

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

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ABSTRACT

In this work, synthesis and characterization of gel-type polymers *via* non-aqueous dispersion (NAD) was studied. The beaded polymers were produced *via* NAD have broad range of potential applications in many distinct area such as solid-phase extraction (SPE), chromatography, catalysis, *etc.* In this study, the experiment was divided into two sections namely one-stage NAD polymerization and two-stage NAD polymerization. For one-stage NAD polymerization, all the monomers, initiator, stabilizer and co-stabilizer namely styrene, benzoyl peroxide, Triton X-305, and poly (N-vinylpyrrolidone) (PVP), respectively were dissolved in ethanol in a 500 mL four-necked round bottom flask equipped with an overhead stirrer, condenser and a gas inlet. Then the reaction flask was placed on a heating mantle at 70 °C and stirred mechanically at 125 rpm and the reaction was allowed for 24 hours. The particle obtained was washed with ethanol and methanol, then it was filtered using vacuum filtration on a 0.22 µm nylon membrane filter and dry overnight in vacuum at 40 °C. The results obtained were analyzed using optical microscope, CHNS analysis and Fourier-transform infra-red spectroscopy (FTIR). The sample contained 78.386 % of Nitrogen, 87.300 % of Carbon, 8.113% of Hydrogen and 0.24% of Sulphur. Nitrogen content was high due to the impurities and contamination from the surrounding environment and also due to PVP may have not completely dissolved during the polymerization which contributed to nitrogen content in particles. FTIR results shown that the polymer belongs to alkene group thus, C=C and C=O bonds portrayed that the crosslinking agent, EDGMA was successfully incorporated in polymers. The polymer also contained C-H₂ bond, belongs to the alcohol group. Based on these results, the gel-type poly(styrene-co-EDGMA) polymer was successfully synthesised *via* non-aqueous dispersion (NAD) polymerization.

Keywords: gel-type polymers, non-aqueous dispersion polymerization, monodisperse

ABSTRAK

Kajian ini mengenai sintesis dan perincian tentang pembentukan polimer gel melalui gel pempolimeran tidak akueus. Polimer manik yang dihasilkan melalui pempolimeran tidak akueus mempunyai aplikasi yang berpotensi tinggi untuk digunakan dalam pelbagai bidang antaranya pengestrakan pepejal-cecair, kromatografi, pemangkinan dan sebagainya. Kajian ini menghasilkan polimer manik, taburan bersaiz kecil, polimer sekata berbagai jenis saiz micron iaitu 3 hingga 5 μm ukur lilit serta pertambahan berskala. Dalam kajian ini, ia merangkumi 2 bahagian iaitu fasa pempolimeran peringkat pertama tidak akueus dan pempolimeran peringkat kedua tidak akues. Bagi peringkat pertama, styrene, benzoyl peroksida, Triton X-305 dan poly(N-vinylpyrrolidone) (PVP) dilarutkan di dalam etanol di dalam kelalang tindak balas bersaiz 500 mL bersama pengacau, kondenser dan saluran gas. Kelalang tindak balas diletakkan di atas pemanas besi bersuhu 70 °C dan dikacau secara mekanikal pada kadar 125 pusingan per minit dan dibiarkan selama 24 jam. Partikel yang terhasil dibilas dengan methanol dan etanol, selepas itu ia di tapis menggunakan pam vakum di atas penapis membran nylon bersaiz 0.22 μm dan dibiarkan kering semalaman di dalam ketuhar pada suhu 40 °C. Partikel yang terhasil di analisa dengan menggunakan mikroskop optik, CHNS analisa, dan Fourier-mengubah infra-merah spectroscopy (FTIR). Berdasarkan keputusan yang diperolehi, sampel untuk 1 jam penundaan agen penyambung, mengandungi 8.39 % Nitrogen, 87.30 % Carbon, 8.11 % Hydrogen and 0.24 % Sulfur. Kandungan nitrogen adalah tinggi disebabkan kehadiran partikel asing dan pencemaran daripada keadaan sekitar dan mungkin disebabkan oleh PVP tidak melarut sepenuhnya semasa pempolimeran dimana ia meyumbang kepada kandungan nitrogen dalam partikel. Keputusan FTIR menunjukkan polimer berada di kumpulan alkene, C=C dan C=O ikatan menunjukkan agen penyambung EDGMA berjaya dimasukkan di dalam partikel. Polimer juga mengandungi C=H₂ ikatan, yang menunjukkan kumpulan itu tergolong dalam kumpulan alkohol. Berdasarkan keputusan di atas, polimer jenis gel melalui pempolimeran tidak akueus antara styrene dan EDGMA telah berjaya disintesis.

