SYNTHESIS AND CHARACTERIZATION OF GEL-TYPE POLYMERS *VIA* AQUEOUS DISPERSION POLYMERIZATION

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ABSTRACT

This study is about synthesis and characterization of gel-type polymer aqueous dispersion polymerization (ADP) that involved two types of dispersion polymerization methodology; one-stage aqueous dispersion polymerization and two-stage aqueous dispersion polymerization. The monomer and crosslinker were used in this study are styrene and EGDMA. Mixture of styrene and solvent undergone under nitrogen atmosphere for one hour at 70 °C before EGDMA was added into the mixture. The reaction was continued further 23 hours before the final product obtained. The polymers are characterized by using FTIR and CHNOS analysis. For one-stage polymerization, the final product was successfully obtained after 24 hours of reaction. The result obtained was not in bead-like shape but in flakes-formed. For two-stage ADP, based on the result from FTIR for two-stage polymerization, it shows that there are functional group that has been identified; alkene and alcohol and phenols reflect to functional group in styrene and EGDMA. It is clearly shown that EGDMA and styrene are incorporated in the back bone of polymer. For elemental analysis, CHNOS shows that there are 6.97% of nitrogen, 88.56% of carbon, 7.66% of hydrogen and 0.01% of sulphur at temperature of 70 ^{o}C while at 72 ^{o}C is 93.73% of nitrogen, 82.07% of carbon, 6.67% of hydrogen and 0.23% of sulphur. In conclusion, the particles were obtained in broad particles size distribution and polydisperse by varying the temperature for the reaction in two-stage ADP.

Keyword: gel-type polymer, aqueous dispersion polymerization, polydisperse

ABSTRAK

Hasil kajian berkaitan dengan sintesis dan pengkriterian polimer berbentuk gel melalui proses akueus serakan pempolimeran. Hasil kajian ini berkaitan dengan sintesis dan pengkriterian polimer berbentuk gel melalui proses akueus serakan pempolimeran yang melibatkan dua peringkat iaitu proses serakan pempolimeran secara akueus peringkat satu dan peringkat dua. Monomer dan agen penyilang yang digunakan dalam kajian ini,antaranya ialah styrene dan EGDMA. Campuran styrene dan pelarut dilakukan dibawah atmosfera nitrogen selama satu jam pertama sebelum EGDMA dimasukkan ke dalam campuran dan seterusnya. Proses tindak balas diteruskan selama 23 jam bagi mendapatkan hasil partikel. Polimer-polimer ini dikriteriakan menggunakan kaedah analisis FTIR dan kaedah analisis CHNOS. Bagi peringkat satu pempolimeran, produk berjaya didapati selepas tindak balas selama 24 jam tetapi produk yang terhasil bukan dalam bentuk manik. Bag peringkat kedua pempolimeran, berdasarkan keputusan daripada analisis, ia menunjukkan bahawa terdapat kumpulan fungsi yang dapat dikesan, iaitu alkene dan alkohol dan phenol. Ianya jelas menunjukkan bahawa EGDMA dan styrene wujud di dalam produk ini. Bagi analisa untuk elemen-elemen tertentu, CHNOS menunjukkan bahawa kandungan elemen ialah seperti 6.97% bagi nitrogen, 88.56% daripada kandungan karbon, 7.66% peratusan kandungan hidrogen dan 0.01% daripadanya adalah peratusan sulphur pada suhu 70^{o}C sementara itu, pada suhu 72 °C ialah 93.73% peratusan nitrogen, 82.07% hasil dari kandungan karbon, 6.67% bagi peratusan hidrogen dan 0.23% ialah sulfur. Konklusinya, dengan mengubah suhu tindak balas, zarah yang diperolehi berbentuk *polydisperse* dalam pelbagai saiz.

