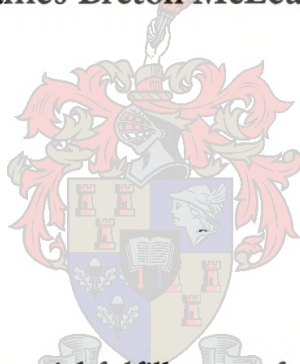


AN INVESTIGATION INTO THE
NANO-STRUCTURE SELF ASSEMBLIES
OF AMPHIPHILES AND THEIR FIXATION BY
POLYMERIZATION

By James Breton McLeary



This thesis is presented as partial fulfillment of the requirements for the
degree

MSc (Polymer Science)

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Stellenbosch
March
2000

Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

_____ on this day _____

James Breton McLeary

Summary

This thesis is a written record of an investigation into the self-assembly of organic monomers in amphiphilic solutions.

The polymerizable surfactant sodium 10-undecenoate was used alone and with different concentrations of styrene and methyl methacrylate monomers and phenyl acetophenone initiator to investigate single particle formation from a simple amphiphilic self-assembly. Reactions were carried out under either ultra-violet light or gamma irradiation.

It was shown that copolymerization between the surfactant and the monomers did not occur to any significant extent. This meant that inclusion of easily modifiable carboxyl functionalities in the polymer by incorporation of the carboxylate surfactant could not be quantified.

Star-like particles were found. The shape of the particles formed, was the result of surfactant self-assembly to create self-assembled particles rather than templating of polymeric material. Polymerization of the unsaturated surfactant particles occurred to low conversions only.

Analyses of formed particles were carried out using scanning electron microscopy, transmission electron microscopy, atomic force microscopy, field emission scanning electron microscopy and light microscopy for structure observation.

The techniques of energy dispersive analysis by x-rays, particle size analysis, differential scanning calorimetry, thermogravimetric analysis, Fourier transform infra-red analysis, nuclear magnetic resonance, small angle x-ray scattering and inductively coupled plasma (for counter-ion analysis) were used for the gathering of physical data.

Opsomming

Hierdie studie is 'n geskrewe rekord van 'n ondersoek van die self-aneensetting van organiese monomere in amfifiliese oplossings.

In die ondersoek is die polimeeriseerbare seep natrium 10-undekenoaat alleen en saam met verskillende konsentrasies van monomere en feniel asetofenoon gebruik om enkelpartikel formasie vanaf 'n eenvoudige amfifiliese templaar te ondersoek. Reaksies is uitgevoer onder of ultra-violet lig, of gamma bestraling.

Dit is bewys dat kopolimerisasie tussen die seep en die monomere nie in enige merkwaardige hoeveelhede plaasgevind het nie. Dit beteken dat insluiting van maklik veranderbare karboksiel funksionele groepe in die polimeer deur middel van insluiting van die karboksilaat seep nie meetbaar was nie.

Ster-vormige partikels is gevind. Dit is getoon dat die vorm van die partikels wat in die vroeëre werk verkry is, die resultaat van seep self-aaneensetting, eerder as templatering van polimeriese materiaal is. Polimerisasie van die seep partikels het net tot lae vlak van omskakeling plaasgevind.

Analise van die gevormde partikels is uitgevoer deur middel van skandeer elektron mikroskopie; transmissie elektronmikroskopie; atomiese kragmikroskopie; veldemissie skandeer elektron mikroskopie en ligmikroskopie vir struktuur bepaling.

Die tegnieke van energie dispersie analiese deur middel van x-strale; deeltjie grootte analise; differensiaal skandeer kalorimetrie; termogravimetriese analise; Fourier transformasie infra rooi analiese; kern magnetiese resonansie; klein hoek x-straal diffraksie en induktief-gekoppelde plasma (vir teenoorn analise) is gebruik om fisiese data te versamel.

Acknowledgements:

My thanks to all the people and organizations that made this investigation possible and especially to:

Professor Sanderson for initiating the project and for the guidance and endless ideas.

The Foundation for Research and Development for the financial resources to carry out this investigation.

The University of Cape Town **Electron Microscopy Unit** for their advice and the use of their instruments.

The University of Stellenbosch **Physics department** for the use of the Electron Microscopy facilities.

The University of Stellenbosch **Biochemistry department** for the ES-MS spectra.

The University of Pretoria **Electron Microscopy unit** for the use of the Field Emission Scanning Electron Microscope.

Hepro (High Energy Processing Cape (PTY) LTD) for the use of the Gamma source, at their expense.

The **Max Planck Institute for Colloid and Interface Science**, Teltow, for the SAXS images and the TEM images.

Charl F.J. Faul for the endless guidance and practical suggestions.

Marcelle Hodgson for her assistance with polymerizations and analyses.

My family and friends, both in Stellenbosch and in Pretoria, for all their support.

With a special thanks to my wife **Engela Elizabeth McLeary** who made it all worthwhile.

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List of Abbreviations

AFM	Atomic force microscope
amu	Atomic mass unit
CMC	Critical micelle concentration
Cocogem	Counterion coupled gemini
DDI	Distilled, deionized water
DNA	Deoxy-ribonucleic acid
DVB	Divinyl benzene
EDAX	Energy dispersive analysis by means of x-rays
EGDMA	Ethylene glycol dimethacrylate
ES/MS	Electrospray mass spectrometry
FESEM	Field emission scanning electron microscope
FT-IR	Fourier transform infra red spectroscopy
Kg	Kilogram
KGy	Kilogray
ml	Milliliter
mm	Millimeter
MMA	Methyl methacrylate
mS	Milli Siemens
Mw	Molecular weight
nm	Nanometer
NMR	Nuclear magnetic resonance spectrometry
pH	Negative logarithm of the hydrogen ion concentration
ppm	Parts per million
PMMA	Poly (methyl methacrylate)
SAXS	Small angle x-ray spectography
SEM	Scanning electron microscope
TEM	Transmission electron microscope
UCT	University of Cape Town
UP	University of Pretoria
UV	Ultra-violet
WAXS	Wide angle x-ray spectrometry

Chapter One

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Chapter One

1.1 Background to nano-shaping

1.1.1 Brief discussion of the nature and purpose of nano-shaping

A nano-particle is by definition a particle with dimensions of the order of nanometers.

A shaped particle is by definition a particle whose shape and formation has been in some way directed by some means.

These two definitions give us a broad outline of what shaping nano-particles is all about. Simply put, it is the formation of nano-particles with some form of shape guidance.

1.1.2 Why nanoshaping?

The simplest answer to the question is : the quest for knowledge and understanding.

The second, and probably more important answer, is: to eventually be able to have finer control of systems on a larger scale, such as micrometers and even millimeters.

The more advanced our knowledge of a system is, the more control we have, and the more cost effective the production of every product should be. Further, we should be able to create different products from the same starting materials.

Nano-structures of different shapes could possibly play a role in separations; in sensors for medicine and even in industrial applications and their importance is increasing due to demand for more effective products.

Many scientists are attempting to understand nano-chemical processes and are approaching the inherent problems of such small scales from different angles. The

approach to nano-shaping in this dissertation is both old and new. It can be considered as a different perspective on an old approach. As such, it carves a niche for itself between templating and surfactant aggregation processes and is completely novel.

1.2 Objectives of study

The main objective of this project was the formation of organic nano-particles and, if possible, to overcome difficulties described in the literature relating to the fixing of these structures by polymerization. This research project focused on the creation of unorthodox single polymeric particles of shapes other than spherical, preferably by a single step reaction in aqueous medium, unlike structures that emerge from traditional emulsion polymerization which are mostly spherical in shape. The idea was that, if successful, the formation of these particles would shed new light on what is obtainable, chemically, in the field of nano-structures taking us beyond spheroids in organic media.

As will be discussed in chapter 2 there are many literature references mentioning that some sort of control may be exercised over the formation of polymeric particles. These and results of earlier research carried out by fellow researchers that suggested that single particles might be formed in situ in aqueous media and led to the initiation this project.

The following materials were selected for use: the polymerizable surfactant sodium 10-undecenoate (as it is commercially available and there is much in the literature concerning its chemistry and polymerization tendencies); styrene and methyl methacrylate monomers; and divinyl benzene and ethylene glycol dimethacrylate as crosslinking agents for the fixation of structures.

The polymerizations were to be carried out in concentrated solutions, in which the surfactant, water and monomer mixture can be a microemulsion, a gel or even form liquid crystals. The compositions of the ternary mixtures were to be varied to determine if and how the different mixtures affected the nano-structure formation. Studying mixtures of this nature as a basis for nano-particle formation, aspects such as

the preparation of new shapes could be studied as a function of the lyotropic phase, conditions of polymerization, nucleation and crystallization of the surfactant.

Six aims were identified as goals for the achievement of the main objective:

Aim one was to investigate preparative variables and determine whether it was possible to form nano-structures from the polymerizable surfactant, sodium 10-undecenoate, in aqueous media, with or without the use of added organic monomers.

Aim two was to determine whether the surfactant sodium 10-undecenoate was fully polymerizable by of ultra-violet irradiation, using of a free radical initiator.

Aim three was to see if the surfactant sodium 10-undecenoate could be more completely polymerized through the use of gamma irradiation than with ultra-violet irradiation.

Aim four was, if nano-structures could be formed, to see if it was possible to achieve an in-depth nano-particle structural elucidation though the use of transmission electron microscopy or field emission scanning electron microscopy.

Aim five was to use light microscopy and small angle x-ray scattering to determine the presence of order in the solutions for the purpose of determining phase interaction with the structures.

Aim six was to see if the structures that could be made had significance in the context of templating of organic polymerizations in organic media, which has not yet been achieved by researchers.

Chapter Two

Concepts pertaining to nano-shaping

(A literature study)

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Chapter Two

Concepts pertaining to nanoshaping

(A literature study)

This is an introduction to the reasoning, approach and some of the concepts that were used in this investigation.

2.1 Liquid crystals

Liquid crystals are an integral part of our everyday lives yet few people actually understand their nature.

By definition, a liquid crystalline or mesomorphic phase (or mesophase, meso meaning in between) is a state of matter in which the degree of order lies between the almost perfect long range positional and orientational order present in solid crystals and the statistical long range disorder characteristic of isotropic or amorphous liquids and gases.¹

Liquid crystals can be divided into several classes and subdivisions, according to the type of order that is present and to the conditions required for the formation of the ordered phases. If the divisions are made according to the type of order then three major classes can be identified; they are smectic, nematic and cholesteric liquid crystals.

Smectic structures are stratified; the molecules are arranged in layers with their long axes approximately normal to the plane of the layers. Nematic structures have only a parallel, or nearly parallel, orientation. Cholesteric liquid crystals are observed mainly in cholesteryl derivatives² and, as such, are not relevant to our discussion.

If the divisions are made according to the conditions required for formation of the liquid crystalline phases, then we also have three major classes; they are lyotropic, thermotropic and amphitropic.

Lyotropic liquid crystals are those liquid crystals which are solvent induced. Thermotropic liquid crystals are temperature induced. Amphitropic phases are caused by both solvent and temperature effects (amphi meaning both).

Among the most well known examples of liquid crystals in small molecules (i.e. non-polymeric) are the large organic compounds, such as p-azoxy-anisole, which are used in liquid-crystal display devices.

2.2 Amphiphilic self assembly

What relationship exists between liquid crystals and emulsion polymerizations? This is dependent on the emulsifier or surfactant used in the polymerization.

Molecules that contain both a hydrophilic and a hydrophobic part frequently display a characteristically strongly cooperative association in aqueous solutions. These molecules are known as amphiphiles. The repulsion between the hydrophilic groups in this progressive aggregation process leads to aggregates, known as micelles. This term was first used by J.W. McBain in 1913³ to describe this aggregation by detergents and soaps (hereafter referred to as surfactants).

A micelle can be described as a spherical aggregate in which the polar (or hydrophilic or lipophobic) end groups are in contact with the polar phase while the non-polar (or hydrophobic or lipophilic) hydrocarbon tails are in the center of the sphere. The tails are in a liquid like state that is similar to that of the pure hydrocarbon phase. In the case of ionic surfactants the polar end groups form a repulsive double layer. Polar solvent molecules interact with the polar ends, providing stabilization. There are only five polar solvents in which micelle formation has been documented, namely: water, hydrazine, ethyl ammonium nitrate, formamide and ethylene glycol. Non-polar solvents also show micellar aggregation but the aggregation behavior differs.⁴

The critical micelle concentration (CMC) is that concentration of the surfactant that leads to the formation of the colloidal aggregates. The Kraft temperature is that

temperature above which aggregation is possible (i.e. below which the monomer solubility in the solution is too small for micelle formation).

As the concentration of surfactant in a solution is increased beyond the saturation limit of the surfactant in the system, the surfactant aggregates change their form. This is the system's way of accommodating the surfactant tails, or hydrophobic portions. The hydrophilic portion of the surfactant, or amphiphile, will continue to be water-soluble but the surfactant aggregate form, that is a thermodynamically stable aggregate at that concentration, is no longer spherical, as seen in Figure 2.1.

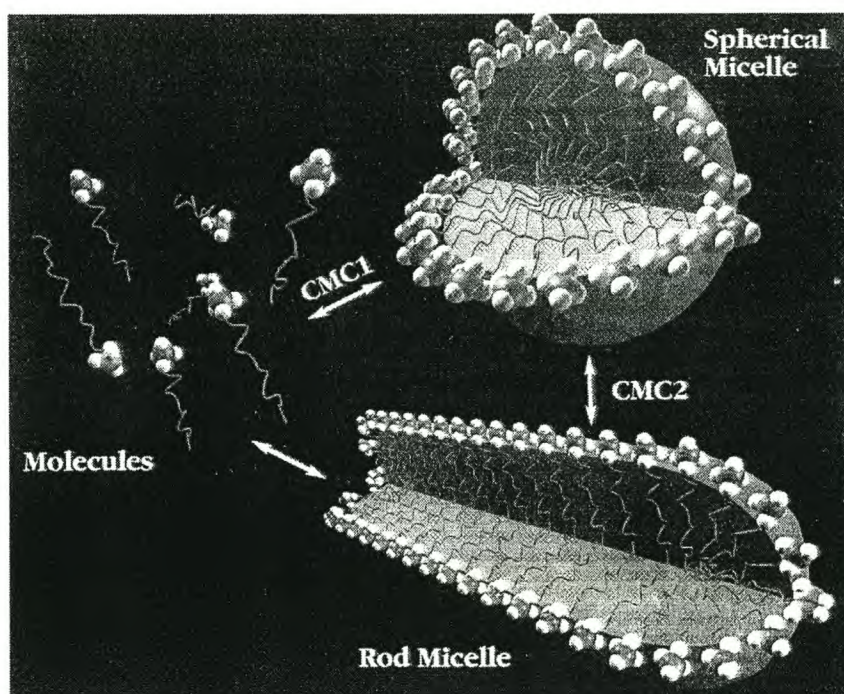


Figure 2.1 A typical representation of the micelle to hexagonal phase transition⁵

Changes in aggregation can be, and have been, studied experimentally as transitions can often be observed in similar fashion to that of the CMC by, for example, the use of light scattering, viscosity, conductivity, ultrasonic absorption, small angle neutron scattering (SANS) or solution calorimetry determinations.⁶

A continuing increase in surfactant concentration leads to various liquid crystalline phases⁷. These structures behave like weak solids, yielding to plastic flow and giving

very high apparent viscosities. Surface shapes that develop include globules; rods; sheets; mesh and struts.⁸ These forms are the surfaces of micelles, cylinders, lamellar planes and bicontinuous surfactant aggregates.

Lyotropic liquid crystals are formed over most of the temperature range between the Kraft point and the surfactant melting point. Between 273-473 Kelvin liquid crystals occur at least as frequently as micellar solutions do.

Lyotropic systems (i.e. solvent induced) commonly consist of the following structural arrangements: solution, micellar solution, liquid crystalline, hexagonal phase (array of rods), liquid crystalline face centered cubic, liquid crystalline lamellar and finally the solid crystalline form. These are not the only forms found nor are they always all found in a specific surfactant system. Many other liquid crystalline forms are found in small concentration ranges and these concentration ranges vary from system to system, but most are simply variations on the basic forms.

The lamellar phase, which is also known as the neat phase in soaps, has surfactant molecules arranged in bi-layers that are separated by water layers. The layers extend over large distances, commonly of the order of microns or greater. For a given sample the thickness of each water layer is very similar, usually within 0.05 nm or less. The surfactant layer thickness is generally 10-30% less than the length of two “all-trans” surfactant chains.⁹

The hexagonal phase consists of rod-shaped micelles of indefinite lengths packed in a hexagonal array and separated by a continuous water region. The cylinder diameter is usually ~ 10-30% less than the distance of two “all-trans” surfactant chains (i.e. similar to the lamellar phase). The distance between cylinders is usually about 1-5 nm.⁹

The cubic phases, which are also known as viscous isotropic phases, have varying structures, including the cubic packing of micelles, but the structures are less well defined.



The lipid systems have been shown to have a large number of cubic phases. The liquid crystalline phases of lipid systems have also been incorrectly ascribed to the bicontinuous systems. This has led to some confusion and references to bicontinuous cubic phases are common.¹⁰

At concentrations higher than the liquid crystalline domains and at temperatures below the liquid crystalline domains a gel phase can occur when the system is no longer fluid. The term gel is used to define a lamellar structure with “solid-like” backbones, which occurs below the temperatures of the lamellar phase region. A coagel is a two-phase mixture of hydrated solid soap and water that may occur due to concentrations of surfactant above the saturation point of the surfactant in the water.⁹

The work of Charvolin *et al.*¹¹ and Kekicheff *et al.*¹² is particularly enlightening as to the degree of variation that occurs between the different surfactant aggregates. They have also studied the narrow border phases between the recognized aggregates. This lends more scope in the use of a phase diagrams for structural identification especially in the case of a phase transition, which is then better understood.

Vesicles, which are double or bi-layer aggregates with a water interface, have been reported as forming from both natural amphiphiles and synthetic surfactants¹³. Bola-amphiphiles (amphiphiles with heads and tails of a polar nature but a significant hydrophobic middle section) have also been found to give rise to microtubes of vesicles¹⁴. This bi-layer assembly gives us more synthetic possibilities as far as surfactant aggregates are concerned as the use of a vesicle type structure allows different approaches to templating (see 2.3).

The nature of the phase present in a mixture of amphiphile and water is also affected by the addition of other molecules. Co-surfactants and organic monomers change the binary phase diagrams of the systems. The subsequent ternary phases retain some of the aggregation properties but they significantly differ in diameter due to swelling of cylinders, micelles or lamellar phases.¹⁵ The ternary systems are also likely to exhibit different phases and shifts in concentration ranges in relation to the binary systems.

The phase is also affected by the addition of electrolytes. The addition of sodium chloride (NaCl) has been shown to alter growth of the aggregates, leading to a phase transition to rod-like micelles (also referred to as a hexagonal phase).¹⁶ The salt addition can be used as a means of phase adjustment, at specific surfactant concentrations, without detrimental effects on the synthesis, in terms of reactivity.

Examples of known self-assembly behavior include phospholipids, which have been used to form long filaments (in the order of hundreds of micrometers) as well as vesicles¹⁷ and inverted cubic phases.¹⁸

2.3 Template-directed synthesis

The use of templates to direct structure formation has been widely examined throughout a number of disciplines¹⁹. The advantage of being able to direct the formation of a material permits the development of materials with new properties.²⁰

A template may be defined as a central structure about which a network forms in such a way that removal of the template creates a cavity with morphological and / or stereo-chemical features related to those of the template.²⁰ The template may be covalently or noncovalently bonded to the material being templated. Kinetic or thermodynamic pathways may be used for formation.

Template synthesis has the advantage that, in principle, any material that forms a unique nano-structure can be used as a mould to obtain negatype (negative imprint) structures of a large variety of shapes.²¹

Examples of templates include lipid tubules. They have already been proven to have industrial uses as slow release mechanisms in anti-fouling paints²². The metallization of these structures has allowed the formation of stable nanotubes that have not yet been fully exploited²².

Templating in the biological realm has long been common knowledge. The replication of DNA is a prime example of the importance of hydrogen bonding and pi-stacking.

The parent/daughter relationship of DNA has been mimicked with varying success in synthetic polymeric systems. Methacrylic acid has proven to be one of the more successful monomers used in this research direction.²³

Inclusion polymerization refers to the polymerization of molecules in constrained media. There is no actual templating occurring but, the product morphology is determined by the form of the host (the mould). The guest molecule is limited not by its interaction with the environment but rather by the lack of a more suitable environment. (Similar to casting a mould of a statue where the metal is confined in the mould not by interactions but by the lack of other options due, in such a case, to gravity and, in our case to concentration gradients). This confined polymerization has been used to provide new materials by post-reaction removal of the mould that was been used to cast the structure.²⁴

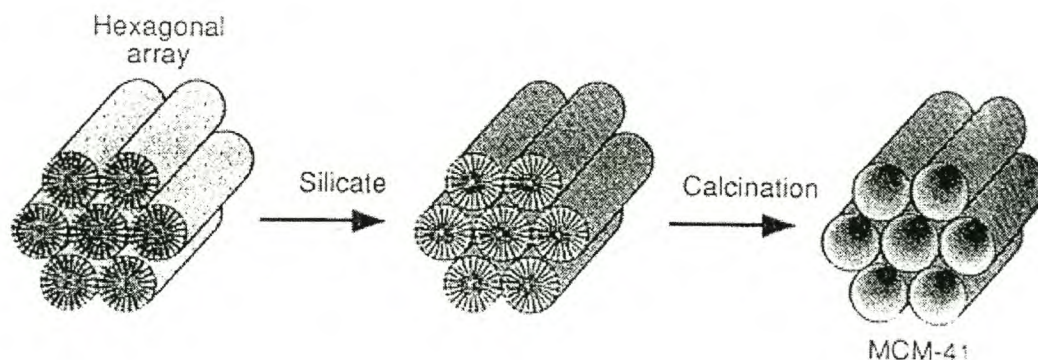
Current opinion on organic templating is as follows: Unlike the aqueous phase templating polymerization of sol-gel systems (see section 2.3.1) the oil phase addition causes the swelling of the lyotropic phase. This disrupts the aggregates and the polymer that forms during irradiation is not sufficiently stabilized to prevent coiling. This leads to the demixing of the polymer from the phase and to microphase separation. Latex particles form, leading to phase disruption, because of the lack of finite interaction between the monomer and the hydrophobic tails of the liquid crystalline phase. The use of liquid crystalline templates has been shown to require strong interaction between the template and the daughter²⁵. This can be achieved through covalent or non covalent bonding but must be strong enough to resist disruption of the template by the forming daughter or copy of the template (in our case the organic polymer)²⁵.

Some success has been achieved by using liquid crystalline phases as structure directing media rather than as templates.²⁵ Even in these cases cocogem surfactants (coupled counter-ion gemini surfactants, in other words having a double layer head and twin tails), amphiphilic block copolymers and the more stable polyelectrolyte-surfactant systems have been required.

2.3.1 Inorganic template-directed synthesis

The sol-gel process of polymerization has been actively studied since the mid 1800s. A sol is a dispersion of colloidal particles in a liquid. Colloids are solid particles with diameters of 1-100 nm²⁶. A gel is an interconnected, rigid network with pores of sub-micrometer dimensions and polymeric chains with average lengths greater than a micrometer.²⁷

Inorganic templating materials are tailored by controlling organic array assembly at the inorganic/organic interface⁵. This interface is between the polar end-groups of the organic self-assembly materials and the polar inorganic materials. The inorganic templating approach has been successfully applied to a surfactant system of hexagonal arrays of cylindrical micelles (i.e. a standard hexagonal liquid crystalline phase). This success shows that the liquid crystalline phases of surfactant assemblies may also be used for templating.²⁸



**Fig 2.2 The extraskelatal templating that occurs in an inorganic sol-gel process²⁸
(The formation of zeolite MCM-41)**

Use has also been made of emulsion particles as templates (see 2.4). The fact that sol-gel systems template on the hydrophilic side of surfactant aggregates means that standard emulsion particles may be used as a template for a sol-gel process.²⁹

Commonly used sol-gel products include the family of the M41S zeolite molecular sieves, specifically MCM-41 that is known to be an hexagonal arrangement of cylindrical pores embedded in a matrix of amorphous silica. The generally accepted view is that liquid crystalline templating occurs, providing the regular arrays of uniformly sized channels.³⁰

Many studies have been carried out to determine the predictability of the host-guest arrangement of molecules during sol-gel type reactions.³¹ Studies in which zeolites such as MCM-41 are used as hosts in inclusion polymerization have shown that the properties of the resultant polymer such as the glass transition, can vary greatly depending on the polymerization environment.³²

2.4 Latex systems

The use of an emulsifier or surfactant is industrially important due to one simple fact.

This fact is also one of the most interesting properties of aqueous solutions and gels of amphiphilic compounds. This property is the ability of surfactants to dissolve significant amounts of substances such as hydrocarbons, which are otherwise insoluble in water. This is possible due to the localization of the hydrocarbon tails in concentrated surfactant solutions, creating a hydrophobic medium in which, for example, an oil, or in our case a monomer can be solvated. The solution of oil in water, aided by surfactant, is known as an emulsion. Emulsions provide an environment for polymerizable monomers to form polymer particles of regular shape under suitable initiation conditions.

The kinetic stability of emulsions is determined by the potential barrier generated between two particles due to the competition between the attractive Van Der Waals interactions and repulsive double layer forces.

Latices are water-based polymers comprising colloidal dispersions of polymer particles in aqueous medium that are formed by polymerizations of emulsions. The

fact that micelles are commonly used as polymerization points to achieve the latex means that the latex particles are commonly spherical.

Smith and Ewart³³ investigated the kinetics of free radicals in the emulsion polymerization. Free radicals are the most commonly used polymerizing agents in emulsion polymerization techniques. They discovered that the principal loci for initiation of latex particles are the monomer-swollen micelles and the aqueous phase.

Some variations of emulsions are commonly used for polymer synthesis, as the basic properties of the hydrophobic domains that are capable of solvating monomers remain the same despite the change in structural arrangement; they are miniemulsions and microemulsions.

2.4.1 Miniemulsions

Miniemulsions are relatively stable sub-micron (50-500 nm) dispersions of oil in water, prepared by shearing (normally through a sonifier or a microfluidizer) a system that contains oil, water, surfactant and often a co-surfactant. The co-surfactant is introduced into the monomer droplets to retard the diffusion of monomer. This allows miniemulsions to be stable for up to periods of months as there is a low interfacial tension and a high resistance to droplet coalescence³⁴. It has been shown that in miniemulsion polymerization the principal loci for initiation are the monomer droplets³⁵. Like emulsions, miniemulsions are slightly blue or white in color due to the size of the particles.

2.4.2 Microemulsions

Winsor³⁶ drew up a set of definitions for the types of mixtures that occur with water and oil systems, with surfactants in quiescent systems. Although somewhat limited for our discussion, they still form a basis for many literature reviews and discussions on microemulsions.

Winsor system I is an organic liquid containing only a small proportion of other components of the system in equilibrium with an aqueous solution of an amphiphilic

compound containing more or less solvated organic liquid. If the organic liquid contains several species there is some enhancement in the proportion of the more hydrophilic species in the solvated organic liquid.

Winsor system II is water or an aqueous salt solution containing only small proportions of the other components of the system which is in equilibrium with a solution of surfactant in an organic liquid containing solvated water.

Winsor system III has free oil and water phases in equilibrium with a solvated phase containing oil, surfactant and water components.

Winsor system IV contains surfactant, water and oil that are mutually solvated. This can also be construed as a microemulsion.

A microemulsion may be defined as a thermodynamically stable isotropic solution of two immiscible fluids, generally oil and water, containing one or more surface-active species. They have been actively studied since about 1980³⁷, although they were first noted by Shulman in the 1940s³⁸. They often exist over a broad range of surfactant concentrations and oil phase concentrations.

Co-surfactants are commonly used to form microemulsions as there are only a limited number of surfactants that are capable of forming microemulsions by themselves. The role of the co-surfactant is to lower the interfacial tension.

Some surfactants or surfactant mixtures reach zero interfacial tension with an increase in bulk concentration. This leads to an increase of the total surface area between oil and water. The lack of interfacial tension gives rise to either microemulsions or to liquid crystals, depending on the system in question³⁹. Microemulsion formation has been proposed as being due to the negative free energy change overcoming the positive product of the low interfacial tension and the large interfacial area generated by the dispersion of one phase into another due to the entropy of dispersion. A second factor that is deemed to be prominent in the formation of microemulsions is the negative change of chemical potential caused by the adsorption of surfactant and co-surfactant on the interface.