Kata kunci: polimer jenis gel, pempolimeran tidak akueus, monodisperse

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LIST OF ABBREVIATIONS

AIBN	2,2-Azobisisobutyronitrile
CBr ₄	Carbon tetrachloride
CPS	Crosslink polystyrene
DCE	Anyhydrous 1,2-dichloroethane
EGDMA	Ethylene glycol dimethylacrylate
FTIR	Fourier- transform infra-red spectroscopy
HPLC	High-performance liquid chromatography
KBr ₄	Potassium bromide
NAD	Non-aqueous dispersion
PS	Polystyrene
PTFE	Poly(tetrafluoroethylene)
PVP	Poly(<i>N</i> -vinylpyrrolidone)
SEM	Scanning electron microscopy
SPE	Solid phase liquid extraction
VBC	4-vinylbenzyl chloride

1.0 INTRODUCTION

1.1 Motivation and statement of problem

There are few types of polymerization which are bulk polymerization, solution polymerization, suspension polymerization and emulsion polymerization. The disadvantage of bulk polymerization is problem with heat transfer during the process. For suspension polymerization, the particle size formed depends on droplet size and rate of agitation, therefore the particle size is proportional to the droplet size as well as are the agitation is crucial in suspension polymerization when the viscosity within the bead increases, the reaction rate increases tremendously and leads to a surge in heat generation. While for solution polymerization, the product formed is not uniform and broad range particles which are 50-150 μm and it was not monodisperse because of extensive agglomeration of the polymer during the polymerization technique (J. M. J. Fréchet, et al., 1998). Dispersion polymerization is an interesting technique for producing micron-sized monodisperse polymer particle in a single batch process. The advantages for dispersion polymerization are the particles were formed in micron sized range approximately 3 μm (M. A. Winnik, et al., 2006). In addition, dispersion polymerization can be scaled up, produced in 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.

Up to now, precursor polymeric materials particles which are produced *via* suspension polymerization, emulsion polymerization and also precipitation are also commonly used in the preparation of hypercrosslinked polymers. Instead of that, dispersion polymerization also has been investigated widely as an alternative method for preparing monodisperse polymeric particles in the micron-sized range in single step (V. A. Davankov, et al., 2009; D. Horak, 1999; T. Wang, et al, 2009; J. McNulty, 1990) because it meet the requirements that are needed in various applications such as separation application in high performance liquid chromatography (HPLC) (I. M. Warner, 2000).

Thus, narrow particles size distributions become important in the applications area in addition to the need for high specific surface area.

Various aspects were explored with a view to study the best operating parameters that may influence the quality of the final product. Several parameters such as, solvent system, swelling time, stirring and crosslinker content were focused on.

1.2 Problem statement

In non-aqueous dispersion (NAD) polymerization process, problem arise when a 'problematic' monomer is used, which intrude the particles nucleation resulting broad particles size distribution to irregular particles and leads to coagulation. Therefore, a two-stage method was introduced involving the delay addition of the problematic co-monomer after the nucleation stage would resolve the problem (M. A. Winnik, et al., 2006).

1.3 Objectives

The following are the objectives of this research:

- To synthesis and characterize gel-type polymers using one-stage polymerization and two-stage polymerization *via* non-aqueous dispersion (NAD) polymerization.
- To compare the effectiveness two-stage NAD polymerization methodology by manipulating the synthesis condition by using different delay time addition of crosslinker after the initiation of polymerization.

1.4 Scope of this research

The following are the scope of this research:

- i) Synthesis polystyrene using one-stage polymerization and using two-stage polymerization.
- ii) Characterize particles of one-stage and two-stage product by using FTIR and CHNOS analysis.
- iii) Make comparison between one-stage and two-stage NAD polymerization methodology.