Kata kunci: polimer bergel, polimeran serakan akueus, *polydisperse*

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LIST OF ABBREVIATIONS

ADP	Aqueous Dispersion Polymerization
CHNOS	Carbon, Hydrogen, Nitrogen, Oxygen, Sulphur
CMPS	Chloromethylated polystyrene
DCE	Anhydrous 1,2-dichloroethane
DVB	Divinylbenzene
EGDMA	Ethylene Glycol Dimethacrylate
FRP	Free Radical Polymerization
FTIR	Fourier Transform Infrared Spectrometry
HCLPS	Hypercrosslinked polystyrene
HPLC	High Performance Liquid Chromatography
KBr	Potassium Bromide
KCl	Potassium Chloride
KPS	Potassiumpersulfate
MEA	2-methoxyethyl acrylate
NAD	Non-Aqueous Dispersion
NaAs	Sodiumascorbate
PEGDA	Poly(Ethylene Glycol) Diacrylate
PPEGMA	Poly(Poly(Ethylene Glycol) Ethyl Ether Methacrylate
PS	Polystyrene
PVP	Poly (N-vinylpyrrolidone)
RAFT	Reversible Addition Fragmentation Chain Transfer
SEM	Scanning Electron Microscope
SPE	Solid Phase Extraction

VBC	4-Vinylbenzyl Chloride

1.0 INTRODUCTION

1.1 Motivation and statement of problem

Precursor polymeric particles which are produced *via* suspension polymerization, emulsion polymerization and precipitation polymerization are commonly used in the preparation of hypercrosslinked polymers. Each synthesis technique has been investigated widely as an alternative method for preparing monodisperse polymeric particles in the micron-sized range in single step (D. Horák et al., 1999; A. J. Paine et al., 1990). This is because such particles meet requirements that are needed in various applications, particularly in separation science, for example in high performance liquid chromatography (HPLC) and solid-phase extraction (SPE). In terms of chemical separation, highly efficient separation is important for example in waste water treatment. Thus, narrow particle size distributions become important in the applications area in addition to the need for high specific surface area.

There are many types of polymerization such as suspension polymerization, precipitation polymerization and dispersion polymerization. Suspension polymerization is a process where heterogeneous polymerization that begins initially as a homogeneous system in the continuous phase, where the monomer and initiator are completely soluble, but upon initiation the formed polymer is insoluble and then it is formed into precipitated form. Suspension polymerization is carried out in a liquid phase (usually water), in which neither the monomer nor the polymer are soluble. Liquid or dissolved monomers are suspended in water containing a dissolved suspension agent. Typical dispersing agents preventing coalescence of the droplets are polyvinyl alcohol and methyl-cellulose.

The particle size of the polymer beads produced is in the range between 10 and 500 µm. The size of the monomer droplets can be adjusted by the agitation speed, the nature and quantity of suspension stabilizers and the volume ratio of the dispersed (organic phase) and continuous phase (aqueous phase). If the dispersed phases consist just of the monomers and crosslinking agents, polymerization yields are hard glassy and transparent polymer beads. Due to their compressibility, column blocking could occur, or at least, large pressures would be required to maintain sufficient flow rates.

Precipitation polymerization is a heterogeneous polymerization process that begins as homogeneous system in the continuous phase whereas the monomer and initiator are completely soluble but upon the initiation the formed polymer is insoluble and then precipitates. After precipitation, the polymerization proceeds by absorption of monomer and initiator into the polymer particles (J. Wiley et al., 1999). The precipitation polymerizations give larger and less regular particles, as a result of little or no stabilizer is present in the process (J. C. Salamone et al., 1998).

Dispersion polymerization is an attractive method for producing micron-size monodisperse polymer particles in a single batch process (S. Kawaguchi et al., 2005). The type and properties of the stabilizer used in a dispersion polymerization determine the colloidal stability and size distribution. A good polymeric stabilizer should be soluble in the dispersant, cover most of the particle surface, and provide a repulsive interaction between particles that is longer-ranged than the attractive van der Waals forces (S. M. Klein et al., 2003). The advantages for dispersion polymerization are the particles form were micron sized approximately 3 µm (M. A. Winnik et al., 2006). In addition, dispersion polymerization can be scale up, produced narrow particle distribution and high yield (M. A. Winnik, et. al., 2006). Therefore dispersion polymerization was used in this work in order to get the desired product.

1.2 Objectives

The following are the objective of this research:

i. To synthesis gel-type polymer by using ADP by manipulating temperature
ii. To study effectiveness of two-stage methodology on aqueous dispersion polymerization (ADP).