Microemulsions differ from standard emulsions in a number of ways. Firstly, a standard emulsion is not thermodynamically stable and has to be maintained through the input of energy, i.e. a kinetic stability, normally by stirring to prevent coagulation. Secondly, the particle nucleation process is continuous throughout the course of polymerization in a microemulsion, unlike in a standard emulsion. Microemulsions are optically transparent as a consequence of the size of the oil (or water) regions, which are of the order of 10 nm, and form spontaneously when mixing the oil and water in the presence of appropriate amounts of surfactant and co-surfactant (normally a short chain alcohol or amine).

The surface active species or surfactants are mostly located at the interface between the domains of polar and non-polar fluids. Microemulsions can be water continuous (oil-in-water), oil continuous (water-in-oil) or bicontinuous⁴⁰.

In their work on microemulsions Gan and Chew studied inverse microemulsions (i.e. water-in-oil)^{41,42}. They produced fine microporous solids, demonstrating that structural direction possibilities exist.

It is also possible to use microemulsions to produce microstructured polymeric solids. Cheung and Sasthav produced a needle-like structured material using sodium dodecyl sulphate and electrolytes⁴³.

Problems that occur in the use of microemulsions include phase separation in the process of polymerization as well as chain transfer via the co-surfactant, limiting the molecular mass of the polymer. The co-surfactant further complicates the system as the interpretation of four component systems become substantially more complicated.

2.5 Polymerizable surfactants or surfmers

The use of copolymerizable surfactants in polymerizations allows a compromise between a classical emulsion system and a surfactant free system. It also provides for inherently hindered surfactant removal, that provides stability and facilitates “core shell” procedures (polymerizations in which a seed latex is used for a second

polymerization, leading to layers of different polymeric materials on a microscale).
44,45

The use of polymerizable surfactants does, however, complicate the polymerization product. It has been found that the reaction kinetics often lead to the formation of oligomeric surfactants that are not incorporated in the particles.⁴⁶

Numerous studies into novel polymerizable surfactants as well as common binary systems have led to a large number of binary phase diagrams being available for the further investigation of such systems.⁴⁷

An advantage of the use of copolymerizable surfactants in polymerization of emulsions is the simple route that they offer for the functionalization of polymeric particles.

2.6 Sodium 10-undecenoate

The surfactant sodium 10-undecenoate offers many theoretical possibilities that researchers have attempted to explore over the last 20 years.

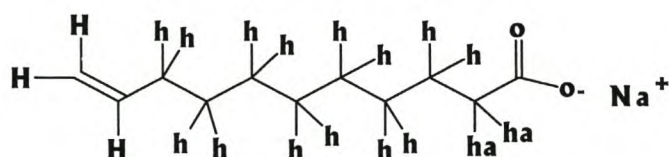


Figure 2.3 Sodium 10-undecenoate

H: double bond associated hydrogens

h: backbone hydrogens

ha: carboxylate neighboring protons

Unlike unsaturation in simple hydrocarbons which tends to increase their solubility by essentially shortening the chain and thus lead to their showing a more hydrophilic tendency, the relative hydrophilicity of the olefinic moiety is negligible in comparison to the ionic head groups in unsaturated surfactants. It has been shown that the

introduction of the allyl group reduces the solubility of the surfactant and the stability of the liquid crystalline phase. The CMC is about a factor 2 greater than that for the saturated analog sodium undecanoate.⁴⁸

Numerous studies on the surfactant sodium 10-undecenoate have yielded a large number of incongruous data. Poly(sodium 10-undecenoate) is formed in aqueous solutions when reacted above the CMC of the surfactant. Studies also indicate that polymerization takes place prior to the CMC in premicellar aggregates. The degree of polymerization is equal to the aggregation number of the monomeric micelles. This aggregation has been shown to be in the region of about 12 monomers. The polymerized micelles have more compact chain packing than the monomeric micelles due to polymeric covalent bonding. This limits the penetration of hydrophobic molecules. At concentrations above 2,06 g/l the poly (sodium 10-undecenoate) ions aggregate under the influence of hydrophobic interactions to form large intramolecular polymeric micelles⁴⁹.

CMCs of 8.24 g/l⁵⁰ or about 0.04 mol/kg have been reported for the surfactant. This has been suggested as being due to pre-micellar aggregation rather than micelle formation. A value of 0.12 mol/kg⁵¹ has been reported using specific conductivity, fluorescence quenching and vapor pressure osmometry.

Mixtures of decyl trimethyl ammonium bromide and sodium 10-undecenoate (anionic and cationic surfactants respectively) have given vesicles⁵². They were uni-lamellar and had diameters between 20 and 100 nm. The vesicles were stable for up to 70 days in 25% ethanol. They were prepared by sonication.

A detailed phase diagram of sodium 10-undecenoate was determined by Kekicheff *et al*¹² using the concentration gradient method and polarizing optical microscopy. The well separated liquid crystalline phases were found at high surfactant concentrations. The investigation was focused on the spiral textures formed by the surfactant lamellar phases when in contact with a wall of a container while evaporating water from the hexagonal phase.

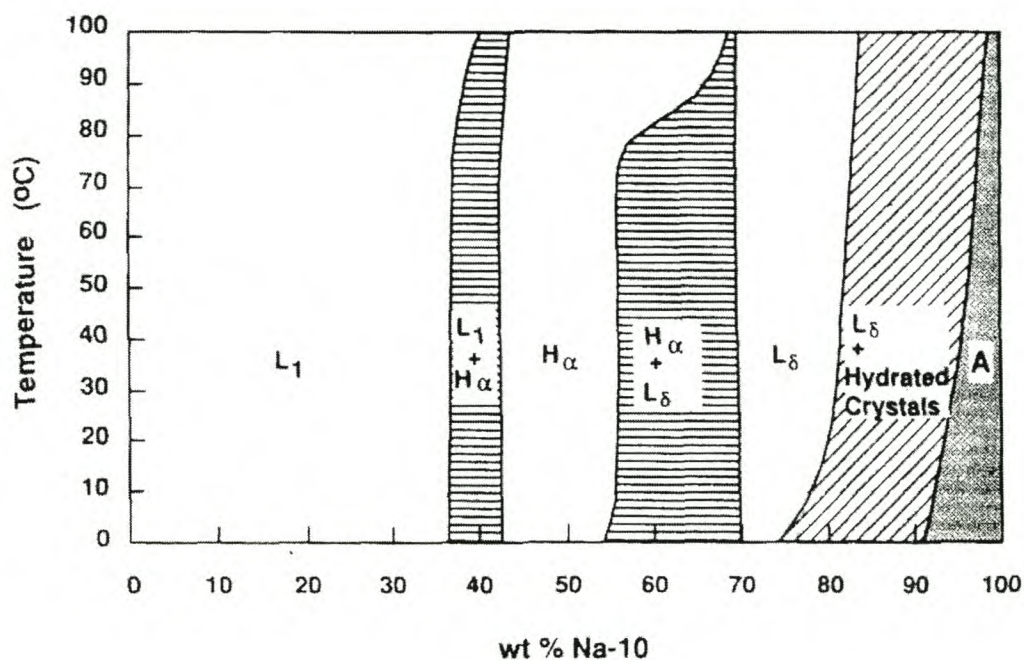


Fig 2.4 Phase diagram of sodium 10-undecenoate

- L₁** : micellar phase
- H_α**: hexagonal phase
- L_δ**: lamellar phase
- A**: solid surfactant /coagel

Analysis of the polymerization of the lyotropic liquid crystals formed by sodium 10-undecenoate at high concentrations using optical methods show a change in the liquid crystalline structure during polymerization,¹². The molecular mass of the polymer that was obtained was in the order of 270 monomeric units.

The hexagonal cylinder radius was determined at 1,414 nm and the number of surfactant molecules as 13,6 per revolution. The theoretical length of a fully extended monomer chain is 1,47 nm, which corresponds well to the radius of the cylinder.⁵³

McGrath studied the polymerization of the surfactant in both its self-assembled and non self-assembled forms⁵¹. While the phase change observed by Friberg et al⁵⁴ was not observed, interesting data was generated. The differences in the polymeric and monomeric phase diagrams have been studied. The different phases that occur in both

have been noted. The low degree of polymerization in the self-assembled form has been attributed to inhibition by aggregate structures.

Hydrocarbon chains in a fluid-like state have a high degree of mobility, unlike when the chains are frozen and are presumed to be almost crystalline in nature. When the chains are in a fluid like state, polymerization may retard their flexibility, whereas for frozen chains the number of degrees of freedom should be increased upon polymerization. This means that the state of the paraffinic chains may have an affect upon the extent or ease of polymerization of the system as well as on the degree of rearrangement that occurs during polymerization ⁴⁹.

McGrath determined the CMC of sodium 10-undecenoate by pH determinations, to be about 0.4 M ⁵¹. The fact that the monomeric form of the surfactant is insoluble in most solvents led to polymerization of the parent acid, followed by derivation. Comparison of the monomeric and polymeric sodium 10-undecenoate liquid crystalline phases showed that in the concentrated region few similarities occur between the two. This indicates that the nature of the hydrocarbon chain plays a critical role in the self-assembly of these systems. The degree of polymerization obtained by McGrath was in the region of 40 monomer units ⁵¹. McGrath also determined that the nature of the head group had little effect on the polymerization mechanism when the double bond was sufficiently isolated from it ⁵¹.

Sodium 10-undecenoate has been used as a copolymerizable surfactant in microemulsions with methyl methacrylate ⁵⁵. The use of pentanol, a common micromulsion formation agent, as a cosurfactant led to interesting structures but the crumbly nature of the polymers, which appeared to show fibrous structure that was attributed to cold drawing of PMMA, made analysis difficult. Furthermore the lack of copolymerization ratios led to the conclusion that although copolymerization took place as witnessed by IR evidence, the degree of incorporation could not be determined.

The use of methyl methacrylate with ethylene glycol dimethacrylate as a crosslinking agent in water with potassium 10-undecenoate was investigated by Raj et al. ⁵⁶ Results of this photo-initiated study showed a large degree of surfactant incorporation as

determined by X-ray fluorescence measurements and extraction studies. The extent of incorporation of the surfactant was found to be dependent on the contents of MMA and EGDMA in the precursor microemulsion. The incorporation was determined by the repeated extraction of the product with boiling water to remove monomeric surfactant. Structures that had plank-like forms were found in samples that contained 45% MMA and 30% potassium 10-undecenoate prior to irradiation. The structures were not templated but appeared regular, though not identical.

Raj *et al*⁵⁶ also reported that the use of microemulsions that were closer to the liquid crystalline domain appeared to result in the microstructure of the resultant polymer being more ordered. The reasoning was that the higher viscosity of the precursor systems would minimize phase separation effects and the rearrangement of the structure on polymerization, which was observed by Friberg *et al*⁵³. Friberg *et al*⁵⁷ used this approach to produce foams that were stabilized by layers of the liquid crystal. The study also suggested that homo-polymer might have been formed as well as low molecular weight polymers as a result of allylic inhibition.⁸

Conclusions of the literature study were that the surfactant has the problem that it polymerizes poorly but that it has the possibility of copolymerizing with monomer.

2.7 Polymerization within liquid crystals

To polymerize within a liquid crystalline system the phase structure must not be disrupted, otherwise the liquid crystalline phase structure cannot be imprinted onto a polymer. Polymerization in bicontinuous microemulsions has shown that the microemulsion cannot be maintained during the reaction⁵⁶. The delicate balance in the phase-separated medium is disturbed by polymerization which, although it leads to a highly ordered product, does not resemble a cast of the parent microemulsion or lyotropic liquid crystal. The ability to partially direct structure formation has nonetheless been shown.²⁵

Polymerization of hydrophilic monomers in the aqueous lyotropic phases of counter-ion coupled gemini surfactants by Antonietti *et al*⁵⁸ showed that the lyotropic phases can be used to generate highly ordered gels for water soluble monomers.

The characteristic size of Antonietti's gels was still 2 orders of magnitude larger than the length scale of the parental lyotropic phases⁵⁸. It was concluded that due to phase separation of the gel from the lyotropic surfactant assembly, a direct cast of the original structure was impossible. It was found that copolymerization of a monomer and the surfactant proceeded easily in these phases.

Antonietti *et al*⁵⁸ explained the order that is generated as follows: The reaction starts from a homogeneous lyotropic liquid crystalline phase and the polymer, once formed, demixes from the continuous lyotropic phases. The growth of the polymer domains is controlled by the anisotropic transport properties of the liquid crystalline phase. An increase in the amount of polymer leads to an interconnected gel structure, embedding the liquid crystalline phase with the majority of the surfactant. This sub-phase can be continuous too.

2.8 Microscopy

The most common analytical method used to study the particles formed via emulsion polymerization type mechanisms is electron microscopy. The use of the electron microscope whether it be scanning (SEM), transmission (TEM) or field emission scanning electron microscope (FESEM), allows the scientist to examine the fine structural features of lattices or other particles.

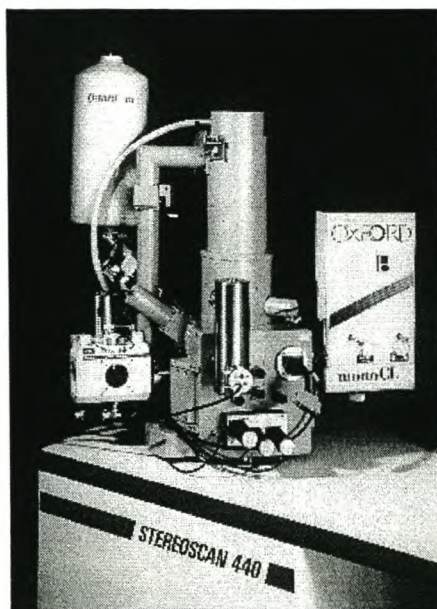


Figure 2.5 SEM at UCT

Many examples of miniemulsion, microemulsion, standard emulsion and other methods of aqueous supported polymer growth can be found in literature⁵⁹. The use of electron microscopy as a tool for the analysis of the latex particles or the micro-structured materials that form is well described in the literature.

The use of SEM offers elemental analysis via X-rays, magnification up to 100,000 times and reasonable resolution (in the range of 10 nm). The disadvantages include working under a high vacuum, which precludes analyzing liquid samples. The sample is also subject to radiation damage by the beam of electrons, the accelerating voltage that is applied allows an increase in resolution but at the risk of sample damage, this occurs despite the coating (C, Cr, or Au/Pd) that is required to create a conductive surface.

The field emission scanning electron microscope (FESEM) offers up to 1000 000 times magnification (this is a National Facility and is only available at the University of Pretoria). The FESEM can be used with low accelerating voltages, allowing a minimal coating and thereby preventing nano-scale features from being obscured.

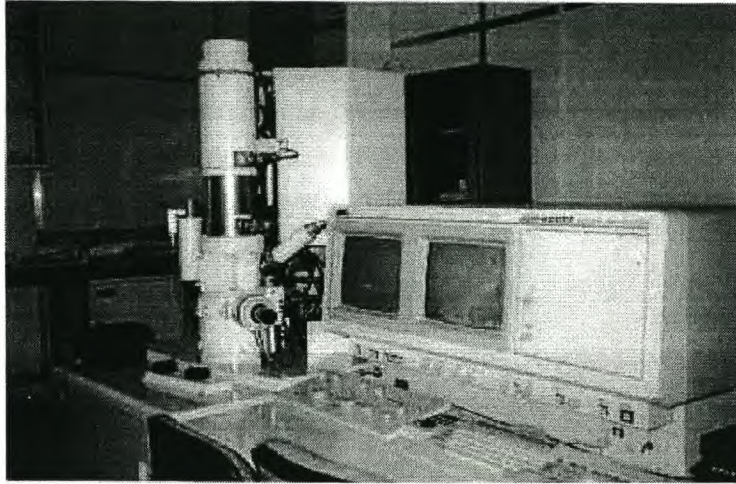


Figure 2.6 FESEM at UP

The scanning electron microscope's image is obtained from interaction between bombarding electrons and the sample's atoms. The SEM images are created by a detector that detects the secondary electrons produced by the incident electron beam from the sample.

The transmission electron microscope produces an image from the electrons that pass through a sample. This technique has been used with frozen samples (so called Cryo-TEM⁶⁰ or freeze fracture electron microscopy⁶¹) and adds a new dimension to electron microscopy in that the sample need not be dried prior to imaging. Disadvantages include the thickness of the sample, which has to be limited to permit transmission, as well as the sample preparation, which is more complicated than for analysis by SEM techniques.

Atomic force microscopy (AFM) allows imaging of insulating materials. Using a flexible force-sensing cantilever stylus the tip is rastered over the surface to be analyzed in one of a variety of modes. The contact mode is capable of imaging individual atoms, while the non-contact or attractive mode can detect Van der Waals forces. The advantages of using this analytical technique are that the sample can be a liquid, the testing is non-destructive and no coating is required. This means that surface features are not obscured.

2.9 In conclusion

The concepts used to approach this investigation have been discussed. The aim of the investigation was to contribute to the understanding of how the structural directing agents work and to provide evidence and understanding about the speculations that exist in literature on the possibilities of organic single particle self assembly, through templating or structure directing properties.

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Chapter Three

Preliminary experimental investigation

(A determination of surfactant suitability)

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Chapter Three

Preliminary experimental investigation

(A determination of surfactant suitability)

3.1 Literature background to preliminary investigation

The polymerization of surfactants has been investigated for a number of reasons. Amphiphilic molecules which form lyotropic liquid crystals have been studied by numerous authors (see 2.2). The fact that long range order occurs in these structures provides many interesting material properties, but the inherent instability of the small molecule aggregates to variations in temperature as well as other environmental conditions has limited their uses. This has led to numerous attempts at their polymerization.

The polymerization of unsaturated surfactants should allow stabilization of dynamic structures. Results of investigations into polymerizable surfactants have however shown that in many cases the liquid crystalline structure is lost or that polymerization is incomplete (see section 2.7).

Self-assembly in the liquid phase has been found to inhibit the polymerization of the reactive species, possibly due to the loss of mobility of the hydrocarbon chains as well as the surfactant aggregate which acts as a cage to inhibit the polymerization ¹

Reasons that have been suggested for the structural integrity loss of polymerizing liquid crystalline systems include the demixing of the polymer from the continuous phase, leading to a disruption of the liquid crystalline structure. The fact that some order remains in the system normally means that the polymeric product will show order although not necessarily that of the parent phase. Microphase separation can also occur.

Due to the changes in the structure of the monomeric unit, specifically the shape of the molecule in solution, it has been found that polymerization can also lead to a change of phase. ²

For retention of the liquid crystalline phase certain inherent properties of the surfactant monomer are required:²

- a) The chain period of the polymer must coincide with the translational period of the monomer crystal lattice (i.e. the translational period of the polymer chain should be equivalent to that of the corresponding crystal lattice).
- b) The overlapping volumes of the monomeric units in the polymer chain should not differ greatly from that of the monomer molecule. (This is normally seen as a decreased side chain volume in the case of the polymer when compared to the monomeric size in solution).
- c) The volume contraction during chain formation should not be in the direction of chain growth. (The bond lengths of a fully formed carbon-carbon bond are significantly shorter than the intermolecular bond lengths in solution).

These limiting factors mean that single particle formation, of an organic nature, on a nano-scale, has not been successful to date.

The polymerizable surfactant sodium 10-undecenoate has been investigated by several researchers and has shown interesting properties in both monomeric and polymeric forms(see section 2.6).

The spiral texture, caused by inherent disclinations in the hexagonal phase, of the monomeric surfactant that is obtained by evaporation of the water from the hexagonal phase was investigated by Kekicheff et al ³ and provides us with insight into the solid phase transitions of this surfactant. The literature reports, however that work done by Shibasaki and Fukuda⁴, resulted in a phase diagram determined via DSC which differs greatly from the commonly accepted one developed by Kekicheff³.

Various initiation methods and reagent concentrations have been investigated for the polymerization of surfactant ⁵. Results of thermal as well as gamma and UV irradiation studies have shown varying degrees of success in the polymerization of

this surfactant in systems above and below the CMC of 0.4 M ⁵, as well as in concentrated solutions, including isotropic systems.

Stoffer and Bone ⁶ briefly investigated the copolymerization of this sodium 10-undecenoate with methyl methacrylate in microemulsion systems. Results of this early work indicated structure directing possibilities was concerned but the authors did consider homopolymer PMMA as a possible artifact creator. A SEM image taken experimentally of the surfactant gel after polymerization under UV irradiation suggested that the phenomenon attributed to cold drawing by Stoffer and Bone may be excess surfactant that had not been removed from the system prior to analysis. (see Appendix B)

The structure-directing properties of the potassium salt of 10-undecenoate were studied by Cheung et al ⁷, with methyl methacrylate as a comonomer. Some promising results for a single tail surfactant in microemulsion compositions giving polymeric products with structured morphology (see Appendix B) were obtained. Again the composition of the product was not determined conclusively but the possibilities for control of structure formation appeared inviting in that the presence of regular shaped separate particles was visible in the SEM analysis.

The fact that previous researchers had found interesting results combined to make the surfactant sodium 10-undecenoate interesting and potentially useful for the self-assembly project that was envisaged.

3.2 Sodium 10-undecenoate polymer preparation

3.2.1 Introduction

The polymerization of the sodium 10-undecenoate monomer was first carried out in the micellar phase using the method of Gambogi and Blum⁸. IR and NMR spectra were recorded.

The aim of the experiment was to provide copolymer IR and NMR data for reference purposes for the self-assembly investigations. A small quantity of MMA (10% by mass) was included.

3.2.2 Experimental

The following experimental procedure was followed for the preparation of the polymeric micelles.

A three-necked flask was placed in a water bath at 70 °C and the following were added: water (200 g), sodium 10-undecenoate (20 g), potassium persulphate (1 g), MMA (2 g).

The reaction mixture was allowed to react at 70 °C for 24 hours. An overhead stirrer was used at 200 rpm to maintain the emulsion. The product was not a white emulsion but a yellow tinged, clear solution, as was expected from the size of the micelles being polymerized.

Polymeric sodium 10-undecenoate was recovered by precipitation of the product in ethanol. Results of IR⁹ and NMR² analyses confirmed the nature of the polymer. Described in 3.2.3 and 3.2.4.

Homopolymer PMMA was not recovered by the ethanol precipitation. No evidence of its incorporation was found (homopolymeric surfactant formed). This disagreed with the results of Cheung *et al* who studied the potassium salt in the concentrated phase⁷.

Cheung and co-workers reported that the potassium salt and methyl methacrylate formed copolymers⁷. The reason for this difference was possibly because of the initiator/MMA ratio used in the experiment. The ratio of 2.2 mol initiator to 1 mol MMA as used here might have led to such short chain homopolymer PMMA that it would have remained insoluble in ethanol and would not precipitate in a short time period. The possibility of the formation of short chain copolymers that remain soluble was also considered as a possible explanation.

Particle size data of the reaction solution was obtained from a Malvern Zetasizer. A multimodal distribution of data showed a bimodal distribution with the majority of particles having with a mean diameter of 50.4 nm. The smaller peak had a mean diameter of 15.9 nm.

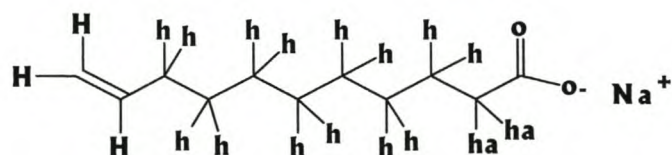
The data was not suitable for analysis as the scan properties were beyond the scientifically accepted values for the instrument (see Appendix C). This meant that the data was only suitable as a rough guide not as exact values. This data was therefore used purely as a reference for the further study. No conclusions were made about the copolymerization of the various monomers.

3.2.3 IR data

The following data was generated for the purposes of identification of polymeric products using a PERKIN ELMER 1600 FT-IR and KBr disks.

The following IR peaks were characteristic of the monomeric surfactant as confirmed via literature²:

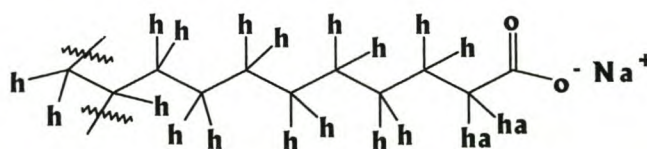
Table 3.1 IR peaks ascribed to the sodium 10-undecenoate



Wavenumber cm ⁻¹	Description	Identity
3084	small	(terminal vinyl)
2920-2940	sharp, strong (two) with shoulders	(C=C-H next to CH ₂)
2851	sharp	(H stretching)
1560	sharp strong	(CH ₂)
1445-1450	multiple peaks (three)	(CO ₂ -), C-H ₂
1415-1420	medium peak with a shoulder	(CO ₂ -)
911	medium sharp	(terminal vinyl)
919	medium sharp	(C-C stretch)
698	small	(C-C stretch)

The following IR peaks were characteristic of the polymeric surfactant:

Table 3.2 IR peaks ascribed to poly sodium 10-undecenoate



Wavenumber cm ⁻¹	Description	Identity
2920-2940	sharp strong	(CH ₂)
2851	sharp	(H stretching)
1560	sharp strong	(CH ₂)
1445-1450	multiple peaks (three)	(CO ₂ -), C-H ₂
1415-1420	medium peak with a shoulder	(CO ₂ -)
919	medium sharp	(C-C stretch)
698	small	(C-C stretch)

In order to determine the conversion from monomeric surfactant to polymeric surfactant by infra-red spectroscopy some authors have followed the decrease in the

vibration at ~ 3085 wave numbers ² but the vibration at ~ 911 wave numbers ³ is more conclusive due to the sharp intensity of the peak.

The distinguishing peaks (at 911 and 3085 cm^{-1} respectively) of the surfactant and the polymeric surfactant are the only changes in the spectra between the two that are clearly and easily identifiable. The PMMA spectrum in the figure below is that of the dialyzed sample. The following figure shows FTIR spectra of the surfactant, the oligomer and the PMMA polymer.

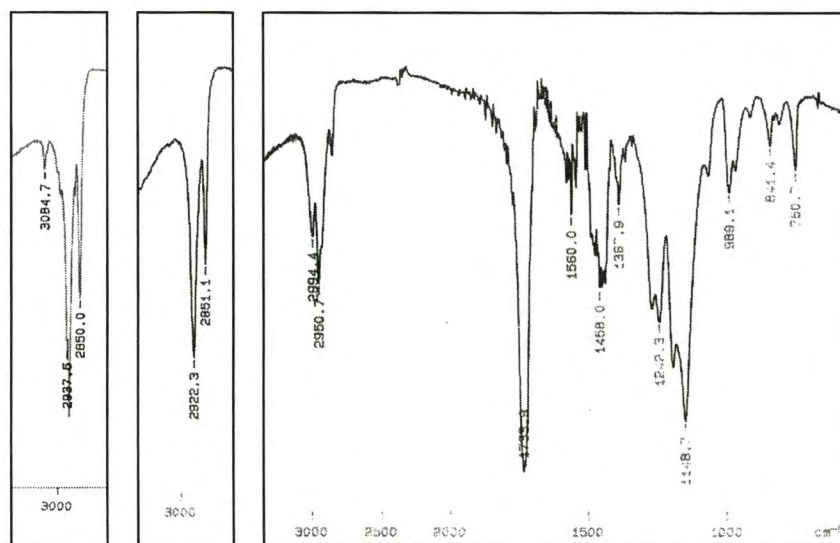
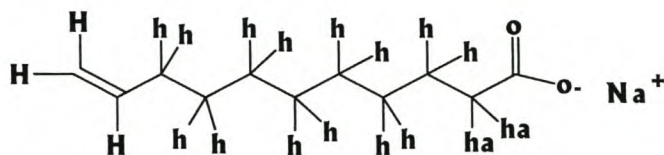


Figure 3.1 FT-IR spectra of surfactant, oligomer and PMMA

3.2.4 H^1 NMR data

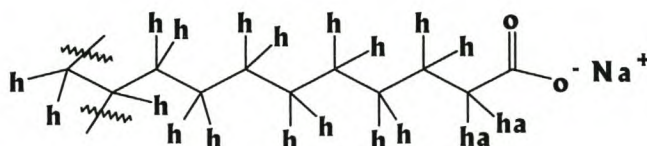
The following proton NMR data was obtained in D_2O solution using a HITACHI PERKIN ELMER R24A high resolution NMR apparatus.