1.5 Main contribution of this work

In this work, the contribution was able to measure the effectiveness of the two-stage methodology. Besides that, the optimum conditions were able to find in order to get the desired product by manipulating parameters by using different delay time of the addition of crosslinker after the initiation of polymerization. These parameters were manipulated in two-stage dispersion polymerization which enhanced the performance and characteristics of the polymers. The particles produced were much sophisticated in terms of micron size, narrow and uniform in size.

1.6 Organisations of this thesis

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

Chapter 1: Gives an introduction which covers the motivation, problem statement and scope of the work. A brief introduction regarding this work was included at the beginning of chapter to gives a clear picture on the field that were focused on.

Chapter 2: Provides a description of the applications and fundamental of dispersion polymerization. General description flow of the processes was included. The chapter also provide a brief discussion of the advanced experimental available for dispersion polymerization.

Chapter 3: Gives a review of the materials and methodology description. The methodology flow chart was also included significantly to show a clear and thorough process.

Chapter 4: Devoted to preliminary results and discussion which were focus on non-aqueous dispersion polymerization. All findings and results were tabulate and analysed in the form of graph and chart. The explanation of the findings was also included.

Chapter 5: Draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

2.0 LITERATURE REVIEW

2.1 Overview of Polymerization

Polymerization can be divided into categories namely, addition polymerization and condensation polymerization. The addition polymerization or conventionally known as chain growth, 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 as by products for examples water and methanol compared to addition polymerization add molecules on the unsaturated monomers backbone. The examples of free radical polymerization methods are atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer agent polymerization (RAFT), reverse iodine transfer polymerization (RITP), free radical polymerization (FRP) and others. This paper was focus on standard the free radical polymerization as the polymer formed by the addition of free radical building blocks onto free radical sites. Therefore, the polymer chains grow rapidly as the addition continues in the chain polymerization mechanism. There are various mechanisms of polymerization such as bulk polymerization, emulsion polymerization, dispersion polymerization and precipitation polymerization.

2.1 Atom transfer radical polymerization (ATRP)

ATRP was also known as transition-metal-catalysed radical polymerization. This technique is the released and captured of the chain radical through single electron transfer process which involving a transition metal and organic halide. The effectiveness of RAFT depends on the nature of the organic halide ability to modify the reactivity of additional free radical. Besides that, the nature of the monomer and environment of polymerization were also affecting the technique (A. Ravve, 2012). The flaws of ATRP are sensitive polymerization environment, highly pure reagents usage and limited number of monomer that can be used (D. Nystrom, 2008).

2.2 Reversible Addition-Fragmentation Chain Transfer Agent Polymerization (RAFT)

RAFT technique was one the first study of controlled radical polymerization. It is actually a degenerative transfer whereby it was proposed to overcome inefficient fragmentation. RAFT techniques replace the electron donating group by an electron neutral group that increases degenerative transfer rate. The efficiency of this method highly depends on the structure of the alkyl precursor.

2.3 Reverse Iodine Transfer Polymerization (RITP)

RITP is a reversible activation-deactivation of the polymer chains, which depends on the strong radical roaming properties of molecular iodine I_2 , to form the iodinated transfer agents *in situ*. The advantages of RITP are it competently controls the molecular weight and the structure of the polymer (P. L. Desmazes, et al., 2013). Besides that, this technique applied in designing copolymers with rare chain microstructures such as gradient copolymers of complex architecture and well-defined graft polymers. RITP is widely used in the application of *ab initio* emulsion and miniemulsion polymerization (B. Boutein, et al., 2007).

2.4 Free Radical Polymerization (FRP)

Conventional radical polymerization most common used in commercial products, using a chain-growth mechanism. Free radical can be describes as a groups of very reactive, short-lived components that consist of one or more unpaired electrons. These electrons form a chain-reaction mechanism that consists of initiation, propagation and termination.

The advantages of FRP are low monomer conversion high molecular weight could be obtained, in addition unlike condensation polymerization, FRP does not produce any by-products. Furthermore, FRP technique was widely used because the initiator can be produced in industrial-scale.

Many works and research have been done by using the technique of FRP. For example, the research of preparation of cross-linked poly(methacrylate) microparticles by solution free radical polymerization by F. Rouzeau, and co-workers. The various poly (acrylate) was produced using FRP produced nanoparticles polymer with high degree of polymerization (F. Rouzeau, et al., 2007). Advanced research have also done by using FRP, for example, Teare and co-workers have successfully initiated radical polymerization from the free radicals present onto the surface of anhydride maleic-based, poly(propylene) fumarate (PPF) (Teare, et al., 2013). The advantage of the free radical reactivity is related to the extended lifetime of the radicals induced on the polymer. The process is called resonance phenomenon, it was actually extend the life span of the short lived radical.