1.3 Scope of this research

The following are the scope of this research:

i) Synthesis linear polymer by using only styrene in one-stage polymerization as comparison study to second-stage polymerization.
ii) Synthesis the crosslink precursor by delayed addition of the crosslinker agent to get desired size of precursor.
iii) Characterization particle by using the characterization equipment such as optical microscope, CHNOS analyzer and FTIR.

1.4 Main contribution of this work

The following are the contributions on the methodology which is to measure the effectiveness of two-stage methodology. Besides, this study is able to find the optimum conditions in order to get the desired product by manipulating parameter which is temperature reaction.

1.5 Organisation of this thesis

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

Chapter 1: Gives a brief introduction which covers the motivation, problem statements, objectives, scopes of the study and main contribution of this work.

Chapter 2: Provides a general design features of dispersion polymerization A general description on the flow of the process was presented. This chapter also provides a brief discussion of the method used in this study.

Chapter 3: Gives a review of the methodology of this process that consists one-stage polymerization and two-stage polymerization. This chapter also provides the materials and equipments used in this study for dispersion polymerization.

Chapter 4: Devoted to result of this study which an experiment on one stage dispersion polymerization and second stage polymerization have been done. All findings and results were tabulated and analysed in the form of graph and chart. The explanations of the findings were also included.

Chapter 5: Gives a conclusion and the future work of this study to improve the way on how to make sure the result is better than the expected result

2.0 LITERATURE REVIEW

2.1 Overview

Dispersion polymerization is an attractive method of producing micron-sized monodisperse polymer particles in a single batch process. There are several applications such as in the medical field, high performance liquid chromatography (HPLC) and solid-phase extraction (SPE) that using this kind of method (S. Kawaguchi et al., 2005). Dispersion polymerisation has been explored widely over the past two decades because of the scientific and commercial interest in such particles; research into their preparation is active until today. However, the biggest challenge that will be faced in this dispersion polymerisation is to obtain the particles in a micron-size range and particles which are monodisperse. A method that has been stimulated by the work of Lok and Ober (K. P. Lok et al., 1985) and was originally developed in 1970s (K. E. J. Barret et al., 1973) which is an alternative method that is known as preparing monodisperse, micron-sized particles in one single step (A. J. Paine et al., 1990).

2.2 Introduction

In a dispersion polymerization process, the reaction mixture started as a homogeneous solution and the resulting polymer precipitates as spherical particles, stabilized by a steric barrier of dissolved polymer (K. P. Lok et al., 1985). The final polymer particle size is determined by the inherent polymer aggregation behaviour under a given set of conditions. In the present study, styrene polymerization was studied in various solvents using cellulosic derivatives as the steric stabilizer. Some of these solvents in certain combinations allowed the direct preparation of particles in the micron size and their size distribution appeared to be highly dependent on the monomer–solvent–initiator system (K. P. Lok et al., 1985).

Dispersion polymerization is an attractive method for producing micron-size monodisperse polymer particles in a single batch process. Great progress in this field has been achieved over the past three decade (W. D. He. et al., 2011 and C. M. Tseng et al., 1986). Micron-size monodisperse particles were usually difficult to obtain because this size is in between the diameter range of particles produced by conventional emulsion polymerization (0.06–0.7 µm) in a batch process (C. S. Chern et al., 2006 and A. Guyot et al., 1994) and suspension polymerization (50–1000 µm) (B. W. Brooks et al., 2010 and H. G. Yuan et al., 1991).

Dispersion polymerization in organic hydrocarbon media was first developed by Barrett (K. E. J. Barret et al., 1973). Dispersion polymerization may be defined as a type of precipitation polymerization in which one carries out the polymerization of a monomer in the presence of a suitable polymeric stabilizer soluble in the reaction medium. The solvent selected as the reaction medium is a good solvent for both the monomer and the steric stabilizer polymers but a nonsolvent for the polymer being formed.

The dispersion copolymerization could be avoided if one delayed addition of the second monomer is used until the nucleation stage was complete and the particle number in the reaction became constant. It has been known for years that the nucleation stage of dispersion polymerization occurs early in the reaction. The very narrow size distribution of the particles obtained is an indication that nuclei with a narrow range of sizes form early in the reaction, followed by a long particle growth stage. The dynamic light scattering studies of the El-Aasser group (M. S. El-Aasser et al., 1986) establish that the nuclei that determine the final number of particles in the reaction form by a rapid aggregation of smaller, colloidally unstable particles produced by collapse and aggregation of growing polymer chains in the continuous medium.