The following proton NMR peaks were characteristic of the monomeric surfactant:

Table 3.3 Proton NMR spectroscopic data of sodium 10-undecenoate

Protons	Shift
Double bond protons (H)	$\delta \sim 4.8-6.2$ (three peaks for the three protons)
Tail protons (h)	$\delta \sim 1.3-1.6$
Protons adjacent to carboxylate (ha)	$\delta \sim 2.1$

The following proton NMR peaks were characteristic of the polymeric surfactant:

Table 3.4 Proton NMR spectroscopic data of poly sodium 10-undecenoate

Protons	Shift
Broadening of the tail (h)	$\delta \sim 1.3-1.6$
Carboxyl adjacent protons (ha)	$\delta \sim 2.1$

The vinyl protons of the surfactant sodium 10-undecenoate were followed to determine conversion of the sample from monomeric to polymeric surfactant.

As can be seen from Tables 3.3 and 3.4 the peak assignments for the polymer were very similar to those of the monomeric species and this simplified the characterization. Most of the polymeric surfactant recovered from samples was slightly contaminated by monomeric surfactant and oligomers due to the precipitation of monomeric surfactant and short chain polymer and required reprecipitation from ethanol to obtain the polymeric product.

3.3 Determination of surfactant stability and quality

The following potential surfactant variables were investigated: surfactant degradation over time, batch quality of the surfactant and counter ion content.

Four surfactant solutions prepared at different times and at different temperatures were made up to 0.16 mol/liter in water and used for pH and conductivity determinations, to determine if any substantial differences in the surfactant batches could be observed.

OA and OB were surfactant batches that had been prepared for the first investigations and were ~ 3 months older than B and C whose preparations are mentioned in the text.

Table 3.5 pH and conductivity studies of surfactant solutions

Soap solution	pH	Conductivity (mS)
OA	8.05	5.9
OB	8.02	5.975
B	7.92	6
C	7.92	5.9

There was no significant variation that might be construed as being due to the age of solutions or preparation methods. Inductively coupled plasma analyses (ICP) carried out by an operator at the Physics Department of the University of Stellenbosch showed the following (in ppm in 0.33% sol)

Table 3.6 ICP data for surfactant solutions

Sample	Na	Al	Ba	Ca	K	Si	Zn
OA	228.8	0.04	0.057	0.987	0.959	0.697	0.027
OB	234.98	0.027	0.028	0.878	0.544	0.539	0.025
B	221.52	0.034	0.047	0.852	0.194	0.421	0.025
C	228.64	0.023	0.055	0.925	0.276	0.377	0.025

The overwhelmingly predominant counter-ion present is sodium. The data also shows that the concentration of sodium is reasonably constant:

Average: 228.485 ppm or around 99% sodium

Standard deviation: 5.50 ppm

Standard deviation is defined as ¹⁰:

$$S = \sqrt{(1/n - 1) \sum_1^n (x_i - \bar{x})^2}$$

Estimated population standard deviation (square root of the variance or second moment about the mean):

4.76 ppm

$$\sigma = \sqrt{\int_{-\infty}^{\infty} x^2 f(x) dx - \mu^2}$$

Assuming a normal distribution with a probability density function ¹¹

$$f(x) = \frac{1}{\sqrt{2\pi} \sigma} e^{-[(x-\mu)/\sigma]^2/2}$$

Unlike the problems encountered by earlier researchers with sodium dodecyl sulphate ¹², where the counter-ion concentration varied widely, the sodium 10-undecenoate system shows that the ionic content is largely standardized. This tells us that the standard of the salts that were purchased is sufficient for use experimentally. This is important as the nature of the counter-ion, be it monovalent, divalent or simply different in ionic strength has significant effects on aggregation behaviour. ¹³

3.4 Conclusions

In conclusion it can be said that sufficient data, both experimental and from the literature, had been gathered to provide an overview of the properties of the surfactant and its suitability for the investigation. The surfactant provided interesting possibilities and was therefore deemed appropriate for the planned experiments.

3.5 References

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Chapter Four

An investigation into nano-shaping and the use of ultra-violet irradiation for initiation of polymerization

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Chapter Four

An investigation into nano-shaping and the use of ultra-violet irradiation for initiation of polymerization

4.1 Background to the intended study

The surfactant sodium 10-undecenoate is normally prepared by neutralization of undecenoic acid with sodium hydroxide. The soap can however be purchased as such from Sigma-Aldrich as was done for this study. The surfactant has a theoretical decay value of 220 °C and a melting temperature of 280 °C.

A decision was made to make use of ultra-violet light for the initiation of polymerization of the surfactant, water and monomer system due to the many advantages as well as the ease of availability.

Quiescent conditions are necessary for the maintenance of order in liquid crystalline and similar systems and an initiation method is required that will sufficiently penetrate an aqueous system of surfactant, water and monomer, to promote initiation.

The initiation method should also minimize the heat generated during polymerization as the kinetic energy will promote aggregate dissociation.

Ultra-violet initiators are easily available for emulsion type systems and are routinely used in industry and were an obvious choice for the investigation.

Sodium 10-undecenoate has been polymerized by Ultra-Violet irradiation in previous studies. Literature states that UV initiation (without an added initiator) has been used to polymerize the self-assembled surfactant ¹. This experiment was carried out over time periods up to 20 days giving up to 20% conversion at 30 °C. The UV lamps used were at a wavelength of 360 nm. This wavelength, unlike 254 nm, is not absorbed by

glass. In the same study azo bis-isobutyro nitrile (AIBN) at 10 mol percent to surfactant was used as a thermal initiator for 24 days at 60 °C giving up to 56 % conversion, the homogenizing of these samples containing AIBN was carried out at room temperature. Kekicheff *et al*² prepared bulk samples of sodium 10-undecenoate by homogenizing, through continual heating at 90 °C, while centrifuging for several weeks and then polymerized through Ultra-Violet irradiation.

These factors namely quiescence, heat minimization and availability of the initiators, were all taken into consideration during the choice of initiating method. Other possible polymerization methods, including gamma irradiation, were not considered at this stage.

The recovery of polymeric surfactant was aided by the following factors. The monomeric surfactant, when cooled to -20 °C or left for a number of hours, was observed to precipitate from ethanol but remained soluble at room temperature for the reasonable lengths of time required for experimental removal. The polymeric surfactant precipitates from ethanol³. Both the monomeric and the polymeric surfactants are soluble in water, while insoluble in acetone and other common organic solvents.

4.2 Practical problems with the surfactant

Although sodium 10-undecenoate was selected as the surfactant to be used in this study, there were certain problems associated with its use. The surfactant has a tendency to form stable foams that dry easily due to increased surface area, leading to lumps in the solutions that are difficult to redissolve. Attempts have been made to polymerize foams of similar surfactants without much success⁴.

The surfactant discolors at high storage temperatures (above 60 °C). Sodium 10-undecenoate also forms gel lumps that are soluble in excess water but are difficult to redissolve in situ. The surfactant when first dissolved tends to have a light yellow color. After extended storage periods and at higher temperatures this color deepens. Neither NMR nor IR analyses reveal any structural changes having taken place.

Unreacted samples appear to contain only monomeric surfactant. A probable explanation for this color would be conjugation in a polymeric system but the surfactant appears stable as a monomer. Further explanations include decarboxylation, radical oligomerization and formation of conjugation, but these have not been confirmed. Further, the quantities of whatever product that has caused the slight color transformation are so low that even very sensitive techniques such as electrospray mass spectrometry do not show what has occurred.

For the purpose of this study it will be assumed that any color change in surfactant solutions can be ignored as the contaminants that form in the system are at such low concentrations as to be negligible. The literature suggests that the surfactant is adequately stable for long periods and indeed should actually be aged in solution for at least a week before reaction ⁵.

4.3 Preparations of samples for SEM analyses

A Hitachi 405 scanning electron microscope was used for standard analysis of samples. The instrument was not suitable for detailed work but was adequate for routine microscopy. The electron microscope of the University of Cape Town (Cambridge Leica S440I) was used for detailed analysis and the field emission scanning electron microscope (JEOL 6000 FE) at the University of Pretoria was used for high-resolution work. The University of Stellenbosch Physics Departments' electron microscopy facilities (specifically the Topcon ABT60 scanning electron microscope) were used for analyses of samples in section 4.7 and chapter six.

The samples to be analyzed in the scanning electron microscope were prepared by placing them on aluminium mounts and then drying the samples in a desiccator. Aluminium mounts were used, as conductivity is required to prevent the charging of the sample. The mount may not be ferromagnetic, as the electrons will be disrupted from their paths. The samples were attached to the mounts (or stubs) using fine carbon in a glue suspension. The samples were coated in a gold /palladium coater at minimum current (~ 4 mA) for 30 seconds to obtain a minimal coating, to prevent

particle damage. The investigations were carried out at accelerating voltages of between 10 KV and 25 KV.

4.4 Preliminary Experiments

Preliminary experiments were carried out to determine the reaction conditions for the nano-shaping experiments. The polymerization of the bulk monomeric systems was carried out to provide a reference for the nano-shaping experiments as far as the product without surfactant was concerned.

4.4.1 *Experiment 1*

The first experiment that was conducted was carried out as a reference for the new polymerizable surfactant system. The experiment used the sodium dodecyl sulphate/ styrene/ divinyl benzene system that had been used in by earlier work at the Institute for Polymer Science by a co-worker C.F.J. Faul ⁶ to provide amphiphilic self assemblies.

The sodium dodecyl sulphate (SDS) experiment was carried out as follows:

A concentrated solution of SDS was prepared (60% weight by weight). Styrene was distilled immediately before use, and crosslinking agent (divinyl benzene) and initiator (phenyl acetophenone) were added to it before addition to the surfactant solution. The divinyl benzene was used as it was obtained from Sigma-Aldrich, (a 70% mixture of isomers). The styrene solution was prepared shortly before insertion into the glove box to prevent prepolymerization.

Nitrogen was bubbled through the surfactant solution, the water (de-ionized distilled water) and the styrene used to prepare the samples to minimize the oxygen content in the system.

The twelve solutions were prepared by volume rather than mass using micropipettes in pill vial no 6 supplied by Lasec (Pty) Ltd, hereafter referred to as polytops. The

reaction mixtures were prepared under a nitrogen atmosphere. The reaction volumes were ~ 15 ml. (For composition of individual samples see appendix D table 1).

A typical composition would be 3.75g SDS (in 12,5 ml water) 0.15 g styrene containing 0.0075 g DVB and 0.00075 phenyl acetophenone and 2,35 water.

The samples were reacted in the polytops with the lids off.

The reactions were carried out in a glove box, which was flushed thoroughly with nitrogen that had been passed through a scrubber. The box did not seal very well and for this reason reactions were carried out under a slight positive pressure.

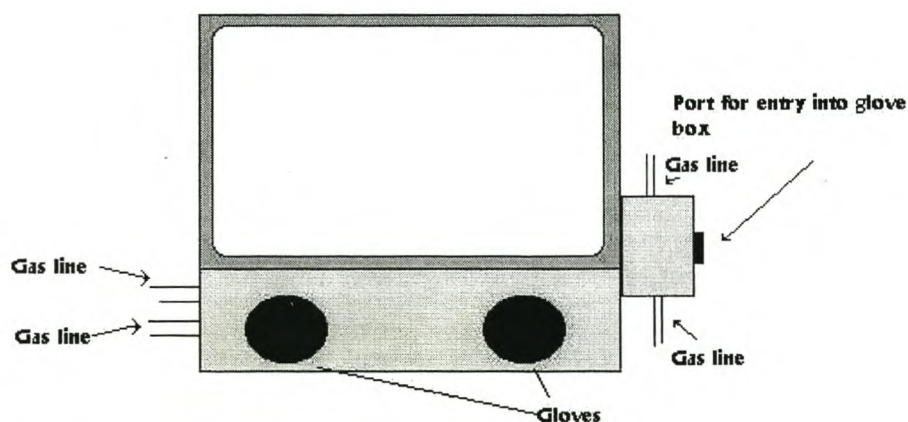


Figure 4.1 Diagram showing glove box

Samples were exposed to two germicidal UV lamps (254 nm) of 15 watt each for a total time of two hours with a thirty-minute intermission at the halfway point (this was to prevent excessive evaporation due to heating of the sample). The lamp distance from the samples was about 150 mm.

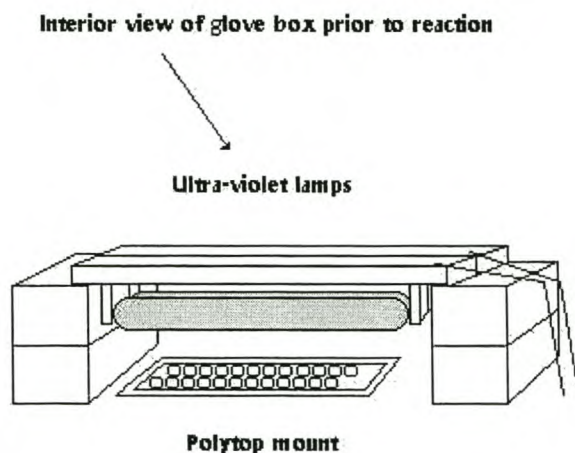


Figure 4.2 Diagram showing interior view of glove box

Particulate shapes were recovered from experiment one sample 7 (see appendix D Table 1 for composition). This was achieved after precipitation in ethanol and washing four times with ethanol (15 ml to 35 ml ethanol) in an separating funnel, followed by filtering through a 0.22-micron filter (Millipore GVWP01300). The filtration was carried out by hand using syringes on a 12 mm radius filter. (Washing with ethanol in the separation funnel was required to remove the excess monomeric surfactant from the system).

Filtration of the same samples using 0.25 ml and 4 x 5 ml ethanol wash while filtering also led to structure recovery. This method proved to be a more rapid form of structure recovery than the separating funnel wash.

The samples were examined under a scanning electron microscope as a standard form of analysis. SEM sample preparation has been discussed in section 4.3.

The structures were fiber-like in form. No image was captured at the time due to the exploratory nature of the experiment and to the fact that similar structures were seen in previous studies ⁶. The form of the structures was as expected, as the suggested environment of the fiber-like particle formation was that of hexagonal phase surfactant aggregates which are rod-like in nature and which should then provide a fiber or wire-like particles after coalescence or structure-directed crystallization.

The SDS system proved limited as the formed structures⁶ were largely surfactant and the surfactant could not be copolymerized to create a fixed structure. For this reason a study of the use of a polymerizable surfactant was initiated.

4.4.2 *Experiment 2*

The bulk systems of the monomers (the systems without water added) were investigated using the same crosslinking agent and initiator concentrations as were used in the samples in experiment one, namely a 5% crosslinking agent content and a 0.5% initiator content. 5 ml bulk samples were placed in polytops and irradiated in the same way as the samples in experiment one and the following was found for both the styrene with divinyl benzene and the methyl methacrylate with ethylene glycol dimethacrylate:

After initiation and radiation the system showed no visible change. SEM analysis of the precipitate showed particles in the micron range. The sample preparation was done according to the filtration and syringe washing method used in experiment one. High concentrations of particles should be observed due to the increased styrene concentration, but this was not the case, in fact, the concentration was quite low. The particles were however of a homogeneous distribution.

4.5 Experiments carried out with sodium 10-undecenoate to investigate nano-particle formation. Part one: the first successes

General information that was relevant to the investigations include the following:

Sodium 10-undecenoate was used as surfactant. The soap was weighed out to prepare 66% by weight concentration solutions in one-liter bottles. The binary phase diagram (section 2.7) predicted the presence of a hexagonal phase between 44 and 55% by weight. This was chosen as the primary concentration range for investigation. This would allow comparison of the binary surfactant/ water and the ternary surfactant/ water/ monomer systems.

The reaction conditions used in section 4.5 were the same as for the SDS experiment (see 4.4.1). The surfactant sodium 10 undecenoate is only partially soluble in ethanol and will precipitate with time. The homopolymer is not soluble in ethanol. This means that washing with ethanol will have a disadvantage in that surfactant contamination of homopolymer precipitation is inevitable. The other solvents which are commonly used for surfactant removal purposes, THF and methanol, were not used as THF causes precipitation of this surfactant and methanol created problems with SDS in that polystyrene has some solubility in methanol⁶.

The reactive solution mixtures that were prepared in section 4.5 are given in appendix D.

The following flow scheme was used for the first part of the investigation into the use of sodium 10-undecenoate for nano-particle formation:

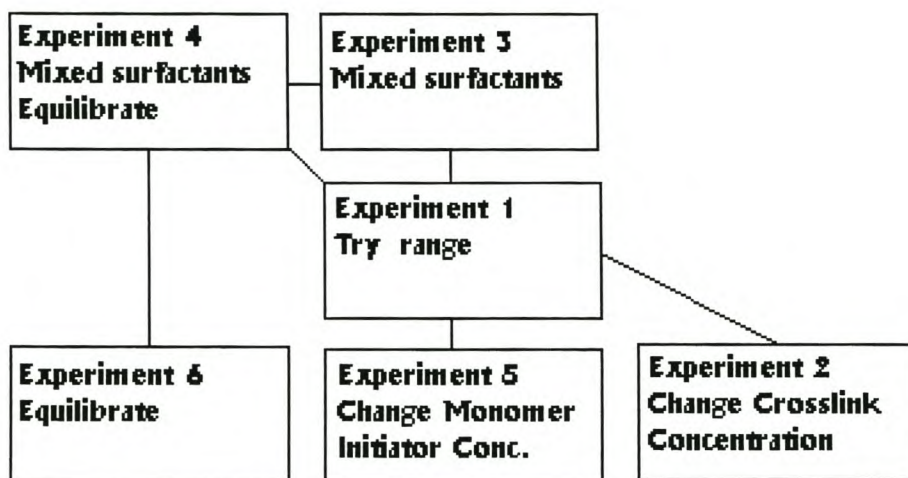


Figure 4.3 Experiments carried out in Part 1 section 4.5

4.5.1 *Experiment 1*

In the first attempt at particle formation a range of reagent concentrations was used: 30-50% sodium 10-undecenoate (in 5% increments). 5% of the styrene solution was used with 0.25% initiator and 5% crosslinker (divinyl benzene). (See appendix D table 2).

Different methods were used to attempt to recover nano-particles as described in test 1-5.

Test 1

The same analysis methods that had been used for section 4.4.1 were carried out. No precipitation occurred in ethanol and no large concentration of any particles was found after filtration and examination under the scanning electron microscope (SEM) (Hitachi 405).

Test 2

An attempt was made to use centrifugation to separate polymer from the solution by destabilizing the high concentration of surfactant and polymer. This was done by centrifuging 5 ml samples for up to 30 minutes. The heavier layer was washed repeatedly with ethanol. The filtration still did not show notable quantities of product under SEM analysis.

Test 3

Addition of an electrolyte to an emulsion will destabilize it and lead to coagulation. This technique was attempted for polymer recovery. Sodium chloride (NaCl) was added but precipitated the surfactant prior to destabilization of the polymer in solution. The natures of both the counter ion and the electrolyte content have been shown to have a large effect on both the product formed and the nature of amphiphilic aggregates^{6,7,8}. These studies showed that the size and type of aggregate formed by amphiphiles changes dramatically with both of these factors.

Test 4

The slow addition of ethanol to a sample of reaction product precipitated by the addition of electrolyte simply redissolved the surfactant as well as the rest of the sample contents rather than giving selective precipitation of the polymeric surfactant.

Test 5

The use of a Soxhlet extraction for the purpose of surfactant removal was attempted. A 20 cm length of dialysis tubing was prepared by placing in running water overnight. The Soxhlet apparatus was run continuously overnight with 5 ml of each sample and 250 ml ethanol in the dialysis tubing. The tubing was removed and pierced, and a sample was dried on a SEM stub. Although a product was obtained the particles did not exhibit any order, they showed a typically coagulated system of amorphous polymer. Ethanol also causes the dialysis tubing to harden. Water is a superior solvent for dialysis.

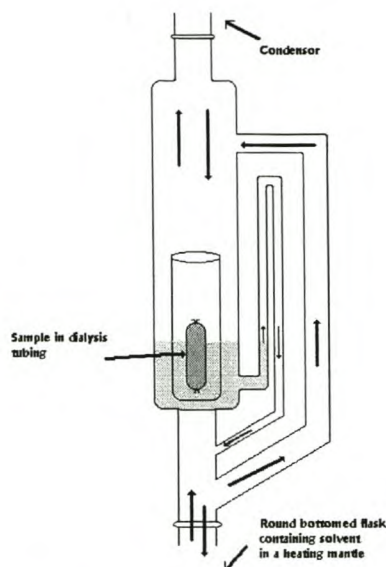


Figure 4.4 Schematic representation of Soxhlet continuous extraction apparatus

The conclusion that was made from these results was that experiment 1 had yielded small, roughly spherical, latex particles in low concentrations. These particles had coagulated in test 5 to provide the amorphous polymer that was recovered. The nature of the polymer in the original reaction mixture was not known.

4.5.2 Experiment 2

The second attempt at particle formation was again carried out with sodium 10-undecenoate with a styrene and DVB mixture as monomer. The concentration of the crosslinking agent was increased from that of experiment 1 in an attempt to strengthen particles more and to maintain the shapes that formed in solution. The monomer concentration was varied to determine the effect of monomer on the swelling of the hexagonal phase. The surfactant concentration was varied to determine any possible phase shift caused by the addition of monomer.

The crosslinking agent was used at 10% by weight of styrene concentration while the initiator was used at 0.5% by weight of styrene. The amount of monomer was varied as follows: 1, 2, 5, 10 % monomer solution was used with 30% surfactant.

5% monomer solution was used with 10-40% surfactant with 10% increments, and blank runs of 10-40% surfactant were carried out in 10% increments. 0.0025 g of initiator were added for every increment to the blanks (samples that did not contain styrene).(see appendix D table 3)

Solutions of 10% and 20% by weight concentration surfactant did not form clear microemulsions with 5% monomer, instead metastable opaque solutions were formed.

The irradiated samples were precipitated according to the procedure described in section 4.4.1 and then filtered. The samples were also centrifuged and filtered as in section 4.5.1.

The samples were analyzed by scanning electron microscopy according to the standard preparation described in section 4.3. The products that were obtained were similar in nature to those that were obtained in section 4.5.1.

No evidence of the effect of the crosslinking agent concentration on the system was found in this experiment. Results of the second sodium 10-undecenoate experiment were also unable to provide any new evidence of the nanoshaping of particles.

4.5.3 Experiment 3

The possibility of using a mixture of surfactants to obtain nano-structures was now investigated. 5% crosslinking agent concentration was used because section 4.5.2 had not provided any new insight into the importance of the crosslinking agent's concentration.

A standard solution of 5% styrene with 5% crosslinking agent and 0.5% initiator was prepared. The total surfactant concentration was varied between 25 and 45% with a maximum of 25% SDS and a maximum of 45% sodium 10-undecenoate. The use of 5% increments, from zero surfactant content, allowed the system to be examined in a broader concentration ranges (see appendix D).

The SDS containing samples tended to precipitate the surfactant. No clear structures were obtained from any SDS containing system. The systems that only contained sodium 10-undecenoate gave low concentrations of roughly spherical particles that had been seen previously in section 4.5.1. The precipitation of the systems was due to the temperature of the glove box, which was uncontrolled as SDS precipitates below 20 °C.

The use of mixed surfactants was not successful due to the temperature of reaction. The validity of the attempt was however questionable as the samples were not clear upon preparation at room temperature, suggesting that interaction between the surfactants was not favorable.

4.5.4 Experiment 4

Following on from work carried out by C.F.J. Faul using SDS⁶ it was decided that extended equilibration of the surfactant mixture prior to reaction might be required for the formation of liquid crystals. Equilibration time has been mentioned in literature^{2,9} but the period of equilibration is rarely given and then only in situations without the addition of a comonomer. Results of light microscopy studies indicate that phase formation occurs rapidly (within minutes) on slides but that larger volumes, when compared to the volumes between the slides, and differing conditions without surfaces for orientation may require longer formation times (see section 5.1). It was decided to equilibrate for a four-day period prior to irradiation.

It appeared that the mixed surfactant system required further investigation as temperature control had played an important role in experiment 3 section 4.5.3.

The experiment containing mixed surfactant samples using sodium 10-undecenoate and sodium dodecyl sulphate in section 4.5.3 was expanded to include higher surfactant concentrations. The concentration range was expanded to include up to 55% sodium 10-undecenoate. Samples that contained no added monomer were also irradiated. These blank runs contained up to 60% surfactant. (*Sample alpha 12, see later in section, a sample that contained no added monomer, was a sample in this experiment prepared at 60% sodium 10-undecenoate as in section 4.5.2).*

A heating mantle was placed in the glove box to attempt to maintain the temperature above the 25 °C required to prevent the precipitation of the surfactant sodium dodecyl sulphate. The solutions were allowed to equilibrate for four days prior to irradiation. They were reacted as in section 4.4.1 and then they were allowed to stand for 3 hours prior to filtration. Reactions carried out with the mixtures of surfactants once more led to precipitation of the surfactant. At no stage were the solutions clear.

SEM images of the samples of this experiment did not show any directed structures. The fact that polymerization would occur during the four days at room temperature that were used as an equilibration period was a factor that was considered detrimental to the study.

At this point it was decided that using this approach, at room temperature, was not suitable, as the surfactant mixture was not homogeneous at high surfactant concentrations at lower temperatures and the mixtures tended to precipitate. The reasons for this precipitation include the chain length of the surfactants as well as the head group interactions. The surfactant chains show a difference in chain length of two carbons (due to the unsaturation of the 10-undecenoate chain). The head groups vary in size, as the sulphate head group is significantly larger than the carboxylate. These two factors will affect the packing of the surfactants at higher concentrations as well as the solubilities of the respective surfactants.

4.5.5 *Experiment 5*

The use of sodium 10-undecenoate alone was tried at up to 60% surfactant concentration by weight. The monomer concentrations used were 5%, 10%, 15%, 20% and 25%, crosslinking agent and initiator concentrations were at 5% and 0.5% of styrene respectively (see appendix D table 6).

The study did not make use of equilibration as the lack of stabilizers in the system were considered as being detrimental to the system over a four day period. The fact that significant polymerization would occur at room temperature in an unstabilized system was thought to lead to the formation of amorphous particles. Results of SEM

studies were not indicative of nano-shaping. In most cases amorphous polymer or spherical particles of less than 600 nm were recovered.

High monomer concentrations (15%+ styrene) formed a clear monomer layer on the top of the sample. This was thought to be either excess monomer (i.e. monomer that could not be phase included due to surfactant constraints) or monomer that had not had sufficient opportunity to diffuse into the surfactant phases.

Sample Alpha 12, an irradiated sample of experiment four, which contained 60% surfactant and 0.5% initiator but no added monomer, was analyzed after it was observed that the sample had discolored strongly. It had been standing for approximately two and a half months. It was found that after precipitation in ethanol followed by filtration as in section 4.4.1 a vast number of star-like particle could be seen under SEM. The use of the Cambridge Leica S4401 SEM instrument at the Unit for Electron Microscopy at the University of Cape Town showed the presence of fine fibers of the range of 70 nm. It was felt that this indicated time dependence as a factor in the particle formation.