2.5 Overview of Bulk Polymerization

Bulk polymerization or known as mass or block polymerization is the polymerization between monomer and initiator. The advantages are high yield of polymer with high purity. On contrast, despite its high yield, the polymer produced is said to be in high viscosity thus makes it challenging to remove heat upon polymerization. (R. J. Young, et al., 2011). The result from this polymerization produced polymer with unreacted initiator and unreacted monomer, thus lead to impurities. Bulk polymerization products were often use in moulding industry where it involves thermosetting compounds.

2.6 Overview of Emulsion Polymerization

Emulsion polymerization is an example of heterogeneous polymerization, which consist three elements, namely monomer, initiator and water. These elements would form suspension where the polymer formed in latex form. The size of a polymer particle ranges from 0.05 to 5 μm . This type of polymerization cannot be run in continuous mode, but it is said that this method overcome the heat control and low degree polymerization. The disadvantage is water-soluble emulsifiers are used, thus making it difficult to demolish from the polymer and might leave little degree of water sensitivity (A. Ravve, 2012). Direct usages of emulsion polymerization final products are paints and coatings.

2.7 Overview of Precipitation Polymerization

As for precipitation polymerization, it is a polymerization of monomer and initiator with water, which act as the medium of heat removal. These synthesise produced suspended bead with the aided of suspending agent such as gelatin and polyvinyl alcohol (PVAL). The polymer produced range from 0.01 to 0.5 cm was mainly used for polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(acrylonitrile) (PAN) production (H. R. Kricheldorf, et al., 2005). These types of polymers are categorized as clear and amorphous solid.

2.8 Overview Dispersion Polymerization

This paper presents the experimental studies of dispersion polymerization, a very auspicious technique for the production of monodisperse particles in the micron-size range. It has been studied extensively as an alternative approach for preparing monodisperse polymeric particles in the micron-sized range in single step (M. A. Winnik, et al., 2006). Beside, this technique applied in the radiation-induced dispersion polymerization of polystyrene particles (PS) in ethanol/water media which results in particles in range of 0.62 to 2.13 μm (Z. Zhang, et al., 2009). Dispersion polymerization contributed to polymer of controlled molar mass and particle morphology and it can be scaled up (B. H. Lee, et al., 2007).

2.8.1 Introduction

In the dispersion polymerization process, problems arise when a 'problematic' monomer is used therefore it is difficult to control such as the crosslinking agent-intrude with particles nucleation. It also results in broad particle size distribution to irregular particles and leads to coagulation. Based on Winnik's study (M. A. Winnik, et al., 2006), a two-stage methodology was introduced involving the delay addition of the problematic monomer after the end of nucleation stage would resolve the problem. In this paper, the dispersion of styrene with ethylene glycol dimethacrylate (EGDMA) were investigated using ethanol as a dispersion medium. The initiator used was 2, 2-azobisisobutyronitrile (AIBN), poly(*N*-vinylpyrrolidone) (PVP) as a stabilizer and ethylene glycol di-methacrylate (EGDMA) as a crosslinker (M. A. Winnik, et al., 2006).

Another example of study on two-stage dispersion polymerization, is atom transfer radical dispersion polymerization (ATRP) of styrene in ethanol by K. Min and K. Matyjaszewski, 2007, was successfully carried out with the formation of uniform sized particles. This was accomplished by using a two-stage polymerization technique, in which the first stage involves a standard free radical polymerization and the second a controlled by living radical polymerization. It has been widely accepted that the key issue for preparation of uniformly sized colloidal particles is a short nucleation stage (K. Min, et al., 2007).

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 broad particle size distribution. Furthermore, the nucleation stage in dispersion polymerization is very sensitive to variations in reaction components or conditions.

