



Faculty of Resource Science and Technology

**SYNTHESIS AND CHARACTERIZATION OF POLYMERIC  
NANOPARTICLES AND THIN FILMS**

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# **SYNTHESIS AND CHARACTERIZATION OF POLYMERIC NANOPARTICLES AND THIN FILMS**

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(Resource Chemistry)

Faculty of Resource Science and Technology  
University Malaysia Sarawak  
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## DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of this or any other university or institution of higher learning.

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# Preparation and Characterization of Polymeric Nanoparticles and thin films

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## ABSTRACT

This project focuses on the synthesis and characterization of colloidal polypyrrole and starch-based microgels. The colloidal polypyrrole were synthesized through the chemical polymerization of pyrrole with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in aqueous solution of methycellulose. Colloidal polypyrrole were being characterized with respect to its particle morphology, particle sizes, stability, chemical structure and electrochemical properties. Starch-based microgels were synthesized in the water in oil emulsion using epichlorohydrin (ECH) as the cross-linker. These microgels were being characterized with respect to their morphology, particle sizes, pasting characteristic and chemical structure. Colloidal polypyrrole appeared to be globular in shape, 100-580 nm in diameter and readily formed aggregations in water. Starch-based microgels were observed to be spherical in shape and of much reduced granule size than native starches. Results of FTIR and UV-VIS showed that both colloidal polypyrrole and the starch microgel samples possessed very similar physical and chemical properties but distinctively different from their original materials. The RVA results showed significant decrease in viscosity of the cross-linked starch microgels as compared to that of the native starches.

Key words: Colloidal polypyrrole, starch-based microgel, chemical polymerization, cross-linking, epichlorohydrin.

## ABSTRAK

*Projek ini berfokus pada penyediaan dan pencirian bagi polipirol koloidal dan microgel kanji. Polipirol koloidal telah disintesis melalui tindak balas kimia pempolimeran pirol dan  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  dalam larutan metilselulosa. Polipirol koloidal telah dicirikan berdasarkan morfologi, partikel saiz, kestabilan, struktur kimia dan sifat-sifat elektrokimia. Mikrojel kanji telah disintesis melalui taut-silang pengemulsian secara air-dalam-minyak dengan menggunakan epiklorohidrin (ECH). Mikrojel-mikrojel ini telah dicirikan berdasarkan morfologi, partikel saiz, sifat pes dan struktur kimia. Polipirol koloidal menjadi dalam bentuk globular yang berdiameter 100-580 nm dan membentuk gumpalan dalam air. Mikrojel kanji didapati berbentuk sfera dan saiznya dikurangkan secara ketara berbanding dengan kanji asal. Keputusan FTIR dan UV-VIS menunjukkan bahawa kedua-dua polipirol dan sampel mikrojel kanji mempunyai sifat fizikal dan kimia hampir sama tetapi menunjukkan perbezaan yang ketara berbanding dengan bahan asalnya. Keputusan RVA menunjukkan kelikatan diturunkan secara mendadak selepas kanji ditaut silang daripada kanji asalnya.*

*Kata kunci: Polipirol koloidal, mikrojel kanji, pempolimeran kimia, taut-silang, epiklorohidrin.*

## 1. INTRODUCTION

Conductive polymers such as polyacetylene, polyaniline, polythiophene and polypyrrole are naturally conducting polymers due to their conjugated double bonds in the backbone of their macromolecule and this allows hopping of electrons in interchain. The field of conducting polymers has attracted the interest of many academic and industrial researchers (Li *et al.*, 2004). Polypyrrole is a five-membered heterocyclic compound and its monomer is pyrrole (Masuda & Asano, 2003). Polypyrrole varies in colour from pale yellow for the fully reduced (de-doped) form to black for the fully oxidized (doped) form. Polypyrrole generally is insoluble in water and common organic solvents and does not melt when introduced to heat but instead decomposes. This is due to a high degree of both ionic and covalent cross-linking (Reece, 2003).