The following images were obtained on the Cambridge Leica S4401 SEM at the University of Cape Town:

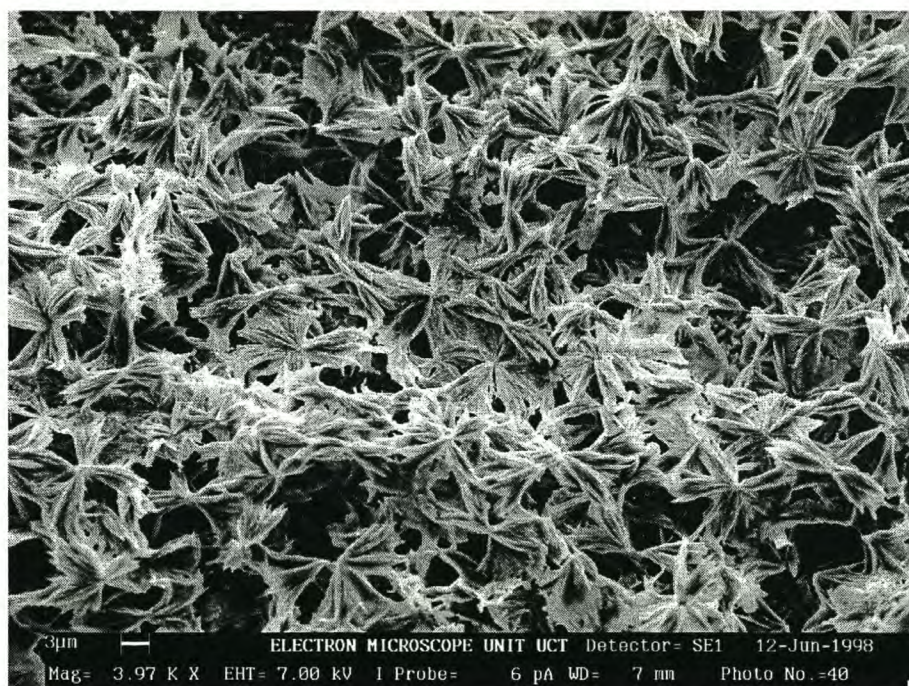


Figure 4.5 SEM image of sample alpha 12 at 1 μm scale

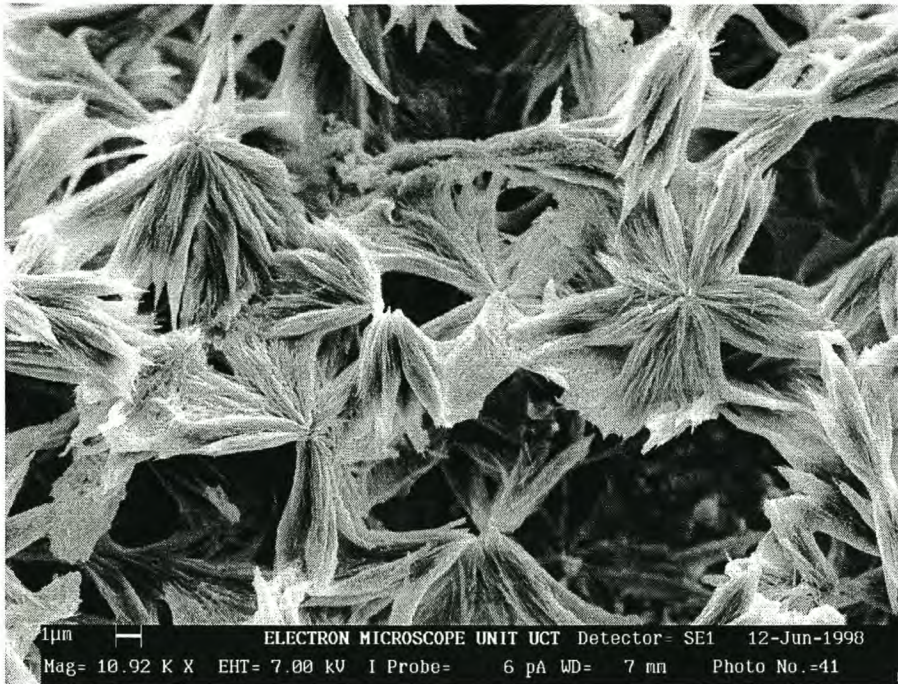


Figure 4.6 SEM image of sample alpha 12 at 3 μm scale

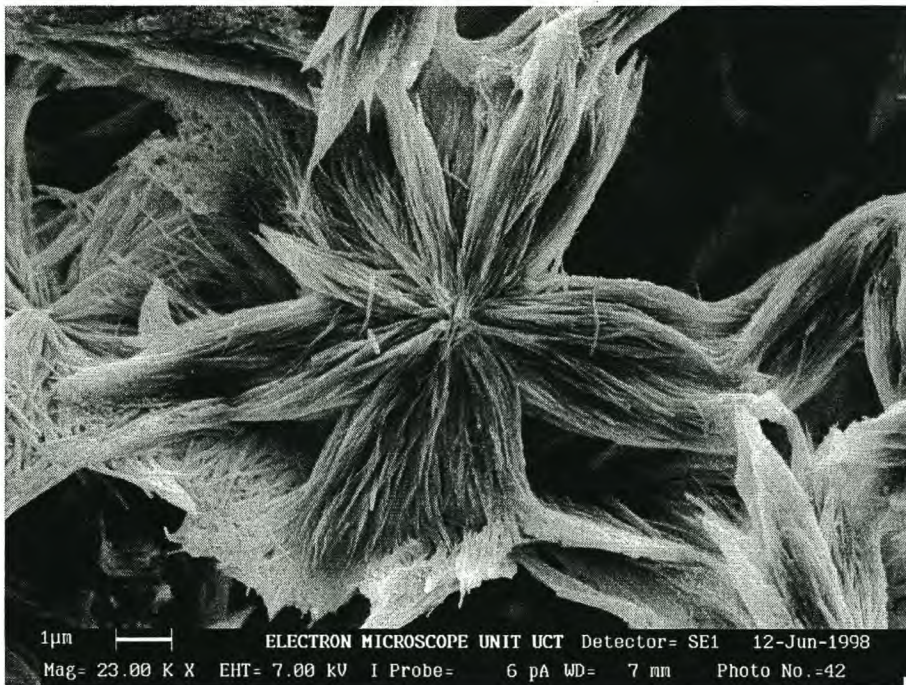


Figure 4.7 SEM image of sample alpha 12 showing a single particle

Field emission scanning electron microscopy (FESEM) work was carried out at the national facility at the University of Pretoria and micrographs were obtained of the sample alpha 12 at high magnification.

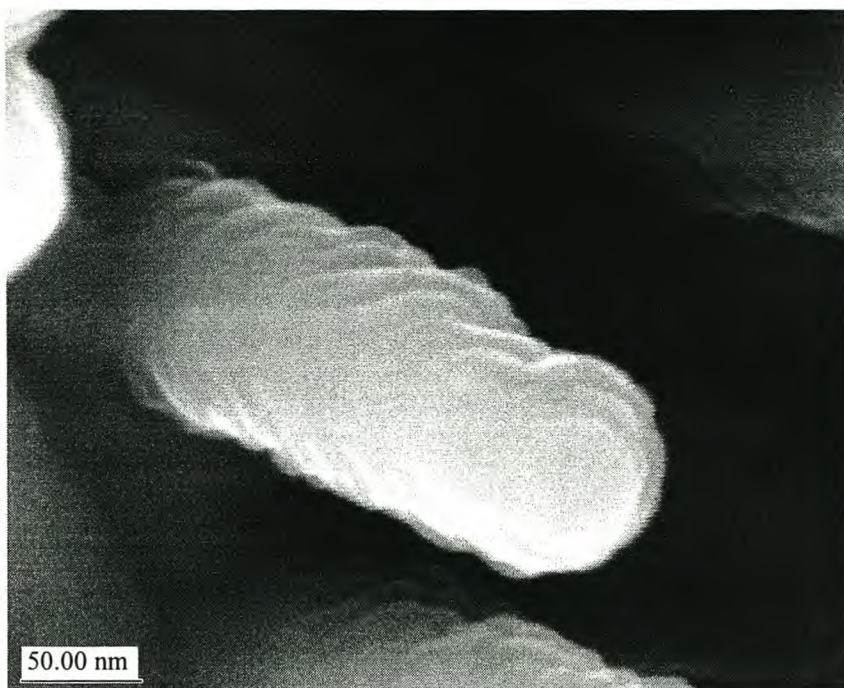


Figure 4.8 FESEM image of the tips of the fibrous structures of sample alpha twelve

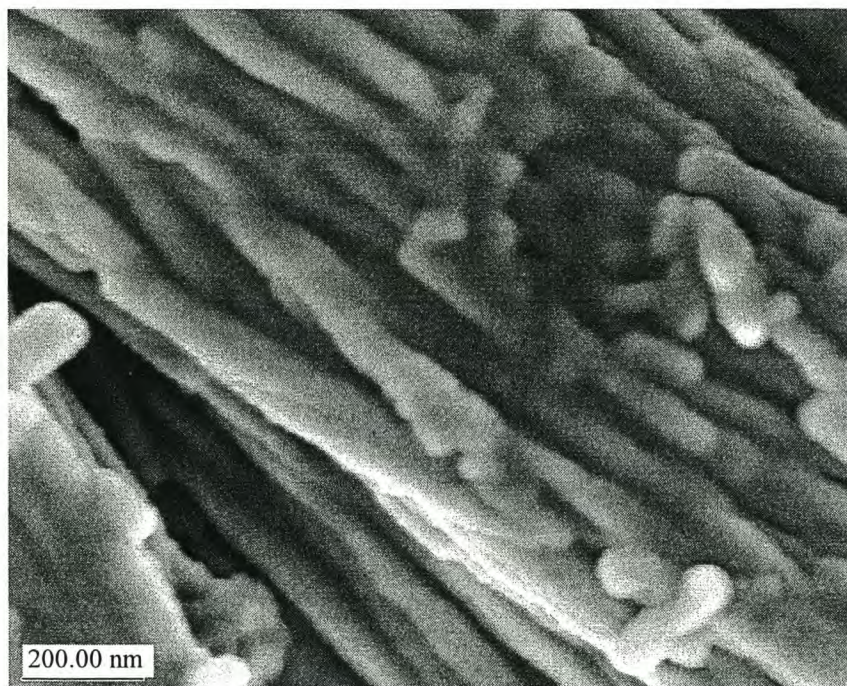


Figure 4.9 FESEM image of the fibrous structures that were obtained, with a cross section of about 70 nm, in sample alpha 12

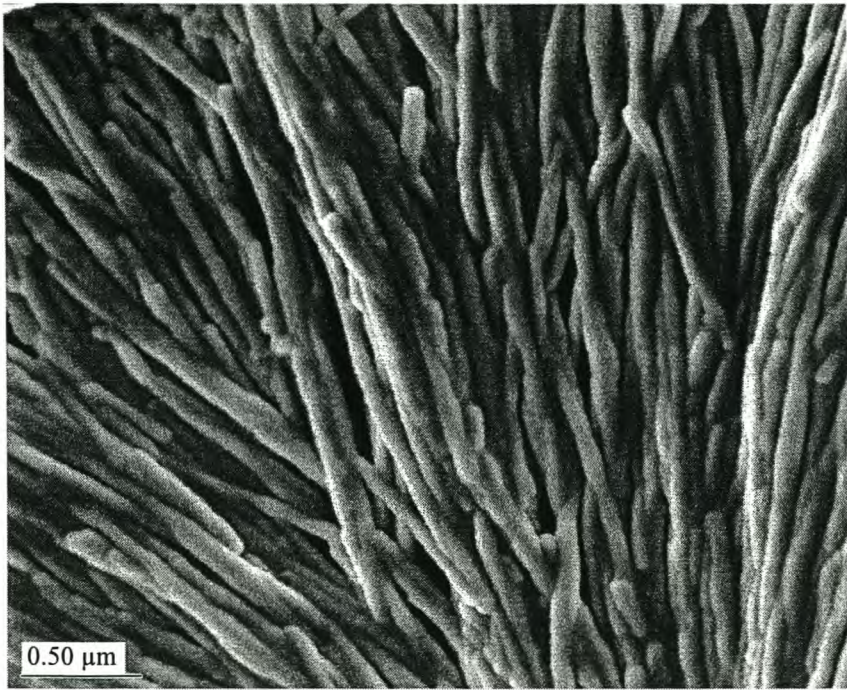


Figure 4.10 FESEM image of the fibrous structure, as seen from above, in sample alpha 12

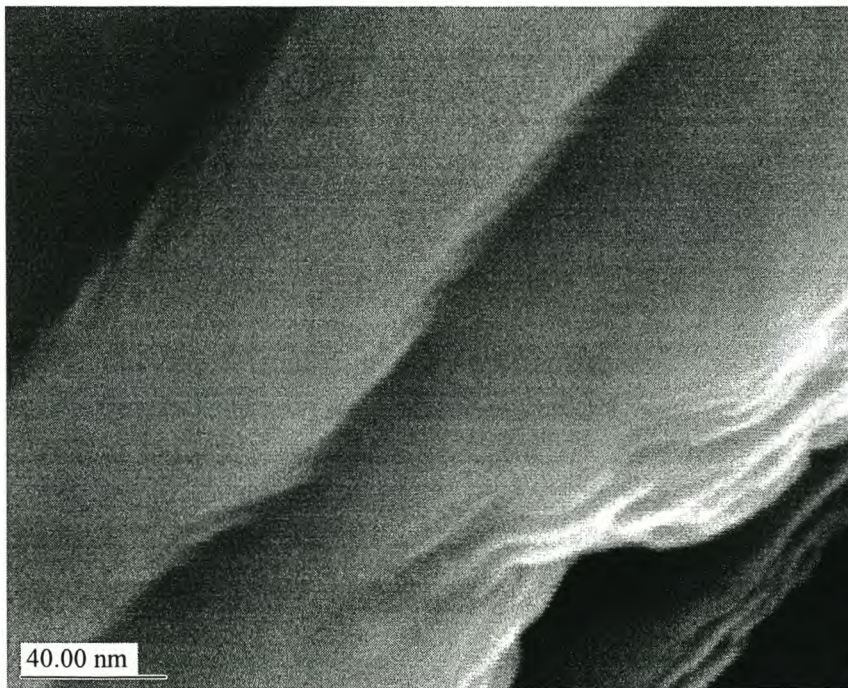


Figure 4.11 FESEM image of an enlargement of the edges of the fibers in sample alpha 12

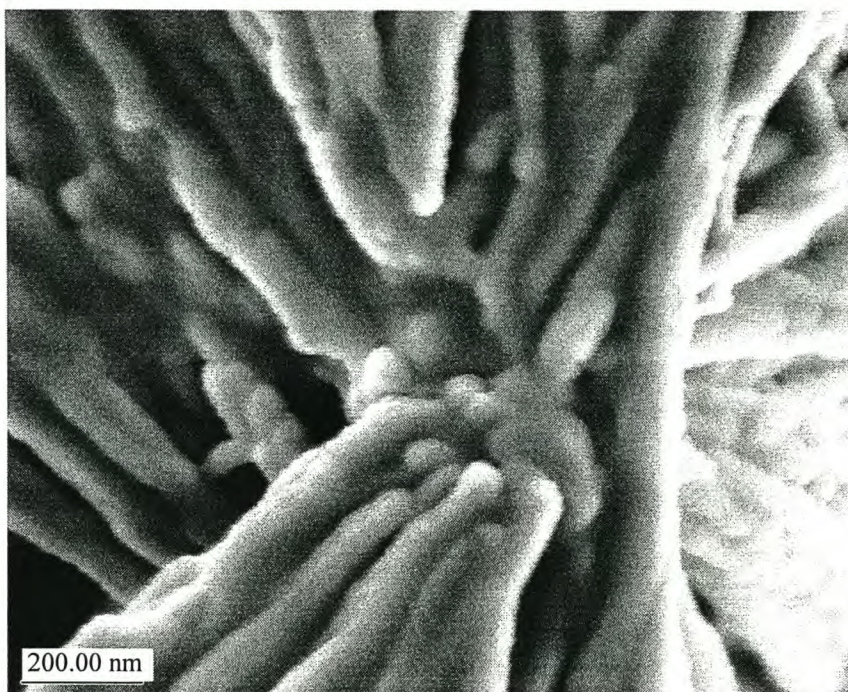


Figure 4.12 FESEM image of an enlargement of the center of a particle in sample alpha 12, clearly showing a central growth area

(This image shows that some of the “leaves” appear to have broken from the central core. The fibers here show sizes between 70 and 100 nm).

Sample Alpha 12 was also prepared for analysis by atomic force microscopy (AFM) by dripping some of the ethanol wash (1:10) directly on the AFM plates. These images did not show the star like particles, due to the preparation method. The surfactant, which would have dried on the plates, obscures the view of any but surfactant surfaces. The AFM images showed only surfactant aggregates (see appendix C 15 and 16). The aggregates are fiber-like which is complementary evidence to the SEM evidence.

The fine fibers seen in SEM analysis were suggestive of hexagonal phase guidance and the aggregates were considered to be shaped into the star-like forms by the natural tendency of the surfactant to form spiral patterns². This was considered to be a success and further investigations were based on these findings.

4.5.6 Experiment 6

The positive results obtained with sample alpha 12 appeared to negate previous theories about stabilization requirements, i.e. no stabilizers in the samples, did not appear to have a detrimental effect. Thus in this experiment equilibration was attempted over a one-week period.

The experiment was carried out in the same manner as set out in section 4.4.1 but was allowed to equilibrate prior to irradiation. The concentrations that were prepared are shown in appendix D table 7.

SEM analyses of the samples of experiment six showed similar star-like particles to those found in sample alpha 12 in certain concentration ranges. The equilibration was thought to be the reason for this phenomenon. The form of the particles was similar, although not identical, to the particles in sample alpha 12, and fibrous structure could be seen in the leaves of the particles.

Samples containing 5% monomer at 50 and 55% surfactant and 10% monomer at 40 and 45 % surfactant showed the star-like particles. The 2.5% monomer run showed low concentrations of star-like particles at 55% sodium 10-undecenoate.

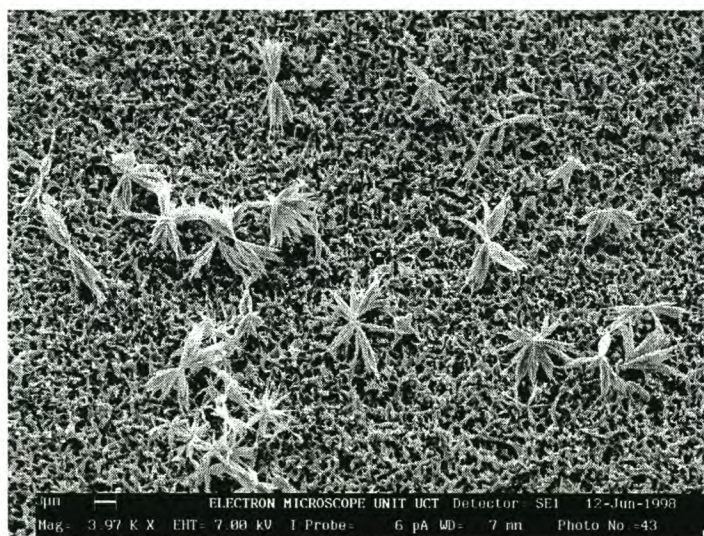


Figure 4.13 SEM image of product containing 5% monomer and 50 % surfactant

This vindicated the supposition of phase prediction for the formation of the particles, as increasing the monomer concentration appeared to decrease the surfactant concentration requirements for the formation of the particles.

4.5.7 *Epilogue*

At this stage the laboratory was moved and a purpose build glove box was taken into commission. This glove box was custom built by the University of Stellenbosch Technical Services with the requirements of the surfactant, water and monomer systems in mind. The glove box was designed to accommodate two persons and was equipped with a temperature regulation system in the form of a heater with a fan and a thermostat. This allowed far more accurate control of the temperature in the system. This also meant that problems, such as different reaction temperatures and surfactant precipitation due to low temperatures, could be eliminated.

The moving of the laboratory did not occur without problems. The new glove box was found to have a low integrity. The purity of the nitrogen was also initially questionable, as a scrubber was not in use. The box continued to cause major problems in terms of atmosphere retention and temperature control and repeatability of the results of section 4.5.6 required two months to establish suitable conditions.

The glove box was sealed with silicone sealant, especially at the gloves. The nitrogen gas supply was changed to a liquid nitrogen supply that was capable of vaporizing the gas as required. The advantage of using a liquid nitrogen supply was that it would condense oxygen and unwanted gases

A large (47 mm) vacuum Millipore filter was commissioned. This allowed large volumes of sample to be filtered. The reason that this was required was the fact that as can be seen from the SEM images the concentrations of the particles were not in sufficient quantity to carry out even the least mass demanding qualitative analysis.

40 samples containing 45% surfactant and 10% monomer were placed in the glove box. They were irradiated in batches, with varied equilibration times, to attempt to

again obtain the reaction conditions that had led to particle formation. The samples were filtered on the large filter after cooling 1:10 ml solutions of sample in ethanol for short periods of time, to encourage precipitation. Those samples that showed any particle formation showed concentrations that were of medium to low intensity see the figure below:

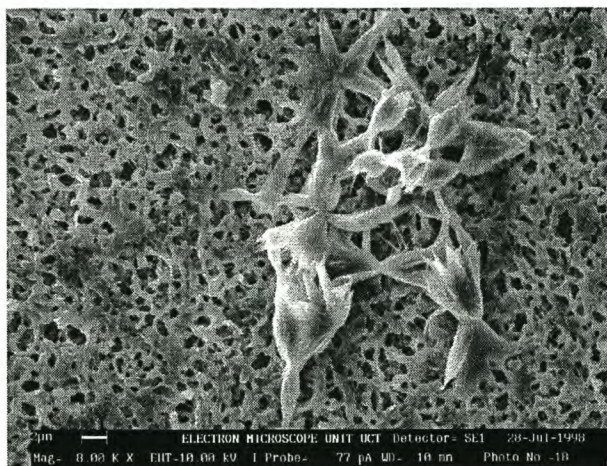


Figure 4.14 Damaged star-like forms

(Sample containing 10% styrene and 45% sodium 10-undecenoate)

The concentration of the star-like particles was much lower in the samples prepared in this manner than those prepared by washing and filtration. The particles also were far less defined than the particles found in the irradiated samples, with 10% styrene and 45% sodium 10-undecenoate, that had been prepared via washing (section 4.5.6). UCT's SEM showed that the shapes were not perfect, in fact they appeared damaged.

Possible explanations for the appearance include the crystallization of surfactant on the surfaces between the cylindrical ribbons. This will occur due to the lowering of temperatures during the cooling period, leading to the damaged appearance of the particles.

As very few of the samples irradiated during the laboratory moving period showed particle formation, regardless of the varied conditions or the recovery method, the nano-particle formation was reinvestigated by exploring the component concentrations and the conditions of reaction. This will be discussed in part 2.

4.6 Experiments carried out with sodium 10-undecenoate to investigate nano-particle formation.

Part two: rediscovery of particles

The earlier success in creating a star-like particle that was achieved using the reaction method discussed in 4.5.6 proved very difficult to reproduce. The use of equilibration as a means to allow the phases to form was now investigated in more depth than in part 1.

In Part 2 the preparations of reaction solutions were done in the temperature controlled and atmospherically sealed glove box that had been specifically made for this purpose and was now fully functional.

Reaction conditions for part two were as follows:

Sample volumes of 7,5 ml of the ternary mixtures of sodium 10-undecenoate/ styrene and water were prepared as the reaction volumes used in part 1 were deemed to have been excessive. The samples were irradiated as before and then removed and analyzed by SEM.

Standard analysis involved filtration of 200 microliters (μl) of the reacted samples with 5 ml ethanol. This was carried out through a 0.22 micron (μm) Millipore filter and the filter paper was then examined under a scanning electron microscope (section 4.4.1).

Previous success in shaped-particle formation had also been achieved in the SDS experiment (see 4.4.1) by precipitation of polymer (5 ml of the sample in 30 ml ethanol) and washing (approximately 4 times) with more ethanol. After treating the washing ethanol with acetone the removal of soap could be clearly seen. Acetone forms an instantaneous gel with any surfactant present. This preparation method was used for the experiments one through three, for comparison to the standard filtration technique described in section 4.4.1 but was also unsuccessful.

Another technique, discussed in 4.5.7, namely the cooling and filtration of 1:10 solutions of irradiated samples in ethanol, had also previously given some success in terms of particle recovery. This entailed placing the solution in ice for a short period but not enough to cause freezing of the sample (this had produced damaged stars in the past but only in low concentrations), and then filtering on the large filtration system. This technique was used as a control for experiment four but success was still limited to damaged star-like particles at low concentrations.

The following flow chart shows the experiments that were carried out in section 4.6:

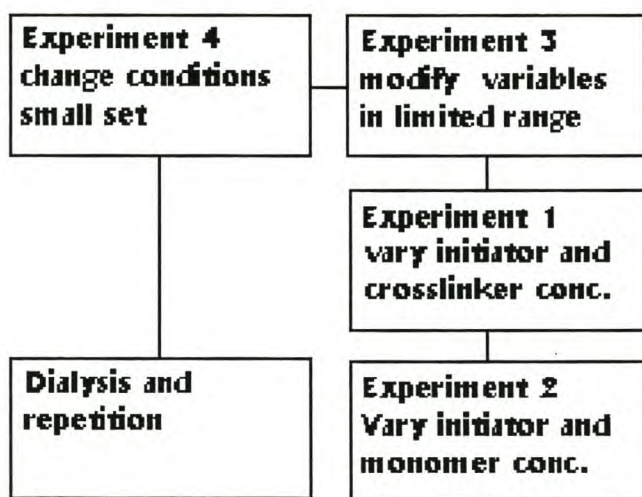


Figure 4.15 Experiments that were carried out in part 2 section 4.6

It was not possible to reproduce the starlike product, which had previously been obtained in section 4.5.6, in the first three experiments. The first time that control was exercised over the styrene containing experiments was in section 4.6.4. The samples were all evaluated by scanning electron microscopy. They were prepared as discussed in 4.4.1 for clear samples but the precipitated samples were filtered and washed with ethanol through the large filter.

The ages of surfactant solutions vary as these results were generated over time. This means that the concentrated solutions had been exposed to different conditions prior to reaction. Equilibration of samples was taken over a one-week period. It has however been shown in section 3.3 that the surfactant is stable in solution for long periods of time and the age of solutions should not be a factor in the study.

4.6.1 Experiment 1

The effect of the concentration of the crosslinking agent and the initiator concentration on the formation of shaped nano-particles was investigated.

Solutions containing 45% soap and 10 % styrene were used, with varying initiator and crosslinking agent concentrations. The following table shows the experiments that were carried out as well as the results that were obtained.

The P is indicative of a system that was unstable and precipitated before or during irradiation and consequent polymerization.

Table 4.1 Results of crosslinker and initiator concentration variation experiment

INITIATOR IN STYRENE	5% DVB IN STYRENE (BY VOLUME)	20% DVB IN STYRENE (BY VOLUME)	100% DVB IN STYRENE (BY VOLUME)
0.5% (by mass)	P	P(yellow)	P(orange)
2.5% (by mass)	P	P(yellow)	P(orange)
5% (by mass)	P	P(yellow)	P(orange)

All the samples were unstable and the precipitates were studied by scanning electron microscopy.

SEM analysis of the 100% DVB samples showed a mixture of spherical and circular plate-like structures. The structures were substantially different from those that were observed in the case of the 5% DVB containing samples, which had been prepared in part one (section 4.5.6), or to standard spherical emulsion particles.

The following SEM micrographs were taken experimentally of these plate-like particles found in the DVB systems.

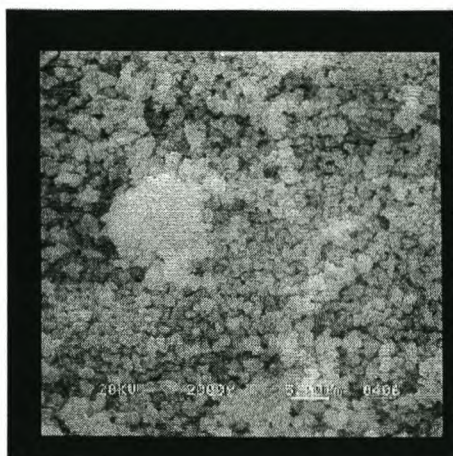


Figure 4.16 Plate-like structures
2000 x



Figure 4.17 Plate-like structures
50 000 x

In no cases were the star-like particles reproduced. The particles varied from spherical to completely random, rough polymer particles of widely varying nature. The high crosslinking agent concentration meant that the systems were not stable, clear samples after irradiation, but were precipitated cloudy solutions, which meant filtration by hand was not possible, and the larger filter was used to recover the polymer.

In systems with high divinyl benzene concentrations the color that was observed in samples was deeper, extending to a deep orange. The DVB system was also the first system in which the polystyrene (poly (divinyl benzene)) precipitation was observed .

The nature of the precipitate was confirmed by the use of FT-IR spectroscopy (see section 3.2). The precipitate was obtained in a fine powder form. The precipitate was particulate in nature with particles in the range of one micron in size in the styrene system.

4.6.2 Experiment 2

The effect of the monomer concentration on the product of the reaction was now evaluated with respect to the initiator concentration to determine the interactions of the effects as well as their effect on the nature of the product.