Figure 2.1 show the images of the polystyrene (PS) particles prepared by one-stage polymerization (batch) method with different values of acrylic acid (AA) and by two-stage dispersion polymerization method. The main highlight from the figure was the size and particles distribution of the two-stage preparation in Figure 2.1(c) was more uniform and evenly distributed compared to the one-stage method in Figure 2.1 (a) and (b). The used of poly(acrylic acid) (PAA) was because of its solubility in ethanol, and copolymers of AA with styrene are likely to be more soluble in ethanol than PS itself. Therefore, the critical molecular weight at which the copolymer begins to precipitate was larger than PS and possibly the rate of the adsorption of the stabilizer-grafted copolymers PVP with poly(styrene-co-AA) on the particles decreases. Eventually, the rate of particles formation and the amount of adsorbed grafted PVP decrease, lead to longer nucleation time which contributed to increases in particles size and broad size particles (McNulty, et al., 1990).

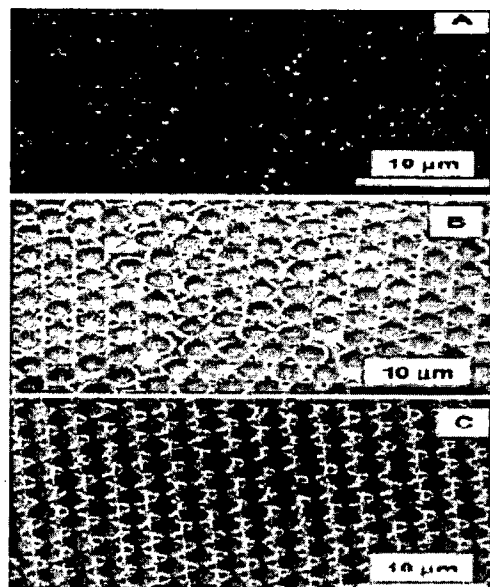


Figure 2-1: SEM images of polystyrene, (PS) particles prepared by different processes (a) one-stage method without acrylic acid (AA), (b) one-stage method with 2.2% AA and (c) two-stage method with 2% AA (M. A. Winnik, et al, 2009)

Research done by K. Min and co-workers on synthesizing a two-step batch dispersion polymerization using atom transfer radical dispersion have contributed to uniform sized polymer beads ranging from 0.5 to 10 μm (K. Min, et al., 2007) . Based on Figure 2-2, the particles sizes were differ for each type. The particles size distributions broadened clearly can be seen to a certain degree with the participation of the components of an ATRP in the reaction media. The disadvantages of ATRP are the chains grow all in at the same rate the time indicated for the preparation of high molecular weight is longer than that in free radical polymerization (FRP). This slower controlled polymerization process directly influences notably extends, the nucleation stage in a dispersion polymerization that will lead to broad particle size distribution.

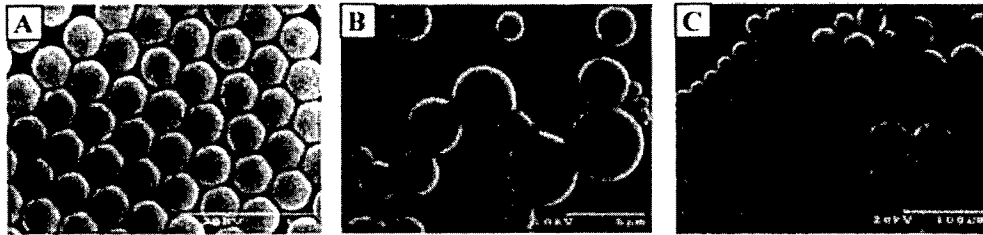


Figure 2-2: SEM images of polystyrene prepared by (a) conventional dispersion polymerization, (b) one-batch direct ATRP, and (c) one-batch reversed ATRP (K. Min, et al., 2008)

2.8.2 Previous study on Two-stage Dispersion Polymerization

The effectiveness of two-stage dispersion polymerization method was also discussed by Winnik, et al., 2006. The study of free-radical dispersion polymerization of styrene was successfully carried out in ethanol, in the presence of carbon tetrachromide (CBr_4) as chain transfer agent. All the monomers, half of styrene, stabilizer and initiator were added into the reaction flask, using ethanol as solvent. The key point used in the study was delaying the addition of problematic co-monomer after the nucleation stage was over which is exactly one hour after the homogeneous solution was formed. As a result, it have produced particles of lower molecular weight, spherical uniform size of approximately 2 μm (M. A. Winnik, et al., 2006) and very narrow size distributions.