Polypyrrole can be prepared by standard chemical or electrochemical polymerization techniques and its surface charge characteristics can be easily modified by changing the anion (X<sup>-</sup>) that is incorporated into the material during synthesis (Anon, n.d.). The electropolymerization is more preferred due to its better control of film thickness and morphology which makes them suitable for use in electronic devices. On the other hand, chemical methods are an attractive technique to obtain polypyrrole in a powdery form for commercial applications and offers mass production at reasonable cost (Can *et al.*, 2003). Moreover, polypyrrole performs significant advantages over other systems used to deliver an electrical stimulus, such as electromagnetic fields, external electrodes, and piezoelectric materials that have been shown to enhance nerve regeneration (Anon, n.d.). However, the brittleness or amorphous and low level of processability constitutes major obstacles to its extensive application. Several attempts have been made to prepare blends or composite

materials containing polypyrrole to improve its structural and physical properties (Migahed *et al.*, 2004).

Starch is one of Nature's most complex materials due to its characteristic structures over a wide range of distance scales and the heterogeneity of structure at all of these different distance scales within a single granule and in populations of granules (Gidley, 2001). Starch is the major carbohydrate used for energy storage and is widely distributed in seeds, roots and tubers as well as in stems, leaves, fruits and even pollen (Perez and Imberty, 1996). Moreover, starch is mainly used in food industries as a thickening, stabilizing, or gelling agent due to its inexpensive and abundant supplies (Ikeda *et al.*, 2001).

Native starch is composed of an amylopectin (70-80%) skeleton in an interpenetrating amylose (20-30%) matrix (Ikeda *et al.*, 2001). The ratio of amylose-amylopectin is specific for each type of starch. Amylose is a linear  $\alpha$ -1, 4-linked D-glucose chain while amylopectin is a highly branched molecule containing short chains of  $\alpha$ -1, 4-linked D-glucose chains with  $\alpha$ -1, 6-linked branches (Fasihuddin *et al.*, 1999). When dry native starch granules are suspended in water followed by heating, it can absorb water and swell to some range (Ikeda *et al.*, 2001). The compactness of the starches was found to be strongly affected by the equilibrium moisture content of the starches, which is dependent on the relative humidity of the atmosphere under which the powders were stored (Bos *et al.*, 1987).

The physical and chemical properties that are most important for starch in commercial applications are dispersion, gelatinization, pasting characteristic, chemical composition as well as physical structure of starch granule that may affect the water absorption, swelling power and solubility of the starch components (Ansharullah, 1997). Normally, the native

starch granules are insoluble in cold water, highly resistant to enzymic degradation and lack specific functional properties. In order to use the starch for industrial applications, the modification of starch is necessary to tailor the required functional properties (Ansharullah, 1997).

According to Spac (n.d.), tapioca is the seventh largest production of staple food in the world and it ranks third in the value of production in the tropics compared to sugarcane and rice. Tapioca gives a carbohydrate production which is about 40% higher than rice and 25% more than maize. As a result, tapioca is the cheapest source of calories for both human nutrition and animal feeding. The proximate chemical composition of tapioca starch are protein ~2.94%, fat ~ 0.88%, fiber ~ 2.94%, ash ~ 0.20% (Ansharullah, 1997). There are two main categories of tapioca, which names bitter (*Manihot palmata*) and sweet (*Manihot aipi*). For industrial purposes mostly the bitter variety is used because of higher starch content. Sweet tapioca is used for food because of taste and its dough forming ability (Spac, n.d.). In Malaysia, growing areas of sago starch covered more than 100,000 hectares (Ansharullah, 1997). Sago starch contains 10.6%-20.0% moisture content, 0.06%-0.13% ash, 0.10%-0.13% crude fat, 0.26%-0.32% fiber, 0.19%-0.25% crude protein and 24%-31% amylase (Fasihuddin *et al.*, 1999). The ratio of amylose and amylopectin for sago and tapioca starch is 27:73 and 17:83, respectively (Ansharullah, 1997).

In recent years, nanoparticles are becoming more significance and the technology of their production and uses is rapidly growing into an important industry. These materials have special physical and chemical properties due to their finite small size with dimension range of 1-100 nanometer (Tang *et al.*, 2000). Therefore they offer many potential applications in areas of chemistry, pharmacy, cosmetics, surface coating agents, textile sizing, paper coating agriculture, and biochemistry (Nakache, 2000). Nanoparticles possess different properties

from the bulk form because the specific surface areas of the finely divided form can be on the order of a million to several million times greater than that of the bulk form of that substance (Otterstedt & Brandreth, 1998). Besides, nanoparticles as polymer additives may have high loading requirements compared to traditional additive (Schmidt & Malwitz, 2003).