The detailed simulations of polymerization and particle growth kinetics was studied by Yasuda et al., 2001) which demonstrated that the nucleation stage of dispersion polymerization of styrene in ethanol is complete at less than 1% monomer conversion, which for styrene under our reaction conditions (70 °C) corresponds to less than 15 min reaction time. There is a good experimental evidence that the number of particles present in the reaction is constant from 10% conversion until the end of the reaction. Winnik and co-workers (J. S. Song et al., 2004) introduced a new method for the dispersion polymerisation which known as “two-stage” dispersion polymerisation method. In this method, they used the delayed addition of second monomer after the end of nucleation stage of the reaction. In an appropriate condition, the micron-sized particles will be obtained. Highly crosslinked micron-sized range particles were successfully obtained by Lee and co-workers (K. C. Lee et al., 2010) with up to 20 wt% of crosslinker has been employed in dispersion polymerization whereas monodisperse polystyrene particle were prepared by using different approach from Winnik.

The SEM images in Figure 1 illustrate the increase in particle size (at low polydispersity) with monomer content. Antl (Antl et. al., 1986) reported a similar trend in the PMMA/ hexane/ poly(12-hydroxy-stearic acid) system, though surprisingly they found a region of colloidal instability at intermediate monomer concentration (10–30%), which they did not observe in their limited trials. They attributed the increase in particle size to an increase in solvent quality for the polymer at high monomer concentration, which allows the polymer chains to grow larger before precipitating and forming nuclei. Another factor contributing to increasing particle size may be decreased effectiveness of the stabilizer in the presence of large amounts of monomer (Winnik et al., 1987).

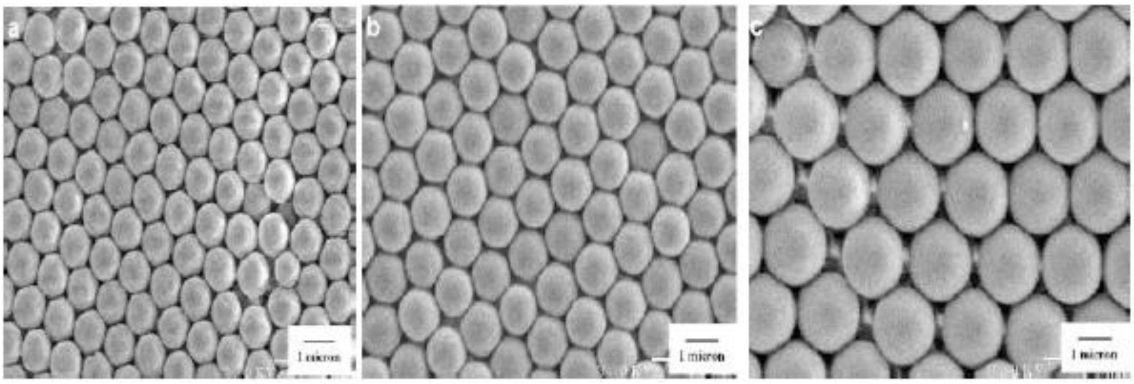

Figure 1: SEM images of monodisperse PMMA particles prepared at monomer concentrations of 15.15% w/w (a) 26.3% w/w (b), and 47.2% w/w (c). All samples are well ordered after drying, but the sample at 47.2% contained aggregates, possibly from evaporation of hexanes, that were separated out and not pictured here. (S. M. Klein et al., V. N. Manoharan et al., D. J. Pine et al., F. F. Lang et al., 2003)

Dispersion polymerization is also defined as a type of precipitation polymerization in which the monomer and all other reactants (including polymeric stabilizers) are initially soluble in the reaction medium, but the polymer is insoluble. Dispersion polymerization starts as a homogeneous solution polymerization, but as polymer (or oligomer) chains grow in size they eventually reach a molecular weight higher than a certain critical value and precipitate from solution and aggregate to form colloidally unstable precursor particles. These particles coalesce and adsorb stabilizers from the reaction medium onto their surface until they become colloidally stable. At this point, the total number of particles in the system is fixed, and the nucleation stage ceases. Subsequent polymerization, also termed the particle growth stage, occurs either inside the swollen nuclei or in the reaction medium depending on the polymer-solvent interactions. However, the newly formed polymers should not form additional nuclei but should be captured by existing particles (Kawaguchi et. al., 2005)

It has been widely received that the key issue for preparation of uniformly sized colloidal particles is a short nucleation stage (Lamer et. al., 1950). The particle number and particle number distribution are determined during the nucleation stage, and no secondary particles or coagulum should be formed during the particle growth stage. A prolonged nucleation stage usually results in abroad particle size distribution.