Another example of two-stage polymerization is by B. Jiang, et al., 2001 studies on monodisperse CPS prepared by the dispersion polymerization method (B. Jiang, et al, 2001). The particle obtained has a diameter of 1-10 μm when divinyl benzene (DVB) (S. E. Lyubimov, et al, 2009).

2.9 Summary

Based on previous discussion, the polymerization synthesis was done based various researchers such as Winnik, B. Jiang, K. Min. Overall the size of particle is said to range from 2 μm (M. A. Winnik, et al., 2006) of particle diameter and also from 0.5 to 10 μm diameter (K. Min, et al., 2008). Free radical polymerization was mainly used in industrial applications such in HPLC (Figure 2.3) because of its advantages such as continuous operating mode, easy to scale up and high molecular weight at low monomer conversion. The polymerization technique chosen in this study was non-aqueous dispersion polymerization. This technique is commonly used as it produced micron-sized particles, uniform range of particles and evenly distributed polymer.

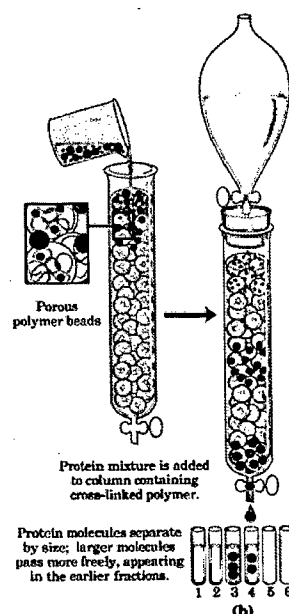


Figure 2-3: An example of application of porous polymers beads in chromatography (Isiah M. Warner, 2000)

3.0 MATERIALS AND METHODS

3.1 *Non-Aqueous Dispersion Polymerization (NAD)*

Polymerization was performed in a four-necked, round-bottomed flask fitted with a flange, condenser, and overhead stirrer fitted with a metal stirrer with three blades. The round-bottomed flask was immersed in a heating mantle. The final products obtained were filtered using vacuum filter and wash one time using ethanol and methanol respectively.

3.2 *Materials*

The reagents used for the polymer synthesis are styrene reagent plus contains 4-tert-Bu4972 (99%), methanol (99.8%), toluene anhydrous (99.8%), ethylene glycol dimethylacrylate (EGDMA) (98%), ethanol (95%) grade, poly(N-vinylpyrrolidone) (PVP) 55 ($M_w \sim 55\,000$) was used as stabilizer. Triton X-305 (70%) was used as co-stabilizer, benzoyl peroxide (98%) was used as initiator. All the materials were supplied by Sigma-Aldrich company.

3.3 *Analysis*

3.3.1 Optical Microscope

Optical microscope was used in order to visualise the product particles at the end of the reactions. A few drops of polymer dispersion were deposited onto a microscope slide and the particles imaged once the solvent had evaporated.

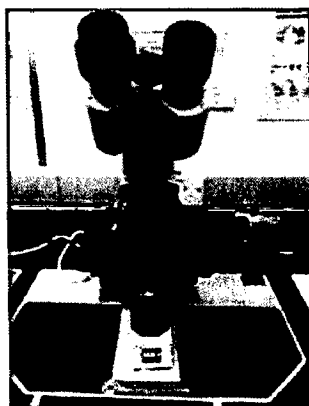


Figure 3-1: Optical microscope Carl Zeiss Model 32080 6398

3.3.2 CHNS Analysis

The sample was sent to CHNSO macro elemental analyzer, brand Elementar, model Vario Macro Cube in the Central Lab, UMP. In-house method was used for simultaneous determination of Carbon, Hydrogen, Nitrogen and Sulphur. In the analysis, sample was burned in an excess of oxygen and various traps, collecting the combustion products carbon dioxide, water and nitrogen oxide. The mass of the combustion products was used to calculate the composition of the unknown sample.

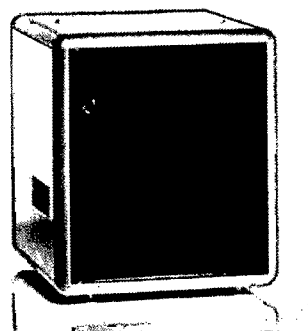


Figure 3-2: CHNS Analyzer, Model Vario Macro Cube (www.Elementar.com)

3.3.3. Fourier-Transform Infra-Red Spectroscopy (FTIR)

The sample was scanned using Nicolet Avatar 370 DTGS 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.