45% surfactant solutions with varying monomer and initiator contents were used. The samples contained 5% crosslinking agent (divinyl benzene).

The following table shows the concentrations of the solutions used and the results of the irradiations.

Table 4.2 Results of monomer and initiator concentration variation experiment

% monomer by volume	0.5% initiator (by mass)	2.5% initiator (by mass)	5% initiator (by mass)
0% Monomer	C	C	C
5% Monomer	C	C	P
10% Monomer	C	P	P

The C solutions are those which were clear after irradiation while the solutions which are indicated as P precipitated.

The higher initiator concentrations as well as the higher monomer concentrations were unable to maintain stability in the sample and the polymeric product precipitated. The nature of the precipitate (in this case polystyrene) was confirmed by FT-IR studies. No star-like particles were found by SEM analysis.

4.6.3 Experiment 3

The sample runs that are shown in table 4.3 are all samples out of Batch X planning (see Appendix D, page xlv). Batch X itself was run before the pressure release system was in place, which allowed a slight overpressure to minimize oxygen contamination,

and before the Dewar (liquid nitrogen supply) was in use as a continuous nitrogen-gas supply and oxygen scrubber. The repeat batches 1(a) through 4(b) were run after the new nitrogen gas supply was in place. The small letters that are indicated refer to the surfactant solution that was used in the preparation of the samples.

The table below (Table 4.3) indicates samples that were reacted as well as their stability after reaction. The P solutions indicate precipitation while the C solutions remained clear. (a) and (b) refer to specific surfactant batches namely solution A and solution B, which was used in section 3.3. The irradiation was as in section 4.4.1.

Table 4.3. Batch X planning and experiments

Weight % Surfactant	Volume % Monomer	% Crosslinker in monomer	% initiator in monomer	Sample number	Batch X (a)	Run 1 (a)	Run 2 (b)	Run 3 (a)	Run 3 (b)	Run 4 (a)	Run 4 (b)
45	5	5	0.5	2	C	C	C				
45	5	10	0.5	5	C	C	C				
50	5	10	0.5	6				C	C		
45	10	5	0.5	8	C	P	C				
45	10	10	0.5	11	C	P	C			P	P
50	10	10	0.5	12		P		P	P	P	P
45	5	5	1	14	C	C	C			C	P
50	5	5	1	15				C	C		
45	5	5	5	17	C	P	C				
50	5	5	5	18				C	C	P	P

When styrene solution that had crosslinking agent and initiator added was allowed to stand for 48 hours at room temperature before use, the samples did not precipitate (see Run 2). This could suggest that the initiator was no longer viable by the time of the glove box preparation i.e. the system had already polymerized.

Precipitation, if it occurred, normally occurred over a period of between 6 and 48 hours, which was during the equilibration period. The samples were kept in the dark in a nitrogen atmosphere at 25 °C during equilibration.

The nature of the surfactant also appears to play a role in the precipitation, as the batch of surfactant that was used for specific samples seemed to allow different samples, with the same component concentrations, to precipitate polystyrene.

Five soap solutions were prepared over time and compared (A, B, C, D and E), they were all 66% by weight. The surfactant solutions were prepared and used in that order and offer varying results in some cases although testing of B and C in section 3.3 in comparison to two older solutions OA and OB showed that there were no obvious differences. Solutions A and B were prepared from the same solid surfactant batch as were C, D and E, for this reason only B and C were tested in 3.3.

There did not seem to be direct correlation between the treatment of the soap and the precipitation, as sample 14 in run 4 prepared from solution A (stored at 70 °C) did not precipitate, while sample 14 in run 4 prepared from solution B (stored at 25 °C) did precipitate. Solution B had not formed any lumps. Previous experience suggests that making up the solutions at lower temperatures leads to less gel lump formation though solution formation is more difficult.

Table 4.4 Batch X planning and experiments cont. (surfactant solution in brackets)

Weight % Surfactant	Volume % Monomer	% Crosslinker in monomer	% initiator in monomer	Sample ident.	Run 5 (a)	Run 5 (b)	Run 5 (c)	Run 6 (b)	Run 6 (c)
50	5	5	0.5	3	C	C	C		
50	5	10	0.5	6	C	C	C		
45	10	5	0.5	8	C	C	C		
50	10	10	0.5	12	C	P	C	P	P

Surfactant solution C showed no precipitation in any of its samples (runs 5 and 6, which were runs specifically for comparison of surfactant batches). Sample 5 (b) 8 did however show an opaque suspension that disappeared over 48 hours to provide a clear solution, and sample 6 (c) 12 precipitated after a period of a month.

Samples (10% styrene sol in 45 % surfactant) that had been standing in the box for three months, as a reference (section 4.5.7), did not show any signs of precipitation. These samples were, however, prepared prior to the sealing of the doors (temporarily) and had thus been exposed to the atmosphere albeit when closed. They were also prepared before the new nitrogen supply was taken into service. That means that they were in contact with oxygen, although closed, and as the seals on the sample vials are not airtight this would have allowed oxygen into the samples, explaining the stability of the samples.

The reaction system was improved by increasing the integrity of the glove box, ignoring equilibration (which had seemed to be important but was now thought to lead to reaction by initiation at room temperature), and flushing all solutions excessively with nitrogen.

None of the samples of experiment 3 showed star-like particles.

4.6.4 *Experiment 4*

The following run was prepared and reacted without being allowed to stand to equilibrate. Surfactant solutions E and D (66% by weight from the same solid surfactant batch) were used for comparison. The styrene was distilled on the day of the reaction preparation and surfactant solution E was prepared one day after surfactant solution D. The reaction was carried out one week after surfactant solution E's preparation.

The table below shows the concentration of the components in the samples for this experiment.

Table 4.5 Monomer and surfactant concentration variation experiment

Sample	Crosslinker % in styrene	Initiator % in styrene	Volume styrene (ml)	Volume % styrene	Vol.surfactant solution (ml)	Weight % surfactant	Surfactant Solution used	Total volume (ml)
4(d)1	5	1	0.75	10	5	44.4	D	7.5 ml
4(d)2	5	1	2.5	33.3	5	44.4	D	7.5 ml
4(d)3	5	1	0.75	10	6	53.3	D	7.5 ml
4(d)4	5	1	1.5	20	6	53.3	D	7.5 ml
4(e)1	5	1	0.75	10	5	44.4	E	7.5 ml
4(e)2	5	1	2.5	33.3	5	44.4	E	7.5 ml
4(e)3	5	1	0.75	10	6	53.3	E	7.5 ml
4(e)4	5	1	1.5	20	6	53.3	E	7.5 ml

Samples with high monomer concentrations were observed to form stable foams that were not able to settle prior to irradiation due to the lack of equilibration time. (4(d)2, 4(e)2 (33%), 4(d)4, 4(e)4 (20%)).

The filtration of the samples was carried out by hand using 0.75 ml of a sample filtered with 5 ml of ethanol.

The following results were obtained from SEM analysis.

Table 4.6 Results of monomer and surfactant concentration variation experiment

Sample	Comment	Sample	Comment
4(d)1	Nothing on filter	4(e)1	Nothing on filter
4(d)2	Stable foam precipitate	4(e)2	Stable foam precipitate
4(d)3	Stars(high concentration)	4(e)3	Stars (high concentration)
4(d)4	Stable foam precipitate	4(e)4	Stable foam precipitate

The following SEM images show the results of the successful nano-particle formations:

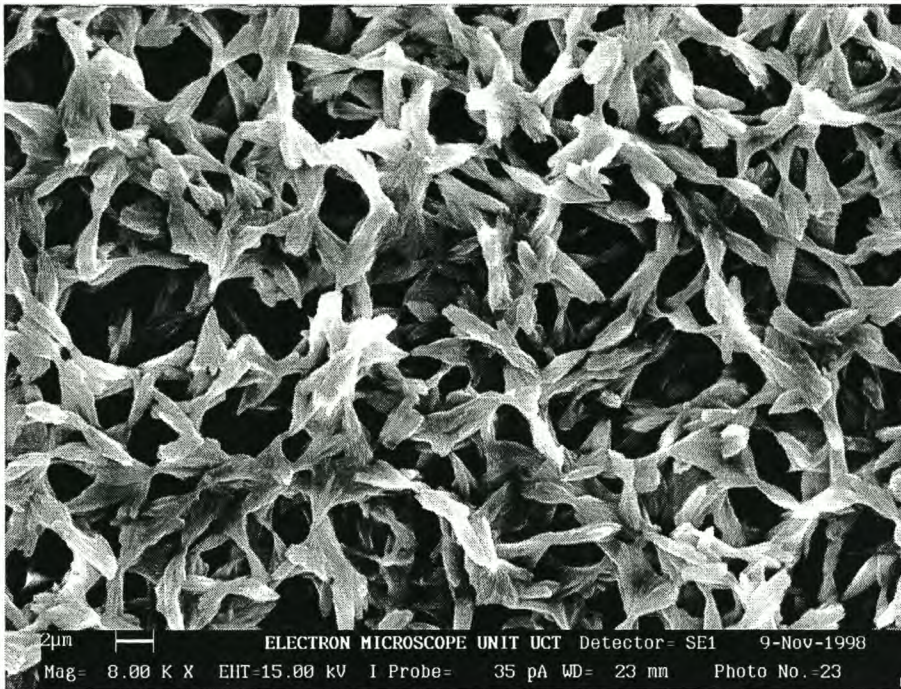


Figure 4.18 SEM image of 4 (d) 3

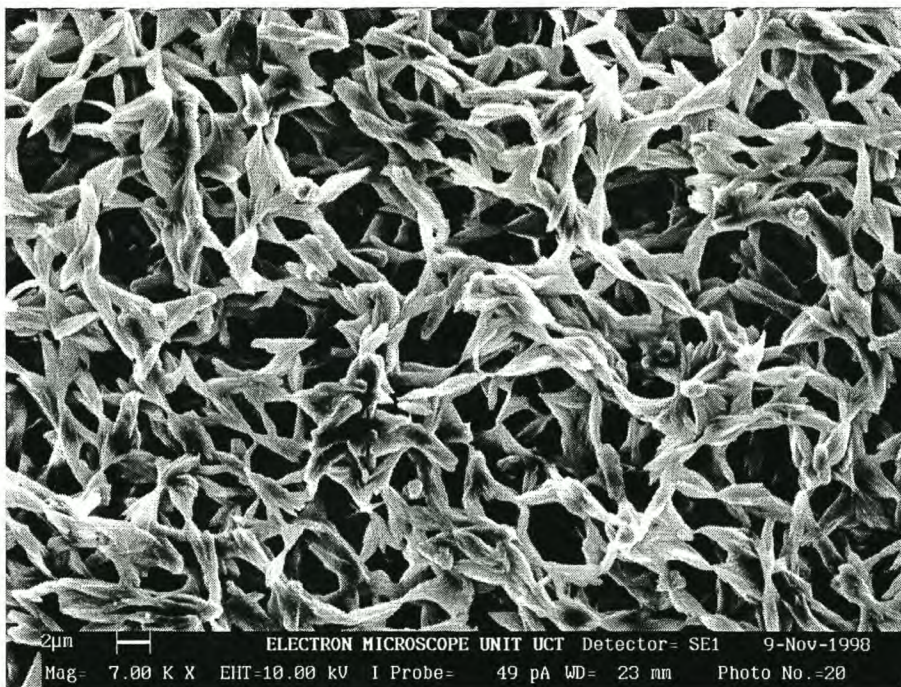


Figure 4.19 SEM image of 4 (e) 3

These images show that under the correct conditions in the glove box, with suitable flushing to maintain nitrogen integrity, as well as immediate reaction, without equilibration, the star-like particles can be prepared. The fragility of the system has not been completely overcome and great care must be taken with the preparation. The concentrations of the components and preparation of the filter paper should be carefully controlled.

The reaction system was now stable enough that the shaped particles could be produced without too much difficulty. The fact that the preparation conditions were now different from those that first proved successful (section 4.5.6) is thought to be due to the difference in the glove boxes that were used e.g. temperature.

4.6.5 *Dialysis*

A duplicate batch of samples to those in section 4.6.4 was used for the purposes of dialysis to allow for polymer recovery without surfactant. The samples were examined under SEM. Four identical samples (4(d)3) were placed in a dialysis tube that had been prepared by placing it in running water overnight and allowing it to stand. The dialysis tube had a molecular mass cut off of 12000 atomic mass units. The samples were washed with ethanol using a continuous system (Soxhlet extraction).

A duplicate sample (of the Soxhlet extracted samples i.e. 4(d)3) was precipitated with THF. THF caused the precipitation of the soap in the system as well as the polymer. THF was discarded as a means of separating polymer from surfactant.

Ethanol was found to cause hardening of the dialysis tubing. Water was the second choice of a solvent. The water extraction required temperatures in the Soxhlet apparatus that were well in excess of room temperature in the dialysis tube. These temperatures are thought to have affected the product, as they would have significantly increased the polymeric product in the system. The dialysis was repeated in water that was manually replaced. The dialysis was taken to completion over a period of one week while replacing the water three times daily.

The dialysis resulted in the recovery of homopolymer polystyrene. There was no visible incorporation of surfactant, as observed in the FT-IR spectra. As expected the structure of the polymer had been lost, but the presence of polymer in the system was confirmed. (The removal of the surfactant is thought to lead to the particles “clumping” as the electrostatic repulsion of the particles has been removed).

4.7 Experiments carried out with sodium 10-undecenoate to investigate nano-particle formation.

Part three: The use of methyl methacrylate as a comonomer

4.7.1 Introduction

The possibility of using methyl methacrylate (MMA) as a monomer in the system was prompted by work carried out by Cheung *et al*, on the potassium salt ⁷. The first experiment yielded results that were cautiously promising (section 4.7.2). The presence of plank-like particles in low concentrations (see figure 4.21), low enough that the possibility of contamination could not yet be ruled out, nevertheless gave hope that the system might have potential as a copolymerizing system for the production of different shaped-particles.

The following general procedure was used for the methyl methacrylate runs. The surfactant stock solution that was used was solution C, as referred to in the surfactant analysis in section 3.3. The crosslinking agent was ethylene glycol dimethacrylate. The methyl methacrylate solutions were prepared in the same fashion as the styrene solutions in section 4.5 in that the initiator was phenyl acetophenone and the solutions were prepared shortly before insertion into the glove box and were first bubbled through with nitrogen gas to remove excess oxygen.

The density of the MMA stock solutions was approximated as 0.944 g/ml. The solutions were made up with distilled deionised water. The samples were prepared in polytops and had a volume of 7,5 ml. The MMA was not distilled but in some experiments was passed through inhibitor removal columns.

The standard filtration for experiments in section 4.7 was carried out immediately. 0.5 ml of each sample was washed with 5 ml ethanol, through 0.22 micron (μm) filter paper.

4.7.2 Experiment 1

Methyl methacrylate was first used with inhibitor present to prevent polymerization during the equilibration period of one day that was allowed. The reaction was carried out for an extra one-hour irradiation period to compensate for the fact that the inhibitor would retard the reaction (i.e. total irradiation of three hours), in the same manner as in section 4.4.1.

The surfactant effect was also partially observed, as different surfactant solutions were used for the two batches, namely A and B. The following table shows the component concentrations in the samples:

Table 4.7 Crosslinker, monomer and initiator concentration variation experiment (1)

Sample	Crosslinker % in MMA	Initiator % in MMA	Vol. methyl methacrylate (ml)	Volume % MMA	Vol. surfactant solution (ml)	Weight % surfactant	Surfactant Solution used	Total volume (ml)
1(a)1	10	1	2.25	30	0	0	-	4.25 ml
1(a)2	10	1	1.5	20	5	44.4	A	7.5 ml
1(a)3	10	1	0.75	10	5	44.4	A	7.5 ml
1(a)4	10	1	0.375	5	5	44.4	A	7.5 ml
1(b)1	5	0.5	2.25	30	0	0	-	4.25 ml
1(b)2	5	0.5	1.5	20	5	44.4	B	7.5 ml
1(b)3	5	0.5	0.75	10	5	44.4	B	7.5 ml
1(b)4	5	0.5	0.375	5	5	44.4	B	7.5 ml

SEM results showed low levels of product that showed trace amounts of typical planks that have been observed in SDS/styrene systems⁶.

Table 4.8 Results of experiment (1)

Sample	Comment	Sample	Comment
1(a)1	Not examined	1(b)1	Not examined
1(a)2	No evidence of particles	1(b)2	Spherical(low concentration)
1(a)3	Pieces of plank/ spherical	1(b)3	Planks (low concentration)
1(a)4	Spheroid	1(b)4	Planks/v-breaks ⁶

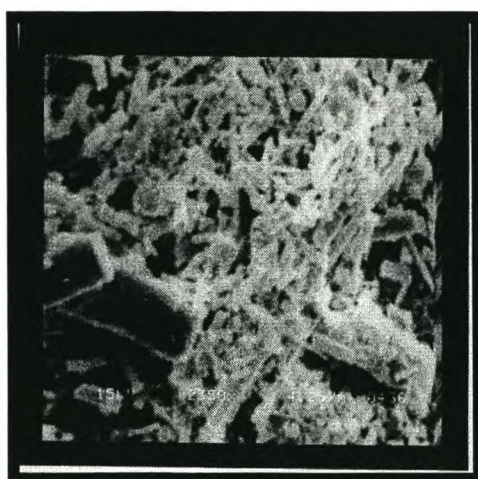


Figure 4.20 SEM image of 1(a) 3

(Plank-like forms that were found. This image is at 2350 x magnification)

The samples 1(a)3, 1(a)4 and 1(b)3, 1(b)4 appeared to give a mixture of structures, including those that have previously only been seen with styrene ⁶. The mixtures of traditional spherical particles and planks occurred in extremely low concentrations and it was thought that the plank-like particles could be due to contamination. For this reason the experiment was changed to improve polymerization by removing the inhibitor.

4.7.3 Experiment 2

In second experiment MMA that had been through an inhibitor removal column was used. The equilibration period was again 24 hours.

The surfactant conditions were retained but concentrations were changed in the less successful batch (a) of section 4.6.3 in that the crosslinking agent concentration was changed to 5 percent and the initiator concentration was increased to 5 percent.

The following table shows the concentrations of the samples of experiment two:

Table 4.9 Initiator and monomer concentration variation experiment (2)

Sample	Crosslinker % in MMA	Initiator % in MMA	Vol. methyl methacrylate (ml)	Volume % MMA	Vol.Surfactant sol(ml)	Weight % surfactant	Surfactant Solution used	Total volume m (ml)
2(a)1	5	5	0.375	5	5	44.4	A	7.5 ml
2(a)2	5	5	0.75	10	5	44.4	A	7.5 ml
2(a)3	5	5	1.5	20	5	44.4	A	7.5 ml
2(a)4	5	5	3	40	5	44.4	A	7.5 ml
2(b)1	5	0.5	0.375	5	5	44.4	B	7.5 ml
2(b)2	5	0.5	0.75	10	5	44.4	B	7.5 ml
2(b)3	5	0.5	1.5	20	5	44.4	B	7.5 ml
2(b)4	5	0.5	3	40	5	44.4	B	7.5 ml

Here precipitated polymer was found in the high initiator concentration systems. The amount of product in the other systems was limited but what was seen in SEM analyses was that star-like product was present.

Table 4.10 Results of experiment (2)

Sample	Comment	Sample	Comment
2(a)1	Bicontinuous polymer	2(b)1	Spherical
2(a)2	Continuous stars (low conc.)	2(b)2	Stars (medium concentration)
2(a)3	----precipitated----	2(b)3	Mat of particles
2(a)4	----precipitated----	2(b)4	Bow-ties/stars (low conc.)

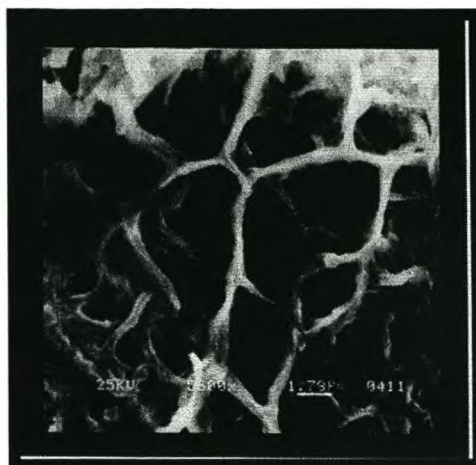


Figure 4.21 SEM image of 2(a)1
(Showing bicontinuous structure)

The second methyl methacrylate experiment i.e. experiment 2 was not successful in principle as a UV initiated experiment, as some polymerization had occurred prior to the reaction time. This was clearly observed in the precipitation of polymer in samples 2 (a) 3 and 2 (a) 4. This means that the use of ultra-violet irradiation is not the primary initiation source for this experiment. The nano-particles were however still recovered and examined.

The fineness of the precipitate prohibited filtration. The precipitate in sample 2 (a) 4 was filtered after being washed with ethanol to remove the excess surfactant. The behavior of the PMMA precipitate was different to that of the polystyrene precipitate. The recovery of the precipitates by washing with large quantities of ethanol allowed analysis of the soap content of the polymer. IR spectrums of the product were recorded. The precipitated polymer that formed in the samples (2(a)3 and 2(a)4) that had 40% monomer by volume was PMMA (polymethyl methacrylate). The FT-IR spectrum did not provide the clarity that would be required to observe the presence of a copolymer. The slight blue tinge in the sample 2 (a) 2 was due to particle size.

The importance of this experiment was the formation of the star-like particles that were present in the lower initiator concentration experiment. This data confirmed the results of section 4.7.2.

4.7.4 Experiment 3

The effect of the equilibration period was re-evaluated by irradiating the samples immediately. The methyl methacrylate that was used had been passed through an inhibitor removal column. A lower initiator concentration was used to determine the comparison to experiment two.

Table 4.11 Initiator and monomer concentration variation experiment (3)

Sample	Crosslinker % in MMA	Initiator % in MMA	Vol. methyl methacrylate (ml)	Volume % MMA	Vol. surfactant used (ml)	Weight % surfactant	Surfactant Solution used	Total volume (ml)
3(a)1	5	2	0.375	5	5	44.4	A	7.5 ml
3(a)2	5	2	0.75	10	5	44.4	A	7.5 ml
3(a)3	5	2	2.5	33.3	5	44.4	A	7.5 ml
3(a)4	5	2	0	0	5	44.4	A	7.5 ml
3(b)1	5	0.5	0.375	5	5	44.4	B	7.5 ml
3(b)2	5	0.5	0.75	10	5	44.4	B	7.5 ml
3(b)3	5	0.5	2.5	33.3	5	44.4	B	7.5 ml
3(b)4	5	0.5	0	0	5	44.4	B	7.5 ml

The following results were obtained. The product occurred at high concentrations. The problem in this system appears to be that the samples without added monomer appear to show product, although in small concentrations. The degree of polymerization in samples that do not have monomer added, under these reaction conditions, is minimal. This suggests high surfactant concentrations in these particles.

Table 4.12 Results of experiment (3)

Sample	Comment	Sample	Comment
3(a)1	Some planks (low.c.)/ spheroid	3(b)1	Separate sticks (high c.)
3(a)2	Partially formed stars (high.c.)	3(b)2	Continuous mat of stars (high.c.)
3(a)3	Huge mat of stars/damaged	3(b)3	Lots of particles less defined
3(a)4	Not a lot but some ex stars	3(b)4	Very little

Low C indicates low concentration

High C indicates high concentration

The following scanning electron microscope micrographs were taken of the samples in experiment 3 on the Topcon ABT60:

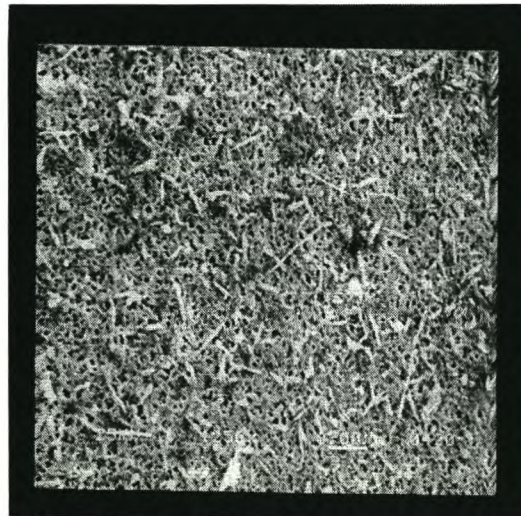


Figure 4.22 SEM image 1 of 3(b)1

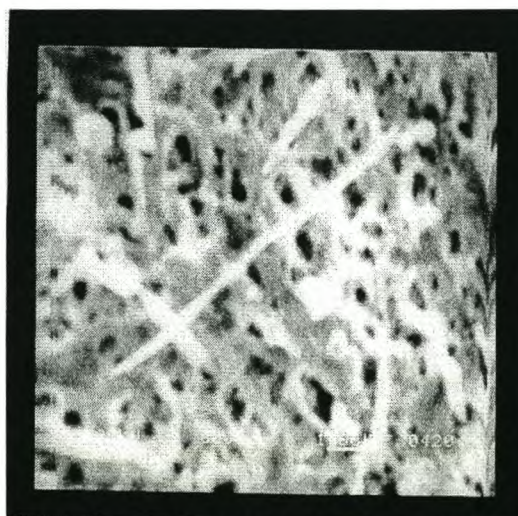


Figure 4.23 SEM image 2 of 3(b)1

The following images were captured on the Cambridge Leica S4401:

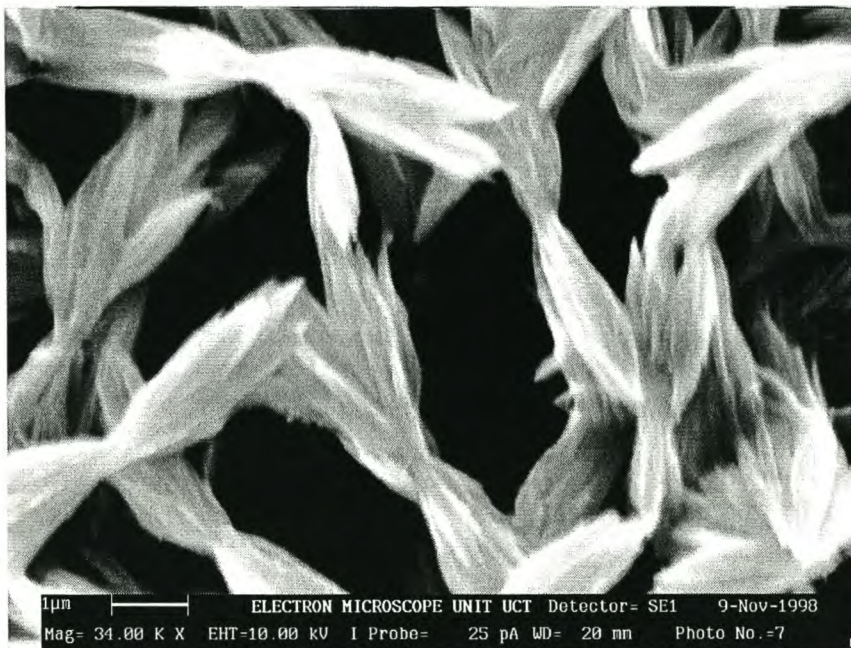


Figure 4.24 SEM image of sample 3 (b) 2

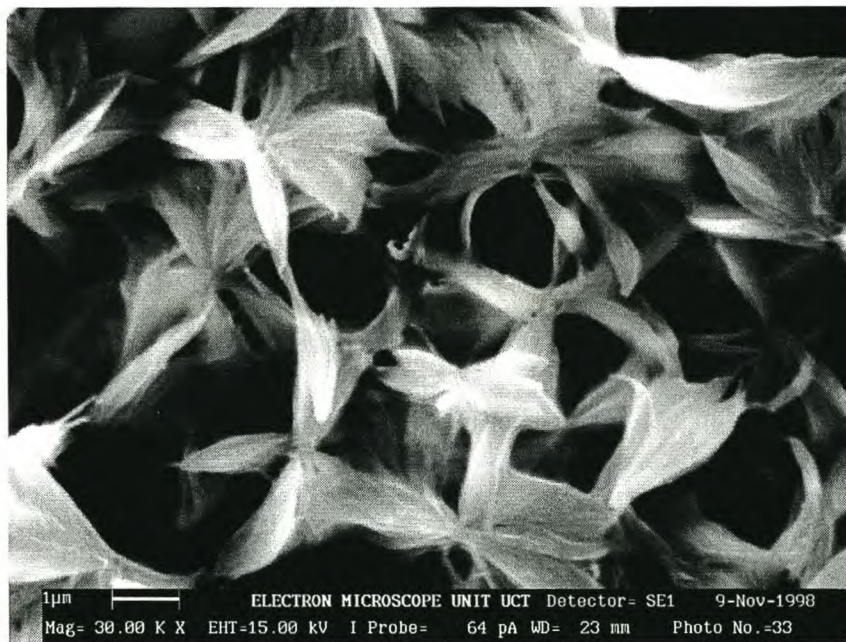


Figure 4.25 SEM image of sample 3 (b)3

The star-like particles that were formed in the systems appeared damaged (i.e. slightly melted) under SEM investigation. This could be due to the coating conditions used for the preparation of SEM samples, which were harsher than usual due to experimentation with the deposition to obtain a better coat for higher resolution images. The stability of the nano-particles to the coating is not accurately known.

