
15.5	0.00235	0.003301132
15.6	0.002380488	0.002137263
15.7	0.002395122	0.002133553
15.8	0.002420732	0.002128605
15.9	0.002419512	0.002123658
16	0.002428049	0.002119947
16.1	0.002392683	0.002115
16.2	0.002385366	0.002111289
16.3	0.002478049	0.002106342
16.4	0.002493902	0.002106342
16.5	0.002491463	0.002106342
16.6	0.002487805	0.002106342
16.7	0.002484146	0.002106342
16.8	0.002459756	0.002106342
16.9	0.002382927	0.002106342
17	0.002363415	0.002106342
17.1	0.002368293	0.002106342

17.2	0.002326829	0.002106342
17.3	0.002331707	0.002106342
17.4	0.002370732	0.002593658
17.5	0.002453659	0.002593658
17.6	0.002459756	0.002593658
17.7	0.002496341	0.002593658
17.8	0.002489024	0.002593658
17.9	0.002514634	0.002593658
18	0.002460976	0.002593658
18.1	0.002419512	0.002016053
18.2	0.002360976	0.002016053
18.3	0.002281707	0.002016053
18.4	0.002245122	0.002016053
18.5	0.002162195	0.002016053
18.6	0.002145122	0.002016053
18.7	0.002134146	0.002016053
18.8	0.002134146	0.002016053
18.9	0.002130488	0.002016053
19	0.002063415	0.002016053
19.1	0.002091463	0.002016053
19.2	0.00205	0.002016053
19.3	0.002065854	0.002016053
19.4	0.002004878	0.001944316
19.5	0.001986585	0.001944316
19.6	0.001968293	0.001944316

19.7	0.001992683	0.001944316
19.8	0.001971951	0.001944316
19.9	0.002003659	0.001944316
20	0.001957317	0.001944316