Figure 3-3: FTIR Model Nicolet Avatar 370 DTGS

3.4 Methodology

3.4.1 One-Stage Non-Aqueous Dispersion (NAD) Polymerization

For one-stage non-aqueous dispersion (NAD) polymerization, 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 a three-bladed metal stirrer at 150 rpm. The reaction was carried out for 24 hours. The particle that had been obtained was washed 1 time in ethanol and 1 time in methanol. The particles then was filtered using vacuum filtration on a 0.22 µm nylon membrane filter and dry overnight in oven at 40 °C.

3.4.2 Two-Stage Non-Aqueous Dispersion (NAD) Polymerization

For a two-stage aqueous dispersion polymerization, all the stabilizer, co-stabilizer, initiator and styrene, half of the EDGMA and half of the ethanol was added into 500 mL four-necked, round-bottomed flask fitted with an overhead stirrer, condenser and nitrogen inlet. Once a homogeneous solution formed at room temperature, the solution was bubbled with nitrogen gas at room temperature for 15 minutes. The flask was placed into a heating mantle set at 70 °C and stir mechanically by using a three-bladed metal stirrer at 150 rpm. The second half of EGDMA was dissolved in the second half of the ethanol at 70 °C under nitrogen. After one hour of starting the polymerization the hot solution that contains EGDMA dissolved in ethanol was added into the reaction flask. The reaction was continued for a further 24 hours. Then, the particles obtained was filtered using vacuum filtration on a 0.22 µm nylon membrane filter and dried overnight in vacuum oven at 40 °C.

The experimental set-up shown in Figure 3.4 was done in a fume hood. A heating mantle was placed on top of four-necked, round-bottomed, reaction vessel of 500 mL volume. A metal clip was used to secure the system. NAD polymerization is a highly sensitive technique and it is crucial to avoid the loss of solvent. Also, a condenser was fitted to the four-necked flask. An overhead three-bladed metal stirrer was used to agitate the system. The position of the stirrer was important to ensure the system is

agitated gently and efficiently. As precautions, if the stirrer is in contact with the bottom of the reaction flask, the particle quality is compromised due to abrasion, in addition if the metal-stirrer blade is set too high, the agitation is inefficient.



Figure 3-4 : Experiment set up for one-stage NAD polymerization

The one-stage NAD polymerizations, was performed under a nitrogen atmosphere. A pressure regulator was used to provide a controlled flow of nitrogen into the NAD polymerization system. At each neck of the flask were sealed with aluminium foil to prevent air from entering the nitrogen circuit. The temperature was controlled and regulated using temperature controller and temperature probe.

The preparation of polystyrene was done using styrene as the monomer, Triton-X305 and ethanol were used without further purification. Based on Table 3.1, styrene (10 g) benzoyl peroxide luperox A89 (0.4 g), PVP (1.6 g) and Triton X305 (0.055 g) were added to the reaction vessel with a volume of 500 mL. Next, 37.31 mL of ethanol was added as solvent and the reaction mixture was stirred at approximately 150 rpm. Nitrogen gas was regulated with pressure regulator and was allowed to enter the reaction vessel to purge the air. Once, a homogeneous solution had formed, after approximately 15 minutes, the reaction was heated to 70 °C using heating mantle and it was maintained using temperature controller. The application of the heat caused the initiator to decomposed, initiating free radical polymerization.

The reaction was left for 24 hours, then the heat was removed and the product particles were inspected under an optical microscope. The polymer suspension was transferred into conical flask and washed 1 time in ethanol and methanol, respectively. The solid product was filtered using a 0.22 μm using vacuum filtered pump. The product then was dried overnight at 40 $^{\circ}\text{C}$ in a vacuum oven in analytical lab.

Table 3-1: Recipe for one-stage and two stage method of NAD polymerization.

Materials	One-stage method (g)	Two-stage method (g)	
		One-stage	Two-stage
Styrene	10	10	not added
EDGMA	0.1	0.05	0.05
Benzoyl peroxide	0.4	0.4	not added
Triton-X305	0.55	0.55	not added
PVP	1.6	1.6	not added