In this research, we wish to synthesis polymeric nanoparticles in the form of colloidal suspensions or microgels. The colloidal methods are known to be technologically simpler and economically more viable than direct manipulation of individual nano-objects. Moreover, this research will produce nanoparticles that may be suitable for fabricating various electrochemical devices with much reduced sizes but enhanced overall performances.

## **2. OBJECTIVES OF STUDY**

The specific objectives of this study are

- to prepare and characterize polypyrrole nanoparticles in the form of colloidal suspensions.
- to prepare and characterize the starch microgels from native starch sources (sago and tapioca starches).
- to prepare nanostructured polymeric thin films and evaluate their electrochemical properties.

### 3. LITERATURE REVIEWS

Hong *et al.*, (1997) had reported that polypyrrole colloidal particles can be synthesized in an emulsion system using water-soluble poly(vinyl alcohol) (PVA) as a stabilizer. Scanning Electron Micrographs showed the resulting polypyrrole blacks were comprised of basically with sub-micrometer particles (colloidal particles). Furthermore, the polypyrrole colloidal particles were distributed in a semi-interpenetrating network (semi-IPN) consisting of linear PAA ( $M = 2,000$ ) in crosslinked poly(acrylamide - methylenebisacrylamide) to produce a new type of composite of polypyrrole colloids and hydrophilic polymers. The weight ratio of polypyrrole in the composite was controlled in the range from 0.2% to 2.3%. This low amount of polypyrrole content caused the composite to be electrically non-conductive in dry state but become conductive when swollen by water. The polypyrrole colloids that can enhance proton transport in water-swollen polymer matrixes could be utilized to improve the humidity-sensing materials as well as proton-conducting electrolytes.

Bjorklund & Liedberg, (1986) has synthesized thin films of composite incorporating colloidal polypyrrole have maximum conductivities  $0.2 \text{ Scm}^{-1}$ . The conductivities of the film can be controlled by varying the several parameters which include concentration of pyrrole, chemical oxidant, and methylcellulose used in the synthesis. In this study, SEM micrographs have indicated that the composites in the solid state were composed of a globular polypyrrole phase embedded in flakes of methylcellulose.

One of the first examples of soluble and fusible liquid crystalline polypyrrole was reported by Chen *et al.* (2001). They also showed that the polymerization of polypyrrole using conventional electrochemical techniques would produce insoluble and infusible



products that show no liquid crystal phases. On the contrary, the soluble polypyrrole could be obtained with two pyrrole-based monomers substituted at the N-position with the mesogenic group 4-cyanobiphenyl. The mesogenic group is separated from the pyrrole moiety by an alkyl chain of either 3 or 11 methylene units length. Besides, the resulting polymer is a linear polymer with relatively low defect population or cross-linking. Moreover, Masuda & Asano (2003) has synthesized polypyrrole with different dopant by optimal the condition and improved the methods for electrochemical polymerization of pyrrole in the presence of dopant in water. The dopants that used in this study were sodium p-toluenesulfonate (PTS), sodium benzenesulfonate (BS), sodium 4-ethylbenzenesulfonate (EBS), sodium 4-n-octylbenzenesulfonate (OBS), sodium dodecylbenzenesulfonate (DBS) and tetraethylammonium p-toluenesulfonate (Et4NPTS). The electrical and spectra properties of these doped polypyrrole were studied.

Studies on colloidal templating of conducting polymers have been repeated recently (Ajayan *et al.*, 2003). Polypyrrole was grown potentiostatically from a solution of pyrrole in acetonitrile through a colloidal crystal composed of SiO<sub>2</sub> spheres with a mean diameter of 238 nm assembled on F-doped SnO<sub>2</sub>-coated glass, followed by removal of the colloidal template with aqueous HF (Sumida *et al.*, 2000; Ajayan *et al.*, 2003). Furthermore, macroporous polypyrrole, polyaniline, and polybithiophene films have been potentiostatically polymerized through a colloidal crystal assembled from 500nm and 750nm polystyrene spheres, on a substrate of gold-coated glass. The polystyrene template was then removed with toluene (Bartlett *et al.*, 2001; Ajayan *et al.*, 2003). In the most recent report, polypyrrole and polythiophene macroporous films were potentiostatically grown through colloidal crystals assembled from 150 nm and 925 nm polystyrene spheres, respectively, on glass coated with

indium tin oxide; the polystyrene was removed with tetrahydrofuran (Cassagneau & Caruso, 2002; Ajayan *et al.*, 2003).