The inability to achieve high-resolution images from the SEM apparatus that was available (Topcon ABT60) was also a problem as the fine structure, if any, could not be observed. This was despite the increased sample coating. (Supplementary images have been added to this experiment taken using the Leica S4401).

The experiment was successful to a degree but preparation damage may be misleading. The experiment was thus broadened and repeated.

4.7.5 Experiment 4

Duplicate runs of the successful component concentrations were carried out, as the product that was sought had now been obtained and reproducibility was required.

The conditions used in section 4.7.4 were used again (i.e. MMA was passed through a column to remove inhibitor and reacted immediately). The initiator and crosslinking agent conditions were still varied. The following table shows the component concentrations for this experiment:

Table 4.13 Crosslinker, initiator and monomer concentration variation experiment (4)

Sample	Crosslinker % in MMA	Initiator % in MMA	Vol. methyl methacrylate(ml)	Volume % MMA	Vol. surfactant solution(ml)	Weight % surfactant	Surfactant Solution used	Total volume (ml)
4(a)1	10	5	0.375	5	5	44.4	A	7.5 ml
4(a)2	10	5	0.75	10	5	44.4	A	7.5 ml
4(a)3	10	5	2.5	33.3	5	44.4	A	7.5 ml
4(a)4	10	5	0	0	5	44.4	A	7.5 ml
4(b)1	5	0.5	0.375	5	5	44.4	B	7.5 ml
4(b)2	5	0.5	0.75	10	5	44.4	B	7.5 ml
4(b)3	5	0.5	2.5	33.3	5	44.4	B	7.5 ml
4(b)4	5	0.5	0	0	5	44.4	B	7.5 ml

0.25 ml of each sample were filtered with 5 ml ethanol due to the large concentration of product that had been found in the systems with a 0.5 ml volume of sample.

The following results were obtained: (h.c: High concentration)
(low conc: Low concentration)

Table 4.14 results of experiment (4)

Sample	Comment	Sample	Comment
4(a)1	Not much (some spheroids)	4(b)1	low.conc. spheroids
4(a)2	Not much (some spheroids)	4(b)2	Spheroids /stars/bow-ties (h.c.)
4(a)3	fibroid artifact and stars	4(b)3	High concentration stars
4(a)4	Not much(some spheroids)	4(b)4	low.conc. spheroids

The following image was captured using the Topcon ABT60:



Figure 4.26 SEM image of 4(a)3 showing the fibroid artifact

The following scanning electron micrographs were captured using the Cambridge Leica S4401 SEM at the University of Cape Town:

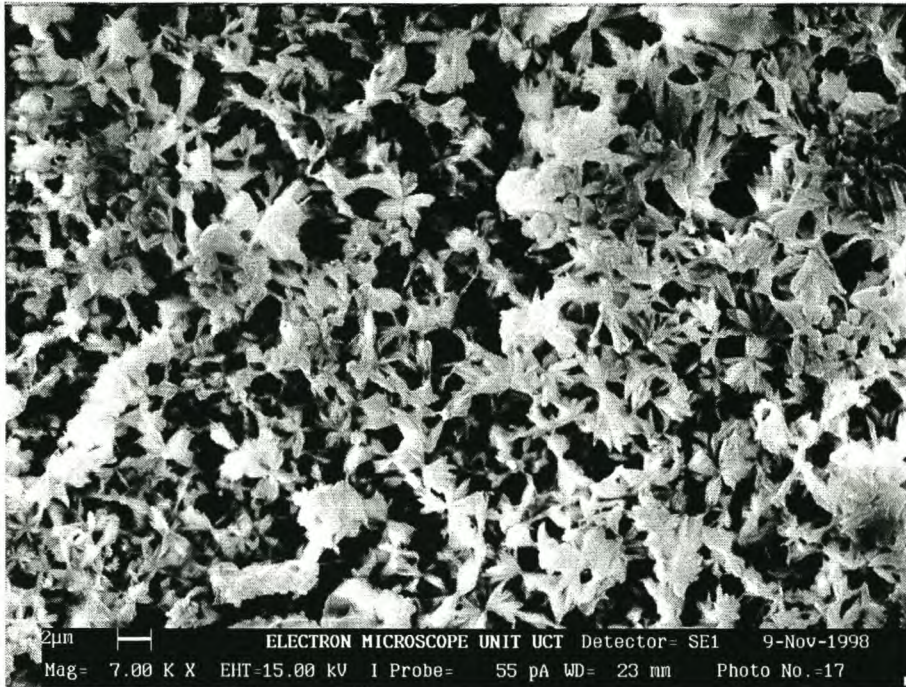


Figure 4.27 SEM image of sample 4 (a) 3 showing the less formed product

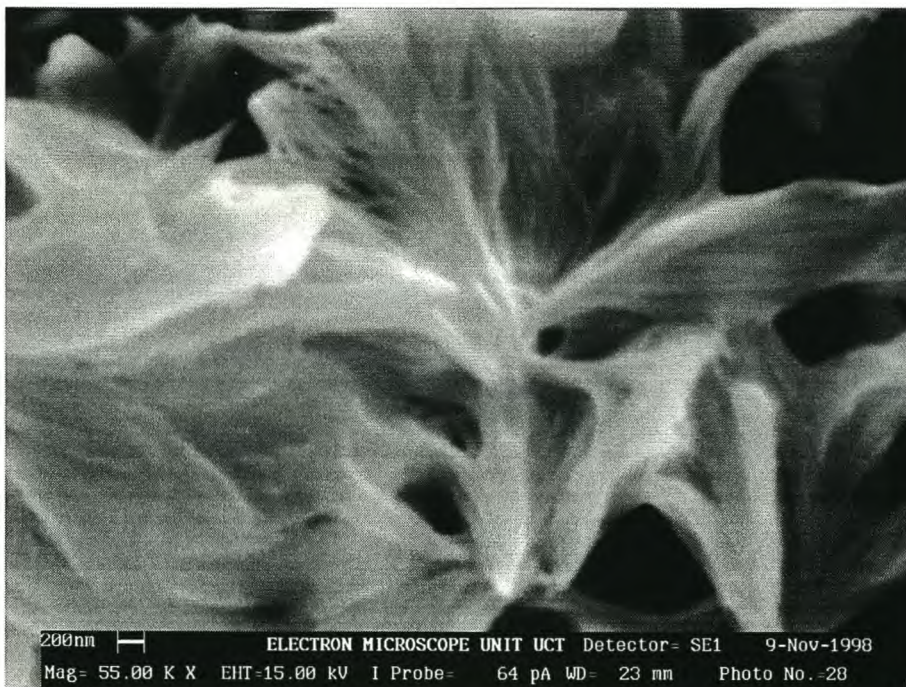


Figure 4.28 SEM image of sample 4 (b) 3 showing fibrous structure

The presence of spheroids throughout was disappointing as it implied that polymer was forming outside of the structures. The lack of product in 4(b)1 was not expected. The possibility of a high crosslinking agent concentration playing a role is suggested by the lack of well-structured product in the (a) run. (It should be noted that 4(a)3 did show some product that was similar to the star-like particles but the presence of a large artifact casts doubt on the sample).

Precipitation of samples 3 (a) 3, 3(b) 3, 4 (a) 3 and 4 (b) 3 was carried out within 1:10 ratios of ethanol. Run 4 (b) 3 showed little sample precipitation, in direct contrast to 4 (a) 3, which showed large quantities of star-like particles, these results were different to the filtration results.

Experiment four showed that this precipitation technique although sometimes successful at providing the star-like structures is not trustworthy due to polymer and surfactant precipitation, while the filtration recovery method appears more repeatable.

The high amounts of product in 4(a)3 could be due to the high initiator concentration used and the better definition could be due to higher surfactant content.

4.7.6 *Experiment 5*

Experiment three was repeated under the known conditions for a second time, to prove beyond a doubt that repeatability had been achieved. High monomer concentrations were used to determine if the product concentration could be improved.

The experiment conditions for experiment five were the same as in experiments three and four.

Table 4.15 Surfactant concentration variation experiment (5)

Sample	Crosslinker % in MMA	Initiator % in MMA	Vol. methyl methacrylate (ml)	Volume % MMA	Vol. surfactant solution (ml)	Weight % surfactant	Surfactant Solution used	Total volume (ml)
5(a)1	5	0.5	2.5	33.3	3	26.6	A	7.5 ml
5(a)2	5	0.5	2.5	33.3	4	31.4	A	8.5 ml
5(a)3	5	0.5	2.5	33.3	5	44.4	A	7.5 ml
5(a)4	5	0.5	1.5	20	6	53.3	A	7.5 ml
5(b)1	5	0.5	0.75	10	3	26.6	B	7.5 ml
5(b)2	5	0.5	0.75	10	4	35.5	B	7.5 ml
5(b)3	5	0.5	0.75	10	5	44.4	B	7.5 ml
5(b)4	5	0.5	0.75	10	6	53.3	B	7.5 ml

5(a)2 had excess water added erroneously.

Samples 5(a)1-4 were filtered in 0.2 ml amounts with 5 ml ethanol, while samples 5(b)1-4 were filtered in 0.75 ml amounts with 5 ml ethanol.

The following results were obtained:

Table 4.16 Results of experiment (5)

Sample	Comment	Sample	Comment
5(a)1	Planks (low concentration)	5(b)1	similar to 5(a)3
5(a)2	Nothing much on filter	5(b)2	Nothing much on filter
5(a)3	(Very thick undefined mat)	5(b)3	Huge numbers of bowties/stars
5(a)4	Planks (very few)	5(b)4	Stars, large numbers

The following scanning electron micrographs were recorded on the Leica S4401:

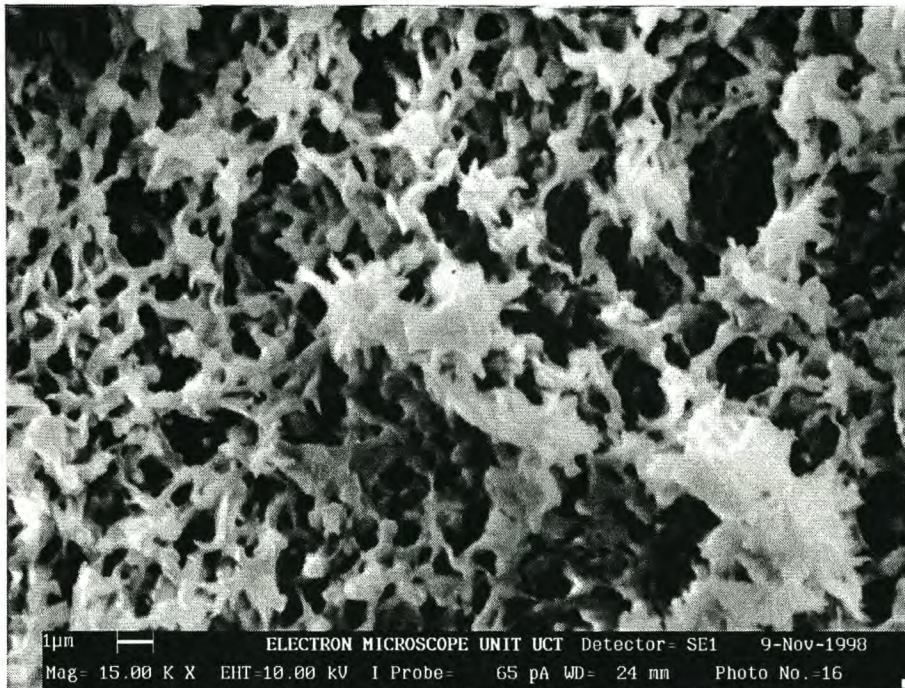


Figure 4.29 SEM image of 5 (a) 3

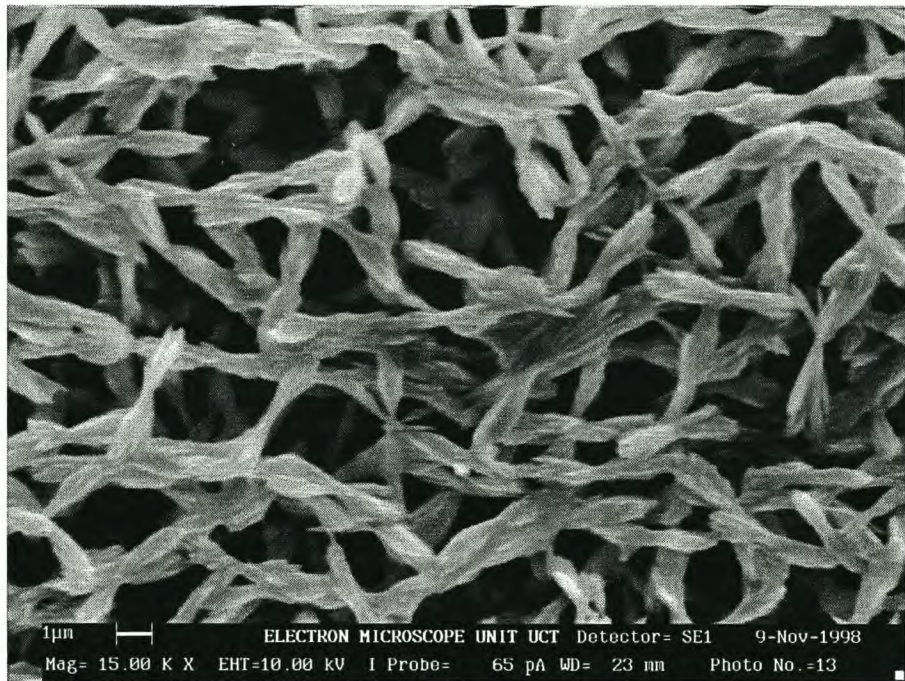


Figure 4.30 SEM image of 5 (b) 3

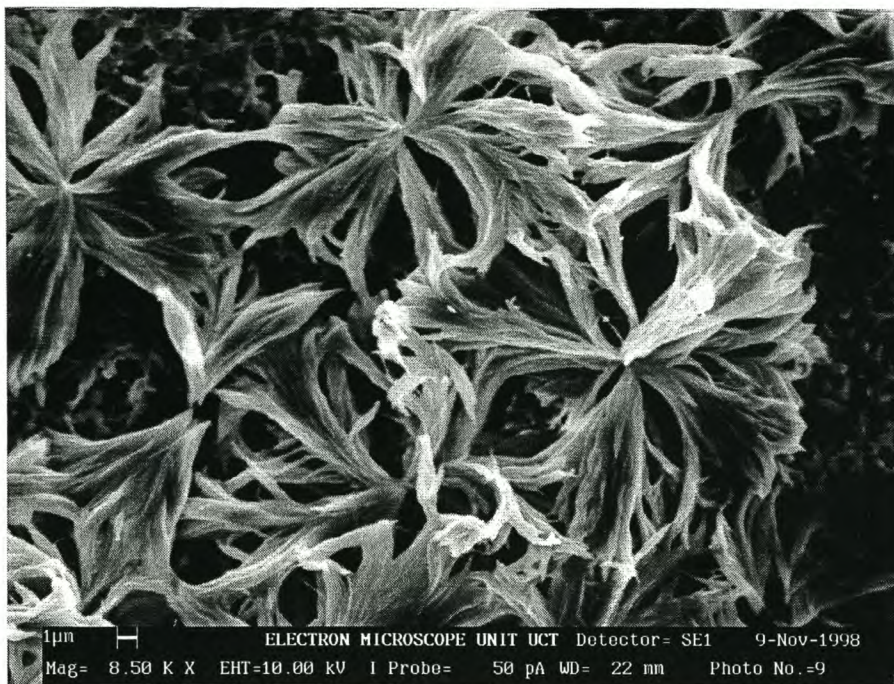


Figure 4.31 SEM image of 5 (b) 4

There is a visible difference between the product of 5 (b) 3 and 5 (b) 4; the bow ties that were predominant in 5 (b) 3 are replaced by fanlike star structures in 5 (b) 4.

This shows the concentration dependence of the particle formation and the changes in product that occur at higher surfactant and monomer concentration ranges.

4.8 Comparison of results of experiments 3,4 and 5

The following table has been drawn up so as to show what the repeatability of the reactions was.

The all important question is whether star-like particles were formed in the reaction.

Table 4.17 Comparison of results of experiments 3,4 and 5 in Part 3

Weight Percentage Surfactant	Volume % Monomer	Weight ratio organic:water	Percentage Initiator In monomer	Percentage Crosslinker In monomer	Sample Yes or No	Duplicate Yes or No	Duplicate Yes or No
26.6	10	1:2.50	0.5	5	5(b)1/N		
26.6	33.3	1:1.15	0.5	5	5(a)1/N		
35.5	10	1:2.00	0.5	5	5(b)2/N		
35.5	33.3	1:1.00	0.5	5	5(a)2/N		
44.4	5	1:1.93	2	5	3(a)1/N		
44.4	5	1:1.93	0.5	5	3(b)1/N	4(b)1/N	
44.4	5	1:1.93	5	10	14(a)1/N		
44.4	10	1:1.67	2	5	3(a)2/Y		
44.4	10	1:1.67	0.5	5	3(b)2/Y	4(b)2/Y	5(b)3/Y
44.4	10	1:1.67	5	10	4(a)2/N		
44.4	33.3	1:0.88	2	5	3(a)3/Y		
44.4	33.3	1:0.88	0.5	5	3(b)3/mat	4(b)3/Y	5(a)3/mat
44.4	33.3	1:0.88	5	10	4(a)3/~Y		
53.3	10	1:1.43	0.5	5	5(b)4/Y		
53.3	20	1:1.11	0.5	5	5(a)4/N		

It can be concluded that one set of component concentrations has been shown to give good results for nano-particle formation in three different batches suggesting that it is the most promising to pursue at this stage.

These component concentrations are tabulated below:

Table 4.18 Optimum sample composition

Sodium 10-undecenoate	5 ml * 66% sol	3.33 gram	44.44% by weight
MMA	0.75 ml * 0.944g/ml	0.67 gram	
Ethylene glycol dimethacrylate	(5% by mass of monomer)	0.033 gram	0.05% by weight
Phenyl acetophenone	(0.5% by mass of monomer)	0.0033 gram	0.005% by weight
Total water	6,75 ml	6.75 gram	
Total volume	<u>7.5 ml</u>	<u>10.79 gram</u>	

Use of these component concentrations gave consistent results for the generation of the star-like particles. The concentration of particles that form is large and the particles that form are well defined. Other concentrations have been successful but at lower concentrations of product as well as less well defined products

4.9 Discussion

Prior to concluding this nano-shaping study it is important that an objective view of the findings to date be taken.

Cross contamination of samples due to monomers that have not been fully flushed from the box is possible due to the fact that the system is exposed during reaction although the system is at atmospheric pressure or slightly above. An open vial is required for ultra-violet penetration into the system at the used wavelength. The biggest problem during irradiation is keeping samples uncontaminated by oxygen to keep radicals active and the difficulty in cleaning the box properly, especially during

operation is also a problem. The thick solutions that are commonly used make it very easy for the micropipettes in the glove box to become contaminated. This is difficult to overcome despite washing, as due to the confines of the glove box, the micropipettes are difficult to clean during use, new tips are used for each preparation.

The star-like particles that were observed in the system were first observed in sample alpha-twelve described in section 4.5.4 experiment four, which was a pure surfactant system that had initiator added and was irradiated. This system was precipitated in ethanol and washed after an extended period of equilibration. The filtrate showed the perfect star-like particles with fine structure that was considered to be possibly polymeric due to the length of time that had elapsed since reaction.

The first one-week equilibration experiment, section 4.5.6, provided the following results: 45 and 50 % surfactant samples showed star-like particles at 5% monomer while 40 and 45 % surfactant samples showed stars at 10% monomer. These samples were prepared for investigation by standard filtration.

This equilibration experiment could not soon be successfully repeated, despite numerous attempts, under varied conditions. The first time that this was repeated with any control was described in section 4.6.4, experiment four.

The size of the fibrous structures, (around 70 nm) seen in sample alpha 12, is of such a nature as to exclude direct templating. Some sort of guidance by the system is however occurring as the shapes produced by the system are not those of the traditional latex particle nor any previously described crystal growth. The exact mechanism of formation is not understood but the crystalline surfaces of the particles suggest a normal growth of crystalline material on at least the surface of the particles. This may also explain the slight variation in sizes of particles that occur.

The question is now whether the interiors of the shaped particles contain a polymeric backbone of fibers on which the surfactant has crystallized. This is not simple to determine as the surfactant that has crystallized may support the particulate shape and the removal of the surfactant by dialysis may lead to the formation of amorphous

polymeric shapes by destabilization rather than to the retention of the particles' interior shape.

The particle formation shows phase diagram dependence and is not found throughout the ternary system. The formation is also dependent on the irradiation. This suggests that the monomer is absorbed into the surfactant aggregates and is initiated in the aggregates. There will be a tendency for coalescence of polymeric particles, which could provide the critical size needed to stabilize a crystal nucleus, which can then undergo secondary crystallization. Under SEM the particles appear to show a central point (section 4.5.5), and FESEM (section 4.5.5) showed that the particles have a central growth area and the star-like shape appears to initiate from a point.

As the surfactant has only previously been polymerized alone in a liquid crystalline system the addition of a monomer that is not stable for long periods at room temperature leads to many questions.

The surfactant has been used with methyl methacrylate in two previously published studies, as discussed in chapter 4.6. The studies are inconclusive as neither discounts PMMA homopolymer inclusion. The first study uses IR¹⁰ to determine the presence of surfactant and the second extraction⁵. Neither of these techniques was used in such a way as to prove that copolymerization between the methyl methacrylate and the sodium 10-undecenoate took place.

Literature reports that the reaction time for the surfactant to reach polymeric states is very long (often more than 24 hours)^{1,9} and this may well be a factor in the particle formation equation. This time delay is however not compatible with styrene that has been distilled or with methyl methacrylate with inhibitors removed, as they will polymerize rapidly. This polymerization would lead to a variety of different copolymers forming from homopolymeric PMMA to copolymers with increasing sodium 10-undecenoate contents.

The use of an UV initiator should, in theory, not cause polymerization in a dark, sealed container. Styrene and methyl methacrylate will however start to polymerize, due to thermal initiation at room temperature, after stabilizers have been removed.

The fact that the system is equilibrated at 25 °C is thus a negative condition for the styrene and the MMA, as they will begin to polymerize prior to irradiation.

As some of the samples (section 4.6.3) show a particulate polystyrene or PMMA precipitate after a period of 6-48 hours it is possible that a week long equilibration period is too long as polymerization has probably already occurred to a large extent by that time. The formation of the homopolymer precipitate is puzzling and the reasons for its occurrence are still undetermined. In the particulate polystyrene precipitate the samples show in the region of a 60% yield, measured gravimetrically. (Section 4.6.3, experiment three, batch X, run 4, sample 18).

4.10 Conclusions

Self-assembly nano-particles have been formed from both styrene and methyl methacrylate containing systems.

The MMA/EGDMA system seems more viable than the styrene/DVB system for the production of the self assembled particles. The optimum concentrations of the components used for the particle formation are given in section 4.8.

The nature of the particles still requires investigation as electron microscopy only provides us with a visual analysis of the nature of the particles.

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Chapter Five

Investigations into the structure of aggregates and particles

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Chapter Five

Investigations into the structures of aggregates and particles

Further proof of the nature of the formation mechanism as well as the structural interior of the amphiphilic self-assemblies formed in chapter four was required. This was to be done by light microscopy, small angle x-ray spectrometry (SAXS) and transmission electron microscopy (TEM). The SAXS and TEM analyses were carried out by Charl F.J. Faul at the Max Planck Institute for Colloids and Interfaces in Teltow, Germany.

5.1 Phase investigations

Light microscopy can be used to determine the presence of liquid crystalline phases. This is done by using twin polarizers, perpendicular to one another, to direct the light. The liquid crystal will rotate the light to allow it to pass through the system being analyzed. The normal state will be a black view, as no light will pass through the polarizers when they are perpendicular to one another.

One of the aims of the structural investigation was to examine the ternary system of water, surfactant and monomer, and ascertain whether liquid crystalline phases were present and if so which specific phases.

The importance of carrying out a phase investigation is in the evidence that it may provide in the context of the nature of the particle formation. Following on from the work of Chueng et al ¹, which suggested that the specific concentrations which showed formed shapes should be closer to a microemulsion, it was decided to conduct light microscopy studies to examine the phases that were present in the solutions used in the study.

The identification of the phases that were observed was done by comparison to the literature. Figures 5.1a and 5.1b show typical hexagonal phases as recorded in the literature.



Figure 5.1a

Typical hexagonal phases of sodium 10- undecenoate as reported in the literature:

5.1a by Friberg ²

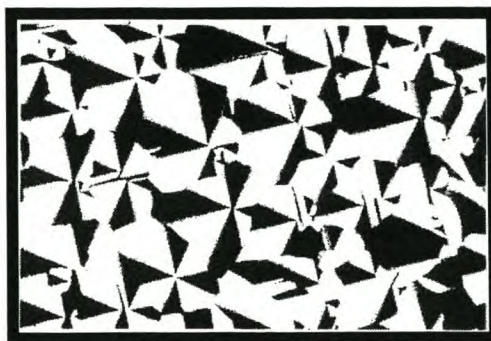


Figure 5.1b

5.1b Kekicheff ³

The typical hexagonal phase will show the well known maltese cross as a product of it's formation. The phase will show extinction angles every 90 degrees, at which no light will pass through the twin polarizers of the microscope.

Both Friberg and Kekicheff show both hexagonal structures and lamellar structures for sodium 10-undecenoate. Such structures were therefore sought in the surfactant solutions that had been prepared in this study for the experimental work.

5.1.1 Experiment one

The following samples, as shown in table 5.1, were prepared to determine the phases present in specific concentrations of sodium 10-undecenoate, water and methyl methacrylate. The liquid crystalline phase for the corresponding binary system is also indicated. The importance of the corresponding binary phase is that it gives an indication of the region in which the ternary phase will begin to show (a binary system is simply a ternary system with one of the components at a zero concentration).

Lam: lamellar phase

Hyd: hydrated crystals or coagel

Hex: hexagonal phase

Mic: micellar phase

Table 5.1 Composition of solutions used in phase investigations

Sample	Mass surfactant(g)t	Mass MMA(g)	Vol water(ml)	Weight % surfactant	Binary phase for Weight % surf	Weight % MMA
1	0.5	0.25	0.25	100	Solid	50
2	0.5	0.25	0.35	83.33	Lam+Hyd	41.66
3	0.5	0.25	0.45	71.42	Lam	35.71
4	0.5	0.25	0.55	62.5	Hex+Lam	31.25
5	0.5	0.25	0.65	55.55	Hex+Lam	27.77
6	0.5	0.25	0.75	50	Hex	25
7	0.5	0.25	0.85	45.45	Hex	22.72
8	0.5	0.25	0.95	41.66	Mic+Hex	20.83
9	0.5	0.25	1.05	38.46	Mic+Hex	19.23
10	0.5	0.25	1.15	35.71	Micellar	17.85
11	0.5	0.25	1.25	33.33	Micellar	16.66
12	0.5	0.25	1.35	31.25	Micellar	15.625
13	0.5	0.25	1.45	29.41	Micellar	14.70
14	0.5	0.25	1.55	27.77	Micellar	13.88
15	0.5	0.25	1.65	26.31	Micellar	13.15
16	0.5	0.25	1.75	25	Micellar	12.5
17	0.33	0.66	0	50	Hex	100
18	0.33	0.66	0.1	43.47	Mic+Hex	86.94
19	0.33	0.66	0.2	38.45	Mic+Hex	76.90
20	0.33	0.66	0.3	34.47	Micellar	68.94
21	0.33	0.66	0.4	31.23	Micellar	62.47

22	0.33	0.66	0.5	28.55	Micellar	57.11
23	0.33	0.66	0.6	26.30	Micellar	52.60
24	0.33	0.66	0.7	24.37	Micellar	48.75
25	0.33	0.66	0.8	22.71	Micellar	45.42

Table 5.1 continued

Sample	Mass surfactant(g)	Mass MMA(g)	Vol water(ml)	Weight % surfactant	Binary phase for Weight % surf	Weight % MMA
26	0.33	0.66	0.9	21.26	Micellar	42.52
27	0.33	0.66	1.0	19.98	Micellar	39.97
28	0.33	0.66	1.1	18.85	Micellar	37.71
29	0.33	0.66	1.2	17.84	Micellar	35.69
30	0.33	0.66	1.3	16.93	Micellar	33.87
31	0.33	0.66	1.4	16.11	Micellar	32.23
32	0.33	0.66	1.5	15.37	Micellar	30.74
33	0.33	0.66	1.6	14.69	Micellar	29.39
34	0.3	0.66	1.7	14.07	Micellar	28.14
35	0.33	0.66	1.8	13.50	Micellar	27.00
36	0.33	0.66	1.9	12.97	Micellar	25.95

The solutions were allowed to equilibrate and were then examined under a polarizing light microscope.