Besides, the nucleation stage in dispersion polymerization is very sensitive to variations in reaction components or conditions. It has been found that incorporation of functional monomers (W. Yang et. al., 2001) or crosslinking agents (J. S. Song et. al., 2005) in dispersion polymerization is more difficult than that in other heterogeneous polymerizations.

2.3 Study on Different Types of Polymerization

Polymerization can be divided into categories namely as addition polymerization and condensation polymerization. The addition polymerization which is also known as chain growth polymerization is the combination of monomers without the elimination of some by product molecules. The condensation of polymerization or also known as step-growth is a formation of polymer through condensation process by releasing small molecules.

2.3.1 Overview of Addition Polymerization

Addition polymerization is characterized by unsaturated monomer. A chain reaction is promoted by an active site. An initiator or catalyst causes one of the electrons of the unsaturated bond to become activated. Additional monomer units react with an activated radical at a rapid rate. As each additional molecule of monomer reacts, the active site translates to the end position of the growing polymer chain. After a typical growth period of a few seconds, two different active sites combine to cease further growth of their chains. An example of this mechanism is polyethylene.

In addition polymerization, a high molecular weight product is produced right from the start, while the monomer quantity decreases slowly with time. Addition polymerization generally is fast, irreversible, and moderately to highly exothermic. On the other hand, step-growth polymerization is usually slow, equilibrium-limited, and isothermal to slightly exothermic. Addition polymerization can be classified as radical, coordination, anionic or cationic polymerization, depending on the type of initiation.

2.3.2 Overview of Free Radical Polymerization (FRP)

The most common type of addition polymerization is free radical polymerization. A free radical is simply a molecule with an unpaired electron. The tendency for this free radical to gain an additional electron in order to form a pair makes it highly reactive so that it breaks the bond on another molecule by stealing an electron, learing that molecule with an unpaired election (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. FRP consists of three chain-reaction mechanisms which are initiation, propagation and termination.

This technique is applied to prepare latexes to be used in paints, high molecular weight poly(methyl methacrylate) for safety glass (Plexiglas), or foamed polystyrene to be applied in coffee cups. Some advantages of radical polymerizations with respect to other techniques, are the relative insensitivity to impurities, the moderate reaction temperatures and the multiple polymerization processes available, e.g., bulk, solution, precipitation or emulsion polymerization. There are other two advantages for conventional radical polymerization: high molecular weight is obtained at low monomer conversion (because every monomer adds directly to the chain end) and unlike condensation polymerizations, radical polymerizations have no by-products. Some disadvantages related to the mechanism of free radical polymerization is the poor control of the molecular weight and the molecular weight distribution, and the difficulty (or even impossibility) of preparing well-defined copolymers or polymers with a predetermined functionality.

2.3.3 Overview of Step-Growth Polymerization

In a step-growth polymerization, the molecular weight of the polymer chain builds up slowly and there is only one reaction mechanism for the formation of polymer. The distinct initiation, propagation, and termination steps of chain-growth polymerization are meaningless in step-growth polymerization. A difunctional monomer or equal molar amounts of two different difunctional monomers are necessary at least to form a linear high molecular weight polymer. The polymerization reaction proceeds by individual reactions of the functional groups on the monomers. Thus, two monomers react to form a dimer. The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer. This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively long period of time, a high molecular weight polymer is obtained. In step-growth polymerization there is a slow increase in average molecular weight of the product. The molecular weight is usually not as high as in chain-growth polymerization, and relatively small amounts of unreacted monomer are present after the start of the reaction.