Due to the poor processability of polypyrrole, several approaches have been taken to improve its properties. One of them is make composite or blend of conducting polymer and insulating polymer. A semiconducting pyrrole-styrene block copolymer film has been successfully synthesized by carried out an electrochemical copolymerization of pyrrole and styrene directly on the surface of the electrode in nitromethane. This copolymer product was a free-standing film and showed better mechanical properties and processability than those polypyrrole. Moreover, the composition and conductivity were found to vary with the ratio of pyrrole to styrene in the polymerization solution. The solvent that used in the experiment must be a solvent with strong polarity and weak nucleophilicity as it is effect greatly electrochemical copolymerization of pyrrole and styrene (Jin *et al.*, 2000).

Several methods for producing polymeric nanoparticles that are useful for drug delivery have been reported: in situ polymerization (Couvreur & Vauthier, 1991; Gibaud, 1998), spontaneous emulsification-solvent diffusion (Espuelas *et al.*, 1997; Yoo *et al.*, 1999) supercritical fluid (Jung & Perrut, 2001) and emulsification-solvent evaporation techniques (Zambaux *et al.*, 1998; Kwon *et al.*, 2001). Polymerization approaches have been popularly studied in recent decades. However the residual monomers as well as surfactant residues or initiator may lead to polymeric nanoparticles being unsuitable for some pharmaceutical preparations such as injectable dosage forms, because of their toxicity (Nakache *et al.*, 2000). Therefore, many applications in natural macromolecules or polymers are studied. For example, Nakache *et al.*, (2000) prepared 5-fluorouracil albumin nanoparticles ~600 nm in

diameter. These interesting particles release the drug with a delayed effect in the organism and that they retard its elimination. Thus the efficiency of the drug is improved and its toxicity may be controlled. Another example is the use of magnetic albumin particles loaded with doxorubicin for cancer therapy to reach the targeted organs (Nakache *et al.*, 2000).

According to Kwon *et al.*, (2002), poly (methyl methacrylate) (PMMA) nanoparticles containing coenzyme Q10 were prepared by using microfluidization and solvent evaporation method. Aqueous dispersions of polymer nanoparticles were prepared by an oil-in-water (O/W) emulsification-solvent evaporation technique. This method has been widely utilized for the production of polymer microparticles. In order to reduce the droplet size to a nanometer size range, high-pressure homogenization was performed with a microfluidizer (Kwon *et al.*, 2002).

Starch-based colloidal microgels were successfully prepared by emulsion cross-linking and combination of gelatinization and emulsion cross-linking (Dziechciarek *et al.*, 2002; Soest *et al.*, 1997). The microgels were negatively charged, spherical and amorphous. The particle size of the microgels ranged from 180nm up to 5µm that showed a large size distribution. To decrease the droplet size, the hydrophilic and hydrophobic phases had to be mixed in a short time at a high mechanical input (Dziechciarek *et al.*, 2002).

Others cross linkers than Epichlorohydrin have been used for cross linking of starches such as Diglycidylether type diepoxy compounds have been used as cross-linkers of dextran and hyaluronic acid, Diepoxybutane has been used for the cross linking of hyaluronic acid. Beside, 1, 2, 3, 4-diepoxybutane (DEB) or 1, 2, 7, 8-diepoxyoctane (DEO) as cross linker

have been used for the modification of native potato starches in the paper of Simkovic *et al.* (2003). The resulting cross linked starch was prepared initial at high speed stirring for the formation of emulsion of water-in-oil particles. Due to the presence of equal volumes of water and oil, the concentrations of starch, NaOH, and cross-linker were doubled. The result has shown that the smaller spherical particles were formed with DEB than with DEO under identical conditions (Simkovic *et al.*, 2003).

The most important chemical characterization of nanoparticles are elemental analysis, total solid, stabilizing agents and soluble salts while the physical characterization are size and size distribution, porosity, degree of aggregation, specific surface area, density, refractive index, and in a liquid medium: pH, viscosity, turbidity (Otterstedt & Brandreth, 1998). Many techniques have been used in the characterization of nanoparticles. This included x-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), Auger Electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), electron microscopy of different types, thermal and desorption spectroscopy (Otterstedt & Brandreth, 1998).