5.1.2 Results of experiment one

The thick hydrated crystal solutions (1-4 and 18-22, which are coagel (note that the samples being ternary, not binary, systems show different behavior from the binary systems)) showed scattering of light but the remaining solutions were dark under the polarizers, indicating no transmission of light.

This led to re-evaluation of the scatter technique that was used to prepare solutions for analysis and a more specific approach was used. Solutions that were known to contain liquid crystals were examined according to the method of Kekicheff *et al.*³

5.1.3 Experiment two a

A 45% SDS solution and a 66% sodium 10-undecenoate solution were compared. These solutions should both contain liquid crystals according to Kekicheff³. Both solutions appeared dark through the twin polarizers. The 66% sodium 10-undecenoate solution, which shows both a gel and a hexagonal phase behavior (mixed phase), according to literature, was examined in both states (i.e. the gel and liquid phases).

5.1.4 Results of experiment two a

The solution of the SDS did not show any polarization of light. The sodium 10-undecenoate solution's liquid phase appeared dark through the polarizers, indicating that no polarization took place. The sodium 10-undecenoate's gel phase appeared light, indicating that light was polarized by the gel allowing it to pass through the twin polarizing lenses. There was no recognizable liquid crystalline phase present.

5.1.5 Experiment two b

A sample of sodium 10-undecenoate at 66% by weight was allowed to equilibrate overnight on the stage, to compensate for disturbances in the phase. The 45% SDS solution was not equilibrated in this way as it cooled rapidly and has a hexagonal phase only when above 40 °C. The microscope that was available for this study did not possess a heating stage.

5.1.6 Results of experiment two b

The solution of the sodium 10-undecenoate at 66% by weight showed no signs of birefringence in the liquid mesophase. The gel phase continued to polarize light but no specific phase could be identified.

5.1.7 Conclusion of experiments one and two

The light microscopy analyses of the surfactant, water and monomer solutions as well as the concentrated surfactant solutions, did not show any sign of the hexagonal phase as had been found in literature but did show that polarization was occurring in gel phases.

5.1.8 Experiment three

Slides containing drops of two specifically prepared solutions, which were covered with slide covers, were prepared as it was hoped that providing a surface for orientation as well as a less mobile environment would allow the hexagonal phase to develop.

The following solutions were prepared:

A 50% by weight aqueous sodium 10-undecenoate solution. The prepared sample should have a standard hexagonal phase according to the binary phase diagram (section 2.7). The phases were examined on slides after they had been covered and allowed to stand for a period of half an hour.

A 66% by weight aqueous sodium 10-undecenoate solution. The prepared sample should have gel and hexagonal phases according to the binary phase diagram (section 2.7). The sample of 66% by weight surfactant was taken and portions of the sample, the solution and the gel were removed and placed on slides. The slides were examined immediately after they were covered.

5.1.9 Results of experiment three

The polarized light microscopy showed a birefringent phase in the solution of 50% by weight sodium 10-undecenoate in distilled de-ionised water that was prepared specifically for the purpose. The phase was confirmed to be hexagonal arrangement by comparison to literature³.

The 66% by weight sample was examined in both the gel and solution and as a whole. Both the gel and solution sides had birefringence that developed rapidly after they were prepared but was not immediately visible. The solution forms a hexagonal birefringence pattern within minutes and the gel appears to have some lamellar (oily streaks) features.

The 66% by weight sample showed mixed birefringent patterns. According to McGrath³ this concentration consists of a mixed hexagonal and gel phase. The lack of order in a 66% solution of surfactant could be seen as the phase was between that of the hexagonal and gel ordered phases and showed micro-separated phases of lamellar and hexagonal structures.

Figures 5.2a and 5.2b show typical hexagonal phases that were obtained from concentrated surfactant solution (66% by weight).



Figure 5.2a
Fan-like structure of the hexagonal phase



Figure 5.2b
Maltese-crosslike structures in an hexagonal phase

Figure 5.3 shows typical lamellar structures that were obtained from concentrated surfactant solution (66% by weight).



Figure 5.3 Lamellar phase structures

5.1.10 Experiment four

The time dependence of the phase formation was investigated as the slides prepared in experiment three showed a far more developed liquid crystalline phase when observed twenty four hours later.

Further investigation showed that the sixty-six percent surfactant liquid phase, when placed on a slide and covered, given a period of time too short for evaporation to have an effect (i.e. ten or twenty minutes), forms mostly hexagonal phase structures.

5.1.11 Experiment five

Samples of typical reaction solutions, both before and after reaction, were now placed on the slides. The reaction solutions that were examined were 10% monomer with 0.5% initiator and 44% surfactant. The development of birefringence and liquid crystalline phases was followed over a period of hours to several days.

5.1.12 Results of experiment five

All these samples showed hexagonal phase development but took considerably longer than the binary systems of experiment four to form the phases (normally over periods of some hours, normally three to four). The evidence that was obtained was similar for all solutions, both before and after reaction.

Typical results of the light microscopy development with time are shown in the following figures:



Figure 5.4 Undeveloped phase
(Immediate image of sample with 10% monomer and 45% surfactant after irradiation)



Figure 5.5a
Developed phases (one day old)



Figure 5.5b
Developed phases (about six hours old)

5.1.13 Light microscopy discussion

The time dependence means that the gel which is birefringent and the 66% surfactant solution liquid phase, which at first glance is not, are able to interact, leaving a hexagonal phase after a period of minutes.

The difference between the solutions, both the 66% and the 45% surfactant, and the slides suggests that the phases are very susceptible to disturbances, which are removed when the solutions are placed on the slides between covers. Other possible explanations include the use of a surface for the alignment of the crystals.

Drops of the liquid that show no sign of birefringence in the vial quickly form phases when placed on a slide. Birefringence was observed in vials with hydrated crystals but

only on the side-walls of the container. The hydrated crystals or coagel tend to sit on the walls, not in the liquid solution in the vial.

The mixed phase, which is present in the 66% by weight samples according to Kekicheff *et al*³ is also supposed to be disruptive in the formation of the stable hexagonal phase. By removing samples of solution and placing them on slides, rather than a mixture of solution and gel, this may be overcome.

5.8 Small angle X-ray scattering

Small angle X-ray scattering (SAXS) can be used for the detection of regular structures in the size range of approximately 2 nm to 60 nm. Wide-angle analyses can be used for the size range smaller than 2 nm, and neutron scattering for the range above 60 nm.

Small-angle scattering arises from inhomogeneities in the refractive index within a material. Inhomogeneities coherently scatter radiation from the forward direction. The intensity distribution as a function of angle is dependent on the shape, the size, the concentration, and the smoothness of the inhomogeneities. Small-angle scattering data are analyzed directly by curve fitting and by comparison to theoretical models.

The SAXS system in use at the Max Planck Institute in Teltow is a Paar Systems Kratky camera. A special sample holder was designed and used for the analyses of liquid samples. Approximately 0.1 ml of the sample is placed in a special borosilicate capillary tube of the following dimensions:

Length: 80 mm, diameter: 2,0 mm, wall thickness: 0,1 mm

The following figure shows the typical setup of a SAXS experiment.

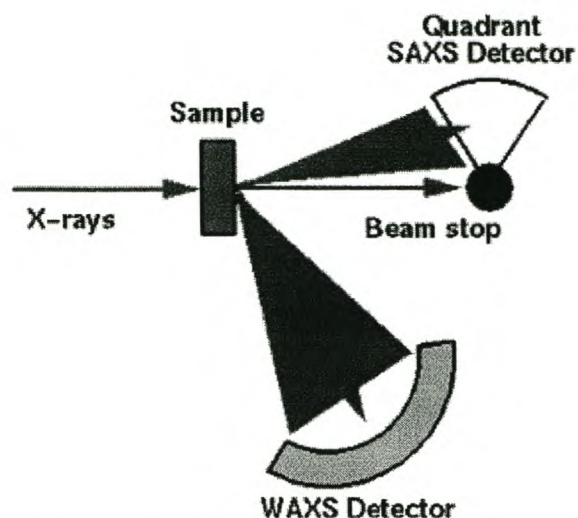


Figure 5.6 SAXS experimental setup

The sample holder is then placed in the mount and the system is evacuated. This is done to minimize scattering due to air, since this can contribute significantly to the scattering of the X-rays at low angles. Due to the low density of the sample (samples are usually solid rather than liquid) the angle is changed after 200 seconds of irradiation this means that the data collection is usually done overnight as the time per data point is relatively long.

5.2.1 Experimental

SAXS analyses were carried out on two samples that contained sodium 10-undecenoate.

- i) A methyl methacrylate containing sample (section 4.7.6 experiment 5 sample 5(b)4) which contained 45% surfactant and 10% MMA.
- ii) A sample of solution D, a 66% by weight solution of sodium 10-undecenoate.

5.2.1 Results

In Figure 5.7, the SAXS scan of sample 5(b)4 from section 5.7.6 is shown. It can be seen from the broad peak at 0.3 s/nm^{-1} that there were some structures in the solution. The hexagonal phase, which was thought to be present, was not detected. This can be

stated, as the sample showed no signs of liquid crystalline structural organization, as the peak that was in evidence was broad rather than the sharp peaks of a liquid crystalline system.

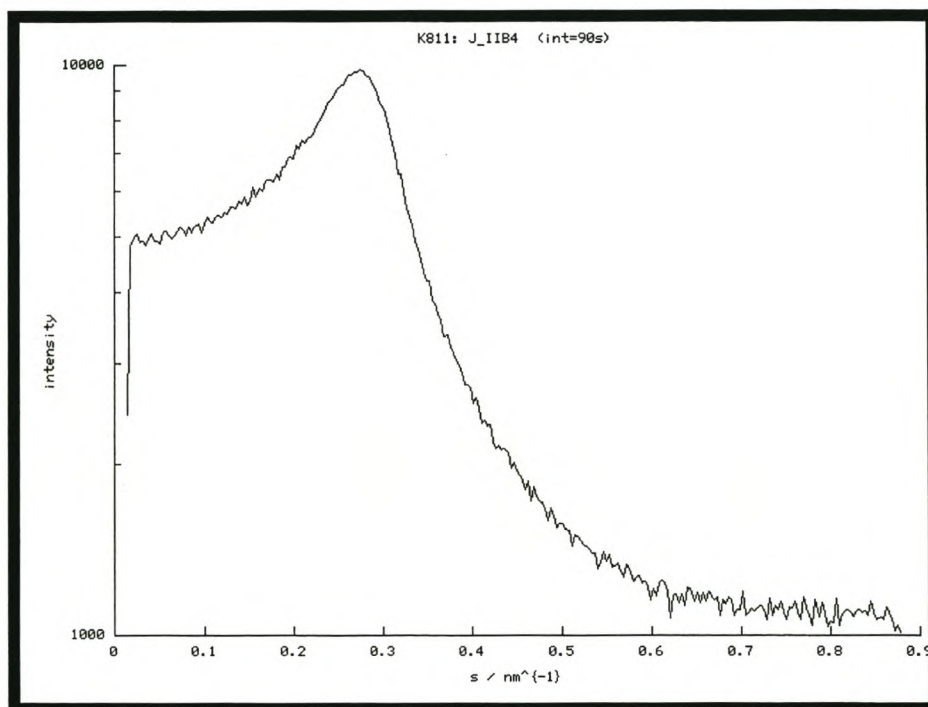


Figure 5.7 SAXS scan of sample 5(b)4

In the second sample, a sample of solution D, the phase that should be present in the sixty-six percent solution according to the binary phase diagram (see 2.7) is that of a mixed hexagonal /gel phase. The peaks show the presence of the fine order repeat units (see the sharp peaks at $<0.1 \text{ s/nm}^{-1}$) The nature of the order shown by the sharp peaks is calculated by the instrument itself, using established mathematical models. This means that for the surfactant solution at 66% by weight there are some repeating

structures present. The broad peak which indicates structures that are not liquid crystalline in nature is still present.

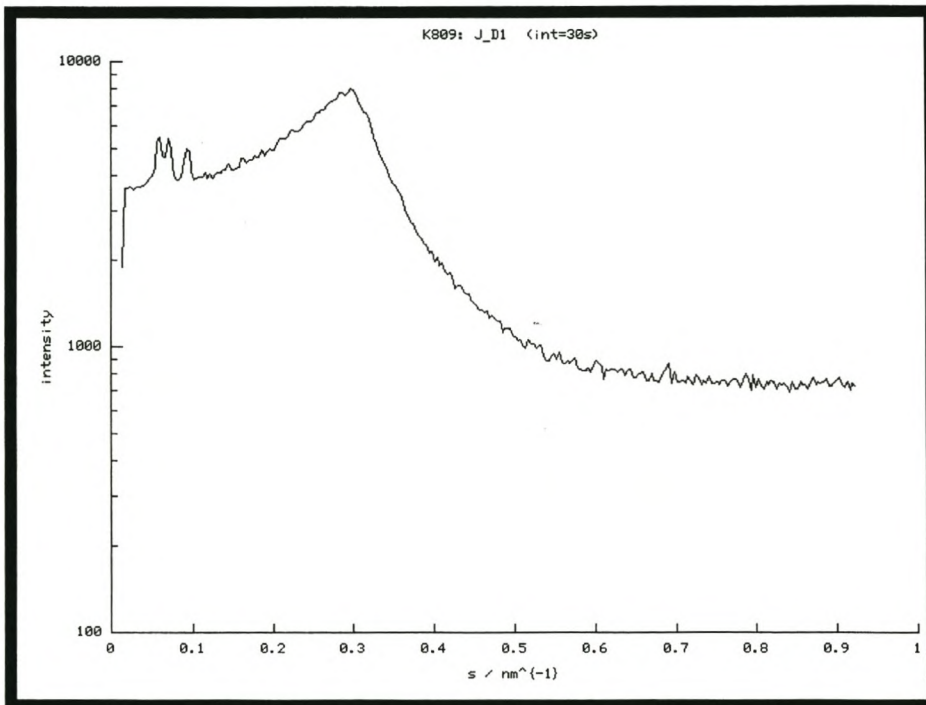


Figure 5.8 SAXS diffraction image of solution D

The SAXS scan of the sample 5(b)4 shows that the order of the system, which can be seen in the scan of the surfactant sample D, is not present.

X-rays have shorter wavelengths than visible light and therefore provide more precise data than light microscopy experiments, for this reason SAXS analyses are deemed the more valid experiments. As only one sample was used for the SAXS analyses, the

fact that no liquid crystalline phase development occurred in the sample cannot however be taken as conclusive. (One possible reason could be the fact that the experiments were carried out by operators rather than the author.)

5.3 Transmission electron microscopy analyses

Transmission electron microscopy allows images to be obtained in a very similar method to traditional optical microscopy. The substantial difference is that instead of passing light through a sample, an electron beam is used.

TEM often finds use in biological applications and can provide additional information to that of a scanning electron microscope and was therefore used to examine samples to see if it could provide more insight into the nature of the particles that had been formed.

As the electron beam has to pass through the sample in the transmission electron microscope, different sample preparation is required to that of SEM.

5.3.1 Experimental

Sample 5(b)4, which contained an irradiated solution of MMA and sodium 10-undecenoate, and a sample of solution D, which was not irradiated, were used for this investigation. The first step was to remove the sodium 10-undecenoate from the samples.

Multiple aliquots (1 ml) of the samples were diluted approximately ten times, and then introduced into dialysis bags (Mw cut off 10 000 – 20 000 atomic mass units). The bags were then placed into approximately 2 liters of distilled, deionised water, and the water slowly stirred. The water was changed three times a day, to ensure a good diffusion rate of the surfactant from the dialysis bags into the surrounding aqueous phase.

After four days the aliquots from 5(b)4 started to show coagulation of particles, and it was decided to remove these samples. Even though the original reaction solution was clear, a slightly turbid solution was obtained from the dialysis.

The aliquots taken from solution D did not show this behavior and were fully dialyzed. The result was that all the surfactant was removed and nothing remained in the dialysis bags.

The aliquots that showed coagulation were diluted and dripped onto transmission electron microscopy grids for analysis. The grids are fine copper grids that have received a thin layer of carbon, which is transparent to the electron beam, on which the material to be examined lies.

5.3.2 Results of experimental

The following TEM micrographs were obtained from the dialyzed sample 5(b)4. The mixture of fibrillar or lamellar structures and spheroidal growths is seen quite clearly in Figure 5.9 and the enlargement, Figure 5.10.



Figure 5.9 TEM image one of the dialyzed sample 5(b)4

TEM showed that there were some composite or conglomerate particles of about 70-100nm cross-section, which contain fibrillae. The presence of fibrillae indicates that surfactant remains in the system as it becomes a surfactant gel during dialysis and encapsulates the fibrillar particles. After further dialysis these gel structures were also lost and the TEM images do not show fibrillar structure. This loss of fibrillar structure follows as surfactant, through electrostatic and crystalline or gel medium, maintains the fibrillar structures and total removal of the surfactant should lead to coalescence and irregular lumps of polymer.

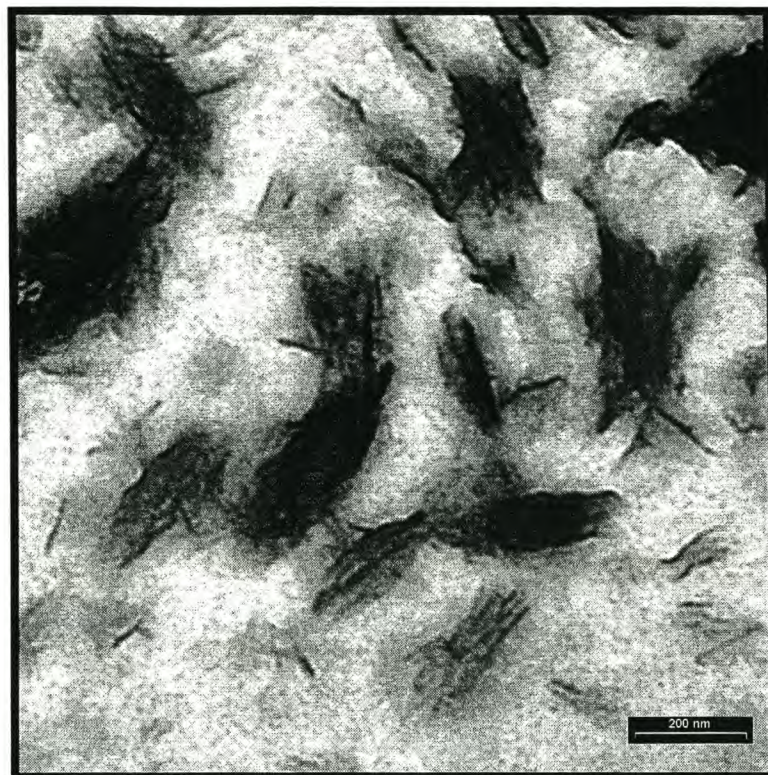


Figure 5.10 200 nm image enlargement of 5(b)4 TEM

Note the fibrillae of the structures. These are between 7 and 10 nm in width.

5.3.3 Discussion

Figure 5.10 shows dark, thick, circular areas of approximately one micron in size are visible. This correlates well with the size of the star-like particles seen in 4.5.5, which were between 3 and 15 microns, if the core of the star is the last part of the structure to dissolve. In Figure 5.10, which is an enlargement of a section of Figure 5.9, an interpretation of the image may be that the surfactant has swollen and become gel-like, but contains the remnants of the star like particles' cylindrical arms with the many short fibrils still encapsulated.

The nature of the fibrillar particles could not be investigated further due to the location of the instruments, in Germany, and the moving of the Max Planck Institute which meant that instruments were off line for a period of eight months.

The fibrillar structures point to many fine polymeric fibers in the 70 nm cross-sections of the star-like particle, that is mostly surfactant, this would mean nano-particle shaping takes place in the initial stages but as polymerization occurs coalescence

occurs increasing the diameter to 7-10 nm for stability. This coalescence occurs in emulsion polymerization, where micelles grow to form spherical nano-particles.

The volume of polymer in the surfactant gel is hard to judge but significantly less than five percent would be expected due to the obvious excess of surfactant that can be seen in the TEM micrographs.

5.4 Conclusions

The star-like particles that were seen under the scanning electron microscope in chapter 4 were not recovered from the dialysis and transmission electron microscopy study. This is indicative that these particles were predominantly surfactant or oligomeric surfactant aggregates but according to TEM analysis the particles appear to contain fine fibers, which could possibly be polymeric.

The phases that were measured by polarizing light microscopy, hexagonal liquid crystalline phases, are taken to be due to the preparation method and time scale. The SAXS scans proved conclusively that the hexagonal phases that had been seen in the solutions with added organic monomer under the microscope were in fact not present in large quantities.

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Chapter Six

An investigation into nano-shaping and the use of gamma irradiation for the fixation of structures

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Chapter Six

An investigation into nano-shaping and the use of gamma irradiation for the fixation of nano-structures

6.1 Background

Use of gamma radiation of polymerizable surfactants for polymerization purposes has been shown to allow retention of macroscopic order in lyotropic phases for certain surfactants, although polymerization is still limited by the structural conformation of the aggregates.¹

Gamma radiation is particularly useful as it has excellent penetration and its use at ambient temperature allows for more control in the quiescent conditions. The fact that the gamma radiation is a more powerful source than ultra-violet for the polymerization of monomers was important to increase conversion. It was hoped that a more rapid and even initiation of the polymerization would occur removing some of the stresses in the guiding surfactant aggregates (caused by the growing polymer) with the hope of improving the product quality in this study in terms of form and polymer content.

The aim of this investigation was to polymerize sodium 10-undecenoate in concentrated aqueous solution, with or without the addition of comonomers and crosslinking agents, and recover fixed nano-particles.

The morphology of the products that were formed was examined using electron microscopy, to determine the structure directing properties of the surfactant under the irradiation conditions. The nature of the product was studied by FT-IR spectroscopy and electrospray mass spectrometry.

The use of the gamma irradiation source would confirm the data that had been generated by the UV investigations to ascertain the possibility of using the surfactant sodium 10-undecenoate as a self-assembly system.

6.2 The gamma source

Use of the commercial gamma irradiation source at Hepro (High Energy Processing Cape PTY (LTD)) was used. The radioactive rods decay continuously and hence the precise ages of the rods are required to determine the dosage that a sample will receive. Hepro had this data available.

The facility is normally used for food and equipment sterilization. The gamma source does not generate heat and this makes it useful for most sterilization purposes. The source is kept beneath eight meters of water when inactive, allowing observation of Cherenkov radiation.

The source was an array of fifty Cobalt 60 (Co^{60}) rods of known ages. The half-lives of the rods were known and with this data the average dosage that the samples would receive could be predicted as a time exposure.

The dosage was measured by dosimeters that were attached to the samples. The dosages above 50 kilograys were approximate, as the dosimeters were not able to give accurate values for the high irradiations. The dosage was an average dosage. This means that the samples were in a package that obtained an average dosage of the required irradiation strength.

The excellent penetration of the radiation requires large concrete blocks in excess of six meters and extreme caution for the use of the facility; for these reasons the samples were reacted by the operator and not by the author.

6.3 Experimental procedure

6.3.1 Background

The reaction vials were the same as those used in the ultra-violet light studies in chapter 4. They were sealed and placed in closed and secured cardboard containers. These containers were then secured to the irradiation trolleys prior to their entry in to the irradiation facility.

Two sets of reactions were carried out. The first set of reactions was carried out at three different dosages namely ten, twenty and thirty kilograys. These values were taken from a gamma irradiation study that had been carried out with the surfactant sodium 10-undecenoate in dilute solution by Larrabee and Sprague.²

The second set of reactions was carried out at three different dosages namely 50, 100, 150 kilograys. This was done after the observation that monomer could still be observed in the reaction vials after the irradiation had been carried out. This was noted due to the strong characteristic odour of the styrene, methyl methacrylate and the crosslinking agents.

6.3.2 The solutions

The solutions C-E are 66% solutions of aqueous surfactant .The standard solutions are 45 % surfactant with a 10% monomer mix containing 5% crosslinking agent (DVB or EGDMA for styrene and methyl methacrylate respectively). This was the solution that proved most effective for particle formation under UV irradiation. The concentrated solutions contained 33% by volume of the respective monomer solutions.

The ethanol solution contained precipitated surfactant. (The surfactant has lower solubility in ethanol than in water). Solid surfactant was irradiated to determine the feasibility of converting solid surfactant structures into polymeric forms. The standard MMA solution that contained no crosslinking agent was prepared for possible polymer determinations. The monomer-in-water mixtures were used as standards to determine the monomer conversion.

The solutions were made up to different volumes. Solutions C, D and E were used in 5 ml volumes while the monomer containing samples were used in 7.5 ml volumes. The ethanol containing samples were made up as 1g in 10 ml.

Table 6.1 Reaction solutions prepared for gamma irradiations

SAMPLE	SURFACTANT WEIGHT %	MONOMER VOLUME %	INITIATOR % IN MONOMER	WATER VOLUME ADDED(MI)
C	66.6	0	0	0
D	66.6	0	0	0
E	66.6	0	0	0
Standard MMA	44.4	10	0.5	1.75
Standard Styrene	44.4	10	0.5	1.75
Concentrated MMA	44.4	33.3	0.5	0
Concentrated Styrene	44.4	33.3	0.5	0
Ethanol solution	10	0	0	0
Surfactant	---	0	0	0
MMA no crosslinker	44.4	10	0.5	1.75
5% MMA in water	0	5	0	5
5% Styrene in water	0	5	0	5

6.3.3 The irradiations

The X marked entries are those samples that were prepared and irradiated.

Table 6.2 Samples dosages for gamma irradiation study

DOSAGE (KGY)	10	20	30	50	100	150
C	X	X	X			
D	X	X	X	X	X	X
E	X	X	X	X	X	X
Standard MMA	X	X	X	X	X	X
Standard Styrene	X	X	X	X	X	X
Concentrated MMA	X	X	X			
Concentrated Styrene	X	X	X			
Ethanol solution	X	X	X			
Surfactant	X	X	X	X	X	X
MMA no crosslinker				X	X	X
5% MMA in water				X	X	X
5% Styrene in water				X	X	X

The surfactant samples C, D and E were compared to determine if the age of the solution had any effect on the precipitation product. These solutions had been made up during the investigation over a period of months, C was substantially older than D and E, which were prepared within weeks of each other. It was decided that having observed no difference in the filtration product of the first set of reactions (10, 20, 30 KGy), that two standards namely D and E would be sufficient for the high irradiation set.

The concentrated solutions of monomer were unstable prior to irradiation and for this reason they were abandoned. The reason that they were made up for the first set was the fact that interesting results had been found in literature ³ at high monomer concentrations as well as the unresolved UV particle formation. It was felt that using a new form of initiation might shed some light on the partially ordered system that had

been found using the potassium salt of the surfactant by Cheung et al³. The study also claimed high percentage incorporation of the surfactant, which has not been found to be the case with the sodium counter ion in the UV studies in section 3.2.3.