2.3.4 Overview of Bulk Polymerization

Bulk polymerization is known as mass or block polymerization where the polymerization between monomer and initiator. It is carried out in the absence of any solvent or dispersant and thus the simplest in terms of formulation. It is used for most step-growth polymers and many types of chain-growth polymers. In the case of chain-growth reactions which are generally exothermic, the heat evolved may cause the reaction to become too vigorous and difficult to control unless efficient cooling.

2.3.5 Overview of Solution Polymerization

Solution polymerization is used to create polymers and copolymers by dissolving a monomer and a catalyst in a non-reactive solvent. During this process, the solvent liquid absorbs the heat generated by the chemical reaction which controls the reaction rate. The liquid solvent used in the solution polymerization procedure usually remains a solvent for the resulting polymer or copolymer. This process is only suitable for the creation of wet polymer types, as the removal of excess solvent is difficult. While removal of excess solvent is possible using distillation, it is usually not considered economically possible in an industrial situation.

The process of solution polymerization offers a few advantages as well as one major disadvantage. The advantages include precise control of the chemical reaction, control of the resulting heat and viscosity, and control over auto acceleration of the process. The disadvantage of the process is the difficulty involved in the removal of excess solvent from the finished polymer.

2.3.6 Overview of Emulsion Polymerization

Emulsion polymerization is a unique chemical process widely used to produce waterborne resins with various colloidal and physicochemical properties. This heterogeneous free radical polymerization process involves emulsification of the relatively hydrophobic monomer in water by an oil-in-water emulsifier, followed by the initiation reaction with either a water-insoluble initiator or an oil-soluble initiator such as sodium persulphate and 2-2′-azobisisobutyronitrile, respectively. Emulsion polymerization involves the propagation reaction of free radicals with monomer molecules in a very large number of discrete polymer particles dispersed in the continuous aqueous phase. The nucleation and growth of latex particles control the colloidal and physical properties of latex products. These emulsion polymers find a wide range of applications such as synthetic rubbers, thermoplastics, coatings, adhesives, binders, rheological modifiers, plastic pigments, standards for the calibration of instruments, immunodiagnosis tests, polymeric supports for the purification of proteins and drug delivery system.

2.3.7 Overview of Dispersion Polymerization

Dispersion polymerization is an attractive method for producing micron-size monodisperse polymer particles in a single batch process. Great progress in this field has been achieved over the past two decades. This study presents an overview of the recent progress in the preparation of polymeric microspheres *via* dispersion polymerization in organic media, focusing on the preparation of novel functional particles, the design of microspheres using macromonomers, and on understanding mechanisms for the control of particle size. Examples of functional microspheres obtained by dispersion polymerization in the presence of linear polymers, block polymers, and macromonomers are tabulated, and new developments are highlighted.

In a dispersion polymerization process, the reaction mixture starts out as a homogeneous solution and the resulting polymer precipitates as spherical particles, stabilized by a steric barrier of dissolved polymer. The final polymer particle size is determined by the inherent polymer aggregation behaviour under a given set of conditions. In the present study, styrene polymerization was studied in various solvents using cellulosic derivatives as the steric stabilizer. Some of these solvents in certain combinations allowed the direct preparation of particles in the micron size and their size distribution appeared to be highly dependent on the monomer-solvent-initiator system. Research on these factors have been suggested that monodisperse particles up to 12 pm can be prepared in a single step: studies of several systems are delineated.

2.4 Previous Study on Aqueous Dispersion Polymerization

Micron-size monodisperse particles were usually difficult to obtain because this size is in-between the diameter range of particles produced by conventional emulsion polymerization (0.06–0.7 μm) in a batch process (C. S. Chern et al., 2006) and suspension polymerization (50–1000 μm) (B. W. Brooks et al., 2010). Methods for producing micrometer-sized polymer particles have been studied by many researchers.

Lok and Ober have reported about the production of 1-10 µm monodisperse copolymer particles which consists of styrene and n-butyl methacrylate with ethanol-water as the polymerization medium. The stabilizer and initiator used are poly(acrylic acid) and benzoyl peroxide, respectively. Micrometer-size monodisperse polymer particles that have been obtained have a wide variety of scientific and technological applications, such as standard calibration, biomedical and clinical diagnosis, high-performance liquid chromatography (HPLC) fillers, catalyst carriers, coatings and ink additives, information storage materials, and colloidal crystals (S. Kawaguchi et al., 2005 and J. Ugelstad et al., 1992).