## 4. MATERIALS AND METHODS

### 4.1 Materials

Pyrrrole monomers, methylcellulose, and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as oxidant were used as delivered without further purification. Sago and tapioca starches were obtained from local market and were used in the preparation of hydrophilic phase. Epichlorohydrin (ECH) was used as the cross-linking agents. Sorbitan mono-oleate (Span 60) was used as the emulsifier and acetic acid as the emulsion breaking agent.

### 4.2 Methods

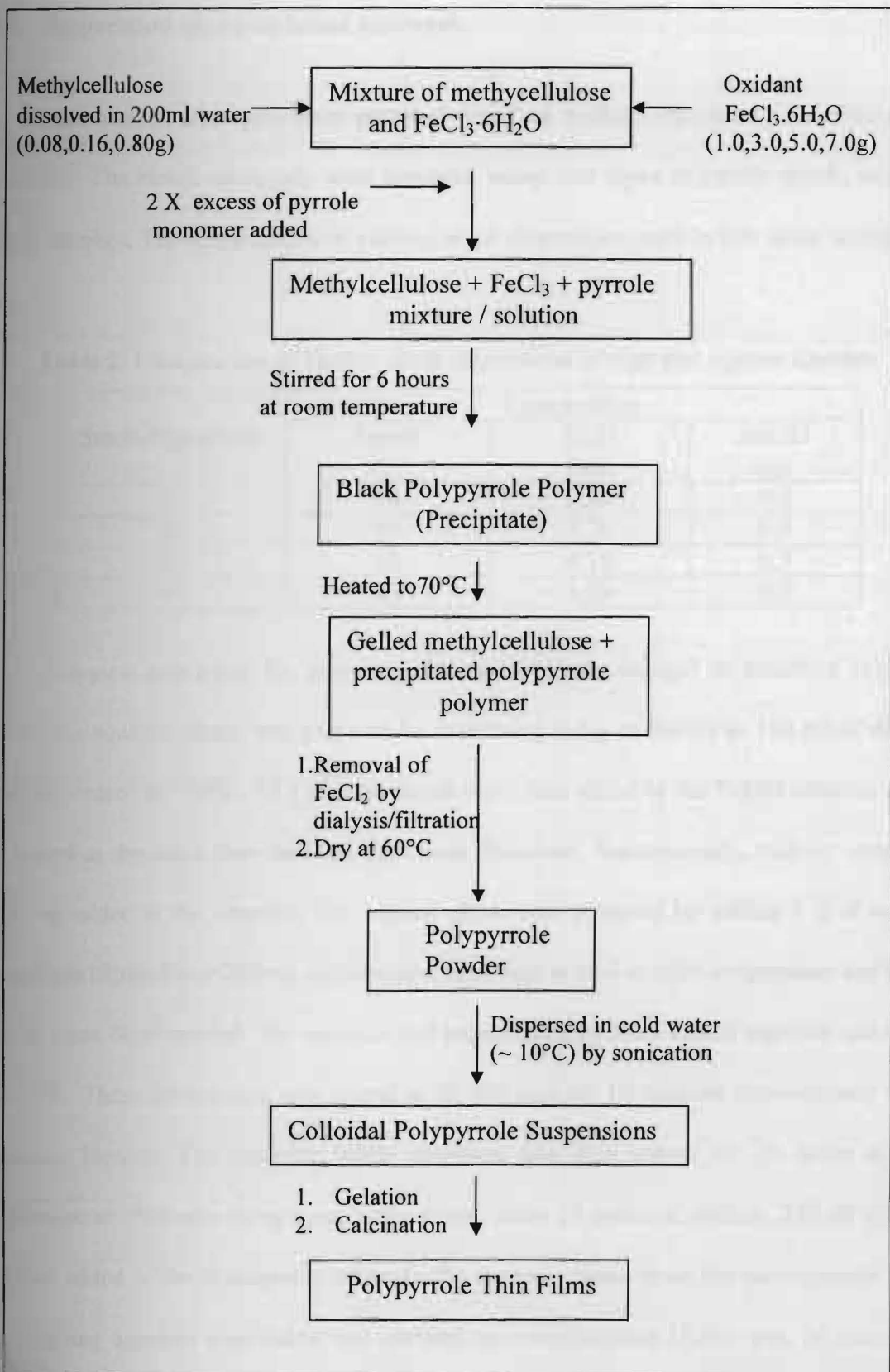
#### 4.2.1 Preparation of conducting polymer nanoparticles

Colloidal polypyrrole was prepared based on method reported by Bjorklund & Liedberg, (1986). The colloidal polypyrrole was prepared by oxidizing pyrrole in an aqueous solution of methylcellulose with varying amount of pyrrole monomer, methylcellulose and oxidant,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  as shown in Table 1.