The ethanol containing precipitated surfactant was irradiated to determine if the particles, which had been found after the ultra-violet irradiation (section 4.4), could be duplicated by irradiation of surfactant in the ethanol solution. These were only carried out at the lower irradiation dosages (the first set of reactions) as higher conversion was considered to be a negative factor due to the formation of viscous solutions, which hindered recovery of any particles.

The solid surfactant was irradiated and compared to literature⁴. McGrath⁴ had also carried out the solid surfactant irradiations, but both his study and this study had poor results, as the conversions were extremely low in this study undetectable.

6.4 Results and discussion

All the styrene containing solutions had precipitated due to the instability of the surfactant/styrene/polystyrene solutions at the temperature of the reactor, which was not controlled and thus sometimes well below 20 °C. The reason that this precipitation had not been seen in the UV studies is attributed to the lack of temperature control, allowing the styrene system, which is less stable than the methyl methacrylate system to precipitate, and the lack of time for the system to equilibrate, as the irradiation was carried out directly after the vials were placed in the reactor. This means that the forming polystyrene was never stabilized by surfactant and the system has the appearance of a thick white heterogeneous solution. This cannot be overcome as the reactor is a commercial facility and cannot be stopped to allow for equilibration of small batches of samples.

This meant that all the data generated from the styrene systems that were subjected to gamma irradiation is not useful for particle analysis. This meant that the focus had to be shifted to the samples containing methyl methacrylate.

Practical problems were encountered with the filtration of the samples by hand due to the thickness of the solutions. The solutions also clogged the 0,22 micron filter in the vacuum filtration apparatus. This meant that dialysis was one of the few options available for the recovery of polymer from the samples.

Filtration was nonetheless carried out with varying success on the standard methyl methacrylate series. Standard analysis involved the filtration of 200 microliters (μl) of samples with 5 ml ethanol. This was carried out through a 0.22 micron Millipore filter and the filter paper was then examined under the scanning electron microscope. The particles that were observed did not have any defined structures that could be considered guided in any way.

As the samples containing 45% surfactant, 10% monomer and 0.5% initiator were found to be the most successful for the production of the star-like particles under the ultra-violet investigation it is thought that preparative techniques and temperature are critical for the formation of these particles. The lack of formation of particles in the gamma study is not proof of the unsuitability of gamma irradiation due to the difficulties in working with these samples and the possibility exists that slight variations in the technique used for the gamma irradiations may lead to success in particle formation.

The solid surfactant that was irradiated did not show any change to the naked eye. When precipitation was attempted from ethanol to separate polymer from these solid state irradiations the results were negligible showing that solid state conversion was minimal as no polymeric surfactant was recovered.

The surfactant precipitated in ethanol also showed very little conversion. On addition of ethanol to the system the precipitate rapidly redissolved. This is an indication that the conversion in the solid form and crystalline precipitated structures was minimal or that the polymer chains that formed had lengths that were too short to precipitate.

The conversion of the concentrated surfactant solutions was determined gravimetrically from ethanol. Ethanol selectively dissolves the monomeric form of the

surfactant. The polymeric surfactant was precipitated and the nature of the precipitate was determined by FT-IR spectroscopy.

The distinguishing peaks of the surfactant and the polymeric surfactant are the only changes in the spectra between the two that are clearly and easily identifiable. The precipitate in ethanol was poly (sodium 10-undecenoate) as observed in section 3.2.

The sodium 10-undecenoate solutions C, D and E were precipitated with ethanol and then filtered to produce the polymeric form of the surfactant in large quantities for the first time from the quiescent systems. This was evidence of the fact that the ultra-violet investigation did not have enough energy to convert the surfactant into its polymeric form in any easily measurable amounts.

The gravimetric conversion of the surfactant solutions shows the following development.

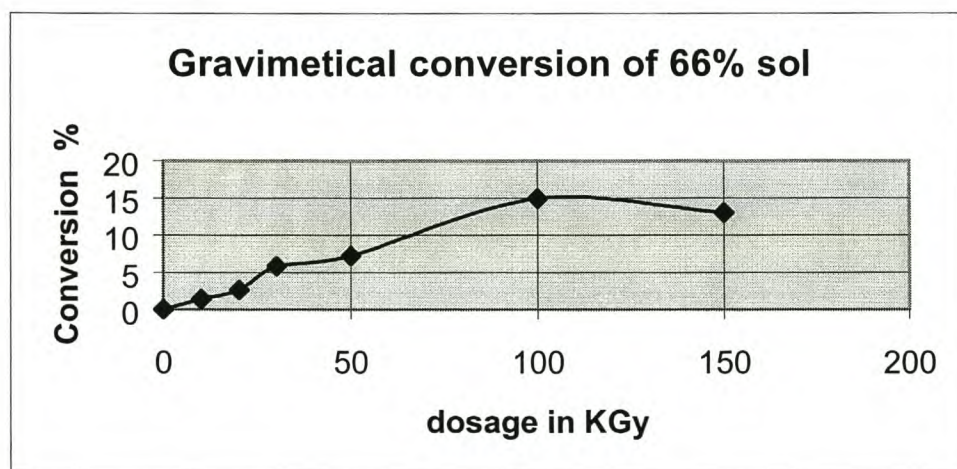


Figure 6.1 Gravimetric conversion of Sodium 10-undecenoate by gamma irradiation

This is in agreement with the results of McGrath's studies⁴ using thermal and UV initiation in concentrated phases of aqueous sodium 10-undecenoate. The degree of polymerization did not improve with time; it in fact showed a decrease which can be attributed to chain breakage by the gamma irradiation leading to shorter chains that are ethanol soluble. The gamma irradiation conversion does differ from the thermal

conversion obtained by Friberg *et al* ⁵ but the reasons for the difference between Friberg's study and the observations by McGrath, as well as the observations of this study, are not known.

6.5 Particle size analysis

Results of the particle size analysis proved particularly disappointing as the Malvern Zetasizer apparatus did not allow distinction between the surfactant aggregates and the polymer particles that formed in solution as the instrument assumes that all dimensions belong to spherical particles. The examined solutions did not show the PMMA particles. This is due to their low concentration and the irregular shapes of the PMMA particles.

Peak analysis by intensity:

Table 6.3 10 kGy particle size data of standard MMA sample

Peak	Area	Mean	Width
1	28.1	834.7	468.2
2	71.9	3740.2	2552.7

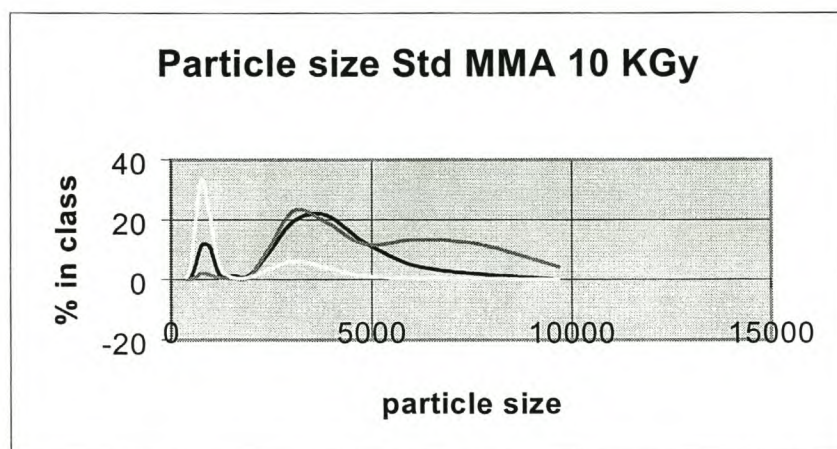


Figure 6.2 Particle size for 10 kGy gamma dose standard MMA sample

The data shows two peaks of micron size (0.84 and 3.7 μm respectively). The solutions were optically transparent. This makes interpretation difficult. There are two options: firstly, that the scan shows the surfactant aggregates and secondly, that the number and shape of the objects in solution are low and non-spherical respectively. The first interpretation would suggest that the two peaks show the nature of the surfactant aggregates as the aggregates in solution will show distributions around their dimensions.

The second interpretation would be that fine fibers could be present, leading to light scattering at the sizes observed but not spheres at those sizes, thereby explaining why the solutions are optically transparent.

The data is not however suitable for in detail deduction as the counts per second as well as the percentage in range were beyond normal ranges for significant inference. (See appendix C)

This meant that particle size analysis was abandoned as a means of analysis of the particles in solution.

6.6 Analysis by means of electrospray mass spectrometry

The biochemistry department of the University of Stellenbosch carried out analysis by ESMS and supplied the following information.

Electrospray mass spectrometry (ESMS) is a technique that is sensitive to charged particles. The technique is capable of detecting m/z ratios of up to 2 000. The samples are normally injected in a mixture of 50% acetonitrile in water. The technique is non-destructive and does not create fragmentation as would normally be expected in mass spectrometry.

Electro-spray ionization takes place in the inlet and source sections of the instrument (Figure 6.3). A mixture of an aqueous solution of a sample and an organic solvent is pumped through a hollow needle held at a high potential (3-4kV). The stream of

liquid issuing at 5-300 μ l/ml is broken up into highly charged droplets of ca. 1 micron to form the electro-spray. Dry nitrogen gas is also introduced through a capillary to enhance nebulisation (Figure 6.3). This occurs at atmospheric pressure.

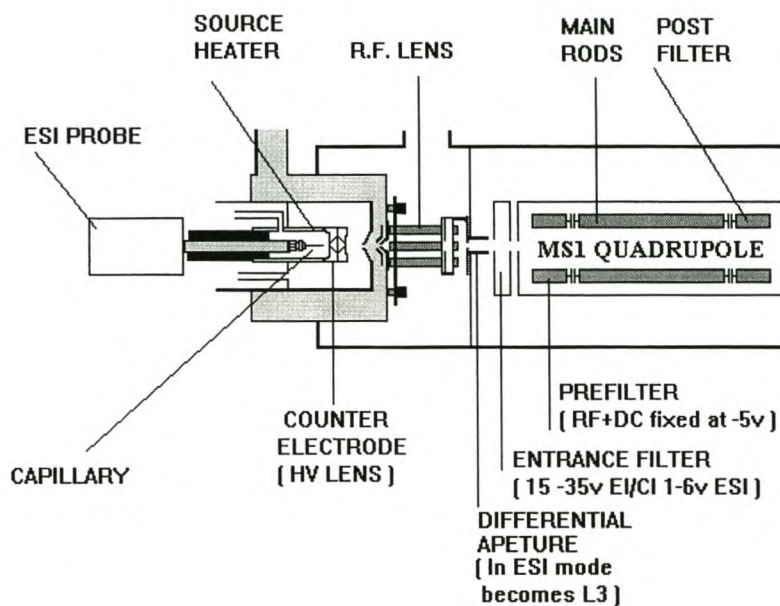


Figure 6.3. Schematic representation of the electro-spray ionization source.

The charged droplets are accelerated in an electric field towards the analyzer section of the instrument held at a high vacuum. Through the combined effects of drying gas and vacuum the solvent in the droplet starts to evaporate, giving rise to smaller, increasingly unstable droplets from which surface ions are liberated into the vacuum (Figure 6.4). The de-solvated ions pass through a sample cone and skimmer lenses and after focusing by the RF lens, into the high vacuum region of the quadropole analyzers where they are separated according to mass and detected by photomultiplier detectors.

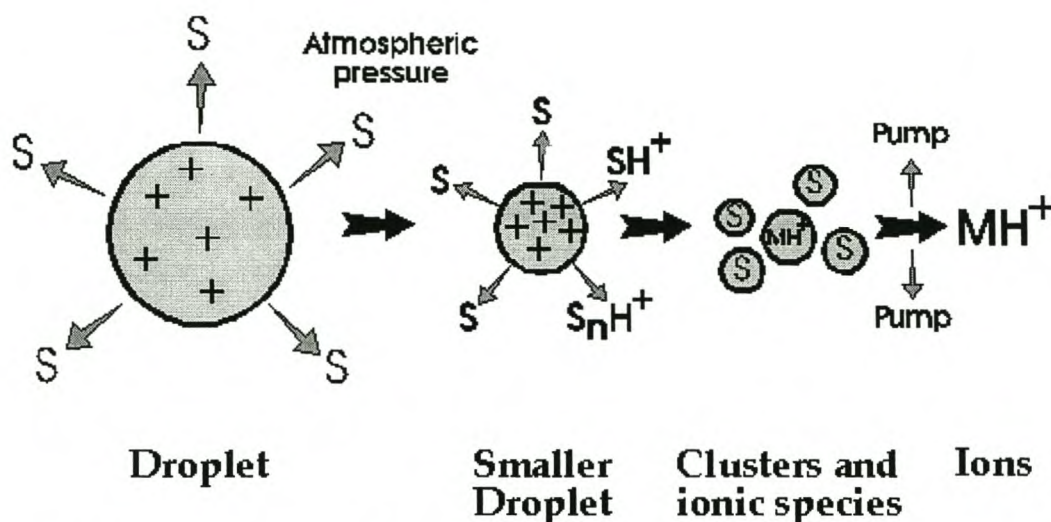


Figure 6.4 The de-solvation process taking place in the electro spray ionization source.

This technique allows single molecules to be detected as well as providing a rough guide to relative concentrations in the solutions. The molecules are separated via the spray, and ionic species are then charged through the addition of protons to the particle. This means that the technique will not detect homopolymer polystyrene or poly (methyl methacrylate). This means that for a single particle with a single charge a second shadow peak will occur in close proximity (a single unit) for a species of double the mass with a double charge. This can be determined by calculations of the expected molecular mass of species and in this way cancelled out.

6.6.1 Experimental and results

Electrospray mass spectrometry was carried out on samples containing MMA and on those containing the standard sodium 10-undecenoate solutions.

The comparison between the polymerized and unpolymerized surfactant solutions was carried out to determine the conversion of the surfactant from monomeric to polymeric form (Figure 6.5).

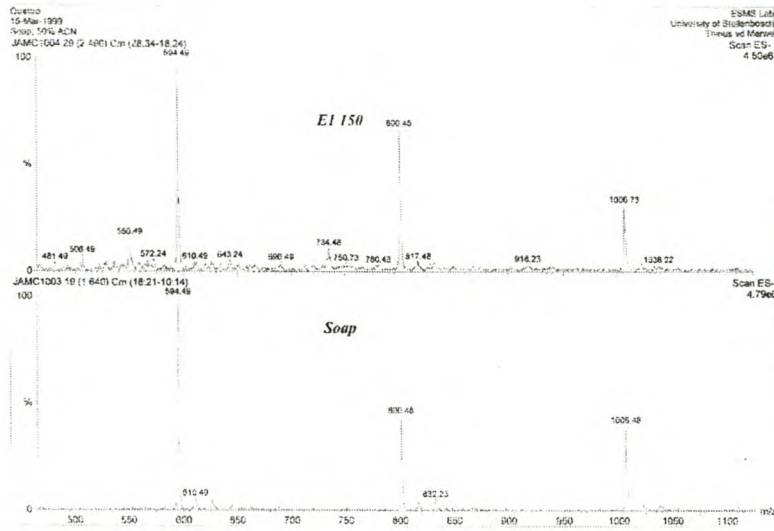


Figure 6.5 ESMS analysis of surfactant at 150 and 0 kGy doses

The comparison between surfactant solutions and irradiated solutions was done to determine the presence of MMA in the short chain oligomers of the surfactant that are formed by sodium 10-undecenoate. This can be seen in Figures 6.6 and 6.7.

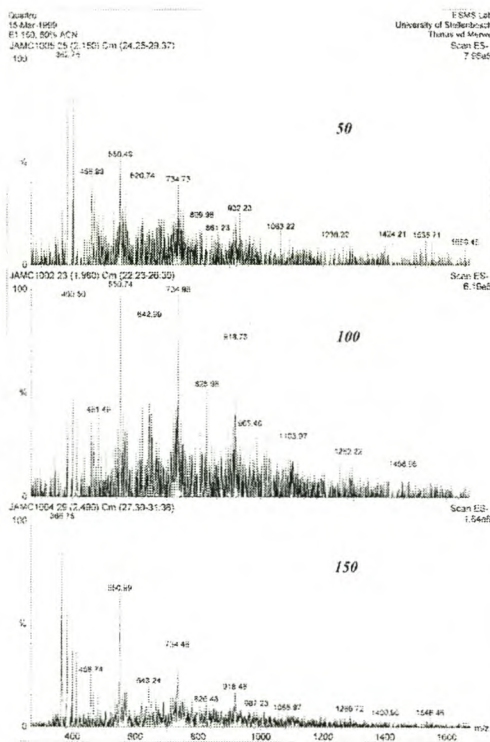


Figure 6.6 ESMS analysis of surfactant at 50,100,150 kGy

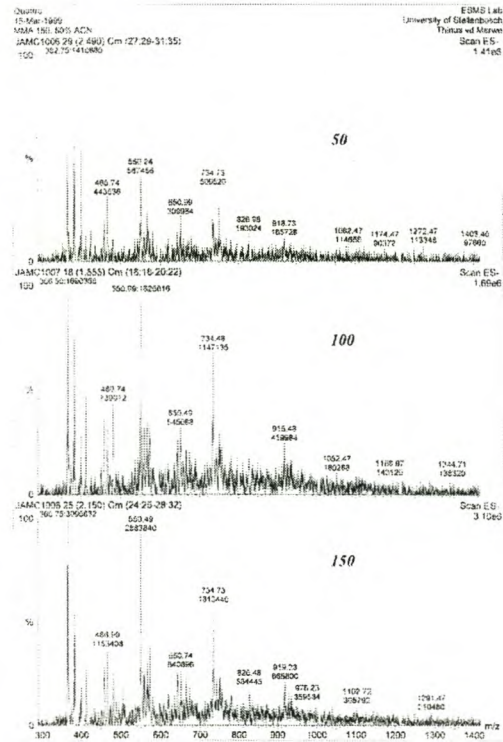


Figure 6.7 ESMS analysis of standard MMA at 50,100,150 kGy

6.6.2 Discussion

The scans shown in Figure 6.5 show that the same peaks are present in both samples for the unpolymerized surfactant but the surfactant that had been exposed to 150 kilograys shows small peaks, due to the formation of oligomers. The data also shows that the vast majority of surfactant is unreacted which agrees with the gravimetric data given in section 6.4.

When the peaks of the oligomers are examined it becomes clear that the same peaks are present in the MMA-containing samples, Figure 6.7, as well as the pure surfactant samples Figure 6.6.

This tells us that the charge bearing oligomers, which are found in the MMA containing samples, are purely sodium 10-undecenoate oligomers and contain no MMA. This suggests that the MMA has all reacted prior to the reaction of the sodium 10-undecenoate. This can be deduced from the large amounts of PMMA which were recovered from the samples (section 6.7). This tells us that the reactivity ratios, even though they are not available in literature nor were they determined in this study, between the methyl methacrylate and the sodium 10-undecenoate are probably unfavorable. The MMA appears vastly more reactive than the surfactant and copolymerization is not favored.

The m/z ratio that can be detected by this technique includes agglomerates up to 2000 amu's. The oligomeric peaks have decayed well before this value, indicating that the chains are considerably shorter. This agrees well with most literature for the polymerizations^{6,7,8}.

The 550 m/z ratio peaks are of particular interest, as their concentration appears to be the highest. The nature of the species causing this peak can be determined if it is taken into account that the molar mass of the surfactant is 206 g/mol while the molar mass of sodium is ~23 g/mol. The ionic species that has no sodium associated has a trimer of molar mass ~549 g/mol. This is in agreement with the 550 m/z ratio, as the technique requires the addition of a unit as the mass of the charge. These peaks do not

appear to be due to double charges. This tells us that trimers are the species of highest concentration.

6.7 Dialysis investigation

Dialysis of the standard MMA polymerizations irradiated at 50, 100 and 150 kilogray dosages was carried out. The samples were placed in water that was continuously stirred and replaced three times daily for ten days. A dialysis tube with a cut off of 12000 atomic mass units was used to ensure that the surfactant, as well as the oligomeric chains, was removed.

After this period the bags were opened to yield a gel of polymer that was analyzed by SEM. The nature of the polymer was confirmed as poly (methyl methacrylate), via FT-IR spectroscopy.

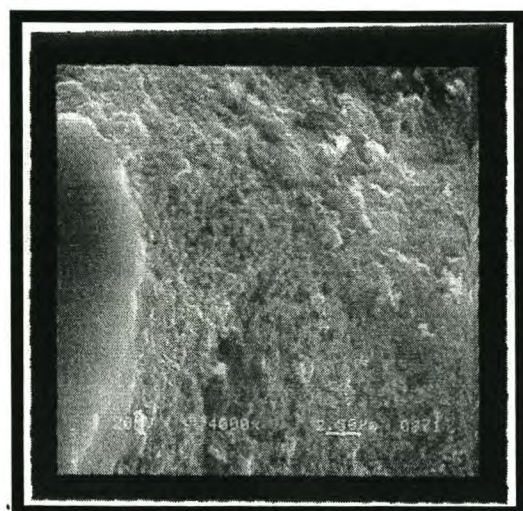


Figure 6.8
150 KGray MMA at 4000 magnification

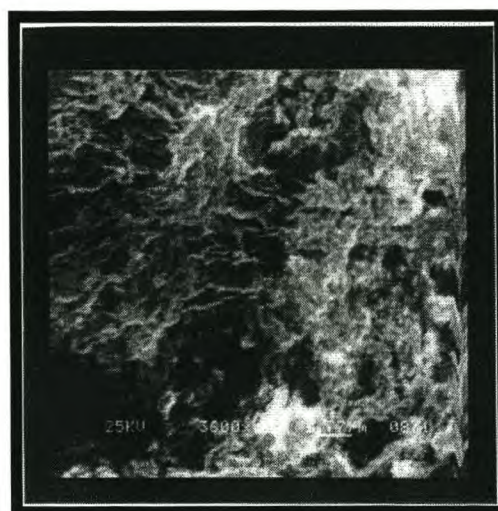


Figure 6.9
100 KGray at 3600 magnification

The PMMA that was recovered by dialysis showed no obvious signs of large-scale order in the product. The morphology shows some finer structure in some of the images but the structure is neither regular nor consistent. This can be examined in the context of the TEM results which show fine structure and can be taken as indicative of coagulation of the smaller particles after removal of the stabilizing effect of the surfactant.

6.8 Conclusions

The polymerization of the surfactant sodium 10-undecenoate by gamma irradiation was greater than the polymerization of the sodium 10-undecenoate by ultra-violet irradiation, as was seen by the precipitation of the polymeric surfactant using ethanol.

This conclusion suggests that the UV irradiation should either be carried out for longer periods, although this is not feasible due to heat generation and evaporation that occurs in the open system, or that a stronger UV source should be used if the aim is to reach higher conversion. This would however require a totally different approach to the irradiation, as a sealed ampoule would be required as well as a sealed and secure UV reactor.

Gamma irradiation is more penetrating than ultra-violet irradiation and thus allows a more controlled reaction. Some practical factors are more problematic than with UV irradiation and will have to be addressed to make this approach viable. These include some decay of the polymeric system that will occur over time and a broad molecular mass distribution that will occur due to the lack of initiator in the system.

The fact that the gamma irradiated solutions contained larger concentrations of polymer than the UV irradiated samples, as evidenced by the thicker more viscous solutions, meant that the standard techniques that had been used for the preparation of the star-like particles formed in the UV studies for analysis, were now no longer effective. (Filtration by hand or by vacuum proved impractical).

Dialysis of samples that contained methyl methacrylate proved that only homopolymeric poly (methyl methacrylate) was formed in significant chain lengths (above 12 000 amu's) and that no defined structures were present. Some finer structure did occur but the irregularity and heterogeneity of the samples meant that the structure could not be assigned as templated or structure directed. This was shown, in the context of TEM results (section 5.4), to be a possible result of coagulation.

Irradiations of the solid sodium 10-undecenoate and the ethanol precipitates did not form solid polymeric particles, as the polymerization that occurred was negligible.

Results of this study provided supplementary data to that of the investigations in chapter 5, which stated that the particles found in the ultra-violet irradiation studies (chapter 4) were predominantly surfactant or oligomeric surfactant aggregates with the possibility of fine polymeric fibers in their interior.

A spin off of the study is a proven technique to make trimers and higher oligomers for use as new structure directing materials in future studies.

6.9 References

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Chapter Seven General Conclusions

Chapter Seven General Conclusions

The objective of this project was the formation of organic nano-particles and, if possible, to overcome difficulties described in the literature relating to the fixing of these structures by polymerization. Unlike structures that emerge from traditional emulsion polymerization, this project aimed at the creation of unorthodox single polymeric particles of shapes other than spherical, preferably by a single step reaction in aqueous media.

The reactants chosen for investigation were the polymerizable surfactant sodium 10-undecenoate; styrene and methyl methacrylate monomers; and divinyl benzene and ethylene glycol dimethacrylate as crosslinking agents for fixation of structures.

Six aims were identified as goals for the achievement of the primary objective in section 1.1 and the following conclusions were reached:

The **conclusion to aim one** was that it was indeed possible to form nano-structures from the polymerizable surfactant sodium 10-undecenoate, with or without the use of added organic monomers, in aqueous media. Star-like self-assemblies were recovered only after photo initiation in the presence of the free radical generator benzophenone.

The **conclusion to aim two** was that the surfactant sodium 10-undecenoate was not fully polymerizable by ultra-violet irradiation with a free radical initiator. In fact, under the chosen conditions polymerization of the surfactant was found to be minimal.

The **conclusion to aim three** was that gamma irradiation proved to be more successful than ultraviolet irradiation for the polymerization of the surfactant sodium 10-undecenoate. Polymerization was found to give conversion of a maximum of fifteen percent.

The **conclusion to aim four** was that structural elucidation of the nano-structures was possible through the use of transmission electron microscopy and field emission

scanning electron microscopy. The fine structure could however not be fully investigated by these techniques beyond five hundred thousand times magnification.

The **conclusion to aim five** was that small angle x-ray scattering studies showed that there was minimal order in the ternary solutions of sodium 10 undecenoate, water and methyl methacrylate. This contrasts with the findings of the light microscopy study, which showed time dependent hexagonal phase formation. This area of the particle development will require more investigation in the future to determine if particle growth occurs in a liquid crystalline phase. The binary phase diagram of sodium 10-undecenoate shows that a hexagonal lyotropic phase would be present for the 45% by weight surfactant concentration that was used, but the addition of a monomer to the liquid crystalline phase may cause disruption. This means that the phase that would be expected from the binary phase diagram would not occur. As only one SAXS sample could be examined, conclusive proof of the nature of the order in the solution was not obtained.

The **conclusion to aim six** was that fine structure of the particles found in transmission electron microscopy studies was indicative of some form of structural guidance in the formation of the nano-structures. This may or may not be templated material but in and of itself is a major step for the formation of polymeric structures if the fine structure could be conclusively assigned as polymeric. Due to the nano-scale of the fine structures and the bed of surfactant in which the structures lie it is not possible to do this at this stage. This is however an interesting and tantalizing glimpse into what the future of polymeric fine structure may well hold.

Chapter Eight Recommendations

Chapter Eight Recommendations

The prospects for the use of the quiescent technique, developed for the nano-structure self-assembly, are limited. Other surfactants beside sodium 10 -undecenoate, with more compatible reactivity ratios should however be investigated in order to determine polymerizable surfactant effects. The use of a polymerizable surfactant that is far more reactive than sodium 10-undecenoate and keeps it's ordered structure during polymerization should allow a more effective examination of this crystalline phenomenon.

Further structural investigation of the particles formed in this study should be done with specific reference to TEM studies, which indicate fine structure in the particles.

The use of a polymerizable surfactant with the polymerizable moiety attached to the head group is an important consideration. The head groups of surfactants are in a more ordered environment than the tails, which means that the polymerizable moiety would be more likely to retain its position in the assembly. The terminal olefinic group of sodium 10-undecenoate is also more hydrophilic than the corresponding saturated terminus, which means that it is a less effective surfactant. A non-terminal unsaturated bond may therefore be more suitable.

The use of bola-amphiphiles (bi-headed systems) and cocogem surfactant systems (bi-tailed systems) for nano-structural direction has been moderately more successful than the use of single tail surfactants. They partially overcome the instability of the structure-directing agent to disruptions caused by polymer chain formation, which has been the main reason for the failure of organic structure directing polymerization to date.

Results using polymeric systems, such as polyelectrolyte surfactant complexes, as stable templates for nano-structuring are cautiously promising, but techniques that may offer in situ single structure directed polymeric particles are not viable at this stage.

Appendices