Other research investigated as shown in Figure 2 dispersion polymerization of 2-methoxyethyl acrylate (MEA) was carried out at solids content >10% w/v relative to water by using poly(poly(ethylene glycol) methyl ether methacrylate (PPEGMA) as both the reversible addition_fragmentation chain transfer (RAFT) controlling agent and the hydrophilic steric stabilizer. Potassiumpersulfate (KPS)/ sodiumascorbate (NaAs) was used as the radical initiator to allow efficient polymerization at low temperatures, either 30ºC or 40 °C. Since MEA and PPEGMA are highly soluble in water, chain extension of PPEGMA is expected to occur in the homogeneous solution. After PMEA grows to a certain length, it produced amphiphilic block copolymer PPEGM_PMEA assembles into core shell nanoparticles. Given its high water solubility and the expected good solubility in its own polymer, MEA will partition in both nanoparticles and water. As polymerization continues in the nanoparticles, MEA in the nanoparticles is gradually consumed, which is continuously supplied from the aqueous solution. To produce cross-linked nanoparticles a water soluble cross-linker poly(ethylene glycol) diacrylate (PEGDA) is used at a constant molar ratio of PEGDA:PPEGMA = 3:1.

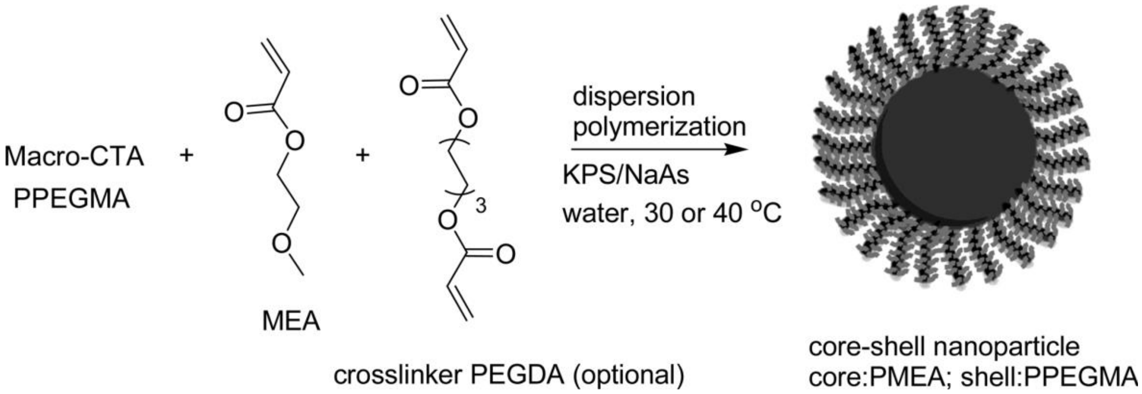

Figure 2: Dispersion Polymerization of MEA Using PPEGMA Macro-CTA in Water (F. Fréchet et. al., 1995)

The typical accepted mechanism for the formation of pores during common polymerization reactions in the presence of an inert solvent (precipitant) is as follow (F. Fréchet et. al., 1995); the organic phase contains the monomers, the porogenic agent and the radical initiator which decomposes at a certain temperature for initiating the polymerization process "in solution". The polymer chains formed in solution precipitate as soon as they become insoluble in the reaction medium, either as a result of the crosslinking density of the polymer network, or depending on the porogenic agent used (thermodynamically "poor" solvent for the polymer).

3.0 MATERIALS AND METHODS

3.1 Overview

This study is about aqueous dispersion polymerization which involved two stages of polymerization which are one-stage dispersion polymerization and two-stage dispersion polymerization.

3.2 Chemicals and Equipments

3.2.1 Chemicals

The reagents used for the polymer synthesis are styrene reagent plus contains 4-tert-Bus472 (99% grade) and ethylene glycol dimethacrylate (EGDMA) (98% grade) and 4-vinylbenzyl chloride (VBC) (95% grade). Methanol (99.7% grade), ethanol (95% grade), Poly (N-vinylpyrrolidone) (PVP) 55 (Mw~55,000) was used as stabilizer and Triton X-305 was used as co-stabilizer were supplied by Sigma-Aldrich. The benzoyl peroxide (98% grade) was supplied by Sigma-Aldrich is used as initiator.