**Table 1:** Synthesis parameters for the preparation of colloidal polypyrrole.

Sample	Synthesis Parameters		
	Pyrrrole (ml)	Oxidant, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (g)	Methylcellulose (g)
1	2.60	1.0	0.80
2	7.70	3.0	0.80
3	18.00	7.0	0.80
4	12.90	5.0	0.80
5	12.90	5.0	0.16
6	12.90	5.0	0.08

Colloidal polypyrrole samples were synthesized with  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  which was dissolved in 200 ml of  $\text{H}_2\text{O}$  containing different weight of methylcellulose. A two-fold excess of pyrrole monomer was then added and the mixture was stirred for 6 hours. The temperature of the mixture was then being raised to  $70^\circ\text{C}$  so that the methylcellulose gelled. The supernatant part of the reaction mixture ( $\text{FeCl}_2$  solution) was removed by dialysis method. Dialysis was carried out by placing the suspension (methylcellulose gelled + precipitated polypyrrole +  $\text{FeCl}_2$  solution) in a dialyzed tube (act as semipermeable) then submersed in a container of distilled water. All  $\text{FeCl}_2$  ions were allowed to pass through the dialyzed tube into the water while the polypyrrole nanoparticles and gelled methylcellulose were retained inside the tube. The distilled water was changed from time to time until the colour of the distilled water no longer become yellowish. Preparation step for the third, fourth and fifth samples were slightly different from those of first and second samples. Dialysis was not able to completely remove the  $\text{FeCl}_2$  ions due to the higher amount of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  used. The particle size of the polypyrrole in third, fourth and fifth samples were bigger than that of the first and second samples so that  $\text{FeCl}_2$  solution was removed by filtering under gravity with filter paper Whatman No 1, washed with hot water and followed washing with ethanol. The black powders obtained after drying at  $60^\circ\text{C}$  were being dispersed in cold distilled water ( $\sim 10^\circ\text{C}$ ) by sonication for as long as necessary to obtain colloidal polypyrrole suspensions. (Figure 1).



**Figure 1:** Flow diagram for the preparation of colloidal polypyrrole.

#### 4.2.2 Preparation of starch-based microgels

Starch-based microgels were prepared based on method reported by Dziechciarek *et al.*, (2002). The starch microgels were prepared using two types of native starch, sago and tapioca starches. The composition of various stock dispersions used in this study is shown in Table 2.

**Table 2:** Composition of various stock dispersions of sago and tapioca starches

Stock dispersions	Composition		
	Starch (g)	ECH (ml)	NaOH (g)
1	10	0.90	0.5
2	10	1.70	0.5
3	10	4.10	0.5
4	20	1.70	0.5

A typical procedure for preparing the starch-based microgel is described briefly as follow. The aqueous phase was prepared by dissolving 0.5 g of NaOH in 100 ml of distilled water and heated to  $\sim 50^{\circ}\text{C}$ . 10 g of sago starch were then added to the NaOH solution slowly and stirred at the same time until all the starch dissolved. Subsequently, various amount of ECH was added to the mixture. The organic phase was prepared by adding 5 g of sorbitan monooleate (Span 60) to 250 ml cyclohexane, and then heated at mild temperature and stirred until all Span 60 dissolved. The aqueous and organic phases were mixed together and heated to  $\sim 45^{\circ}\text{C}$ . Then, the mixture was stirred at 22,000 rpm for 10 minutes intermittently with a laboratory blender. The resulting white emulsion was then stirred for 20 hours at room temperature at 1100 rpm using a magnetic stirrer. After 20 hours of stirring, 250 ml of acetic acid was added to the emulsion to separate the aqueous phase from the non-aqueous phase. The resulting aqueous suspension was purified by centrifugation (5000 rpm, 30 mins) with distilled water and ethanol successively. The starch suspensions were then dialyzed at  $4^{\circ}\text{C}$  against freshly demineralized water until the conductivity of the resulting aqueous