3.2.2 Equipments

For the one-stage and two-stage of aqueous dispersion polymerization, the polymer synthesis has been performed in a five-necked round-bottomed flask fitted with a flange, condenser and overhead stirrer with a metal blade. The reaction flask had been put into a thermostatically-controlled heating mantle as shown in Figure 3.

Figure 3: Apparatus for Dispersion Polymerization

3.2.3 Analysis

3.2.3.1 Optical Microscope

This analysis device is used in order to visualize or find out the particles at the end of the reactions. A few drops of polymer dispersion had been deposited onto a microscope slide and the particles imaged once the solvent had been evaporated.

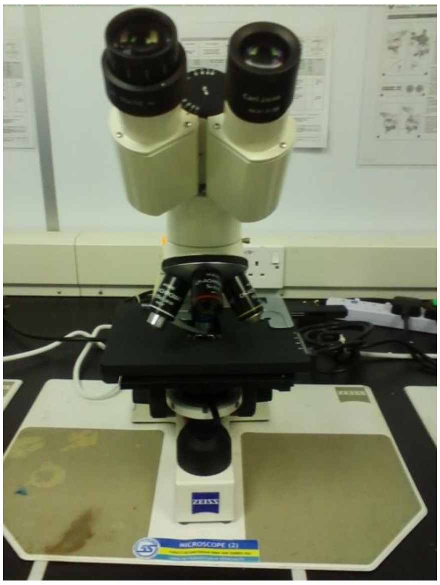

Figure 4: Microscope used for analysing the morphology of the samples

3.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The sample was scanned using Nicolet Avatar 370DTGS in the analytical lab. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. Next, it was compressed into a thin pellet which can be analysed using FTIR.

Figure 5: FTIR device for analysing functional group of the samples

3.2.3.3 CHNS Analyser

This device is used for the rapid determination of carbon, hydrogen, nitrogen and sulphur in organic matrices and other types of materials. The analysers are often constructed in modular form such that they can be set up in a number of different configurations to determine, for example, CHN, CHNS, CNS or N depending on the application. The result received will be the percentage of the elements appeared in the sample.

Figure 6: CHNS Analysis (P. Stevanato et. al., 2014)

3.3 Methodology

3.3.1 One-Stage Aqueous Dispersion Polymerization

For one-stage aqueous dispersion polymerization (ADP), all the monomers, initiator, stabilizer and co-stabilizer was dissolved in ethanol in a 500 mL four-necked, round-bottomed flask equipped with overhead stirrer, condenser and a gas inlet. The solution was bubbled with nitrogen gas for 15 minutes after the homogeneous solution had formed at room temperature. The reaction flask was placed in a heating block at 70 °C by using temperature controller and stirred mechanically using three-bladed metal stirrer at 150 rpm. The reaction was carried out for 24 hours. The particles that had been obtained were washed for one time in ethanol and one time in methanol. Then, the particles were filtered by using vacuum filtration on a 0.22 µm nylon membrane filter and dry overnight in oven at 40°C.

3.3.2 Two-Stage Aqueous Dispersion Polymerization

For a two-stage aqueous dispersion polymerization, all the stabilizer, co-stabilizer, initiator and styrene, half of the VBC and half of the ethanol followed by water (ratio 2:1) was added into 500 mL four-necked, round-bottomed flask fitted with an overhead stirrer, condenser and nitrogen inlet. Once the solution became homogeneous solution which was formed at room temperature, the solution was bubbled with nitrogen gas at room temperature for 15 minutes. The flask was placed into the heating mantle at temperature of 70 °C and stirred mechanically using three-bladed metal stirrer at 150 rpm. EGDMA and the second half of the VBC were dissolved into the second half of the ethanol at 70°C under nitrogen gas. After one hour of beginning of the polymerization, the hot solution that contained of EGDMA and VBC were added into the reaction flask. The reaction was continued for further 23 hours. The particles were filtered using vacuum filtration on a 0.22 µm nylon membrane filter and dried the sample overnight in vacuum oven at 40 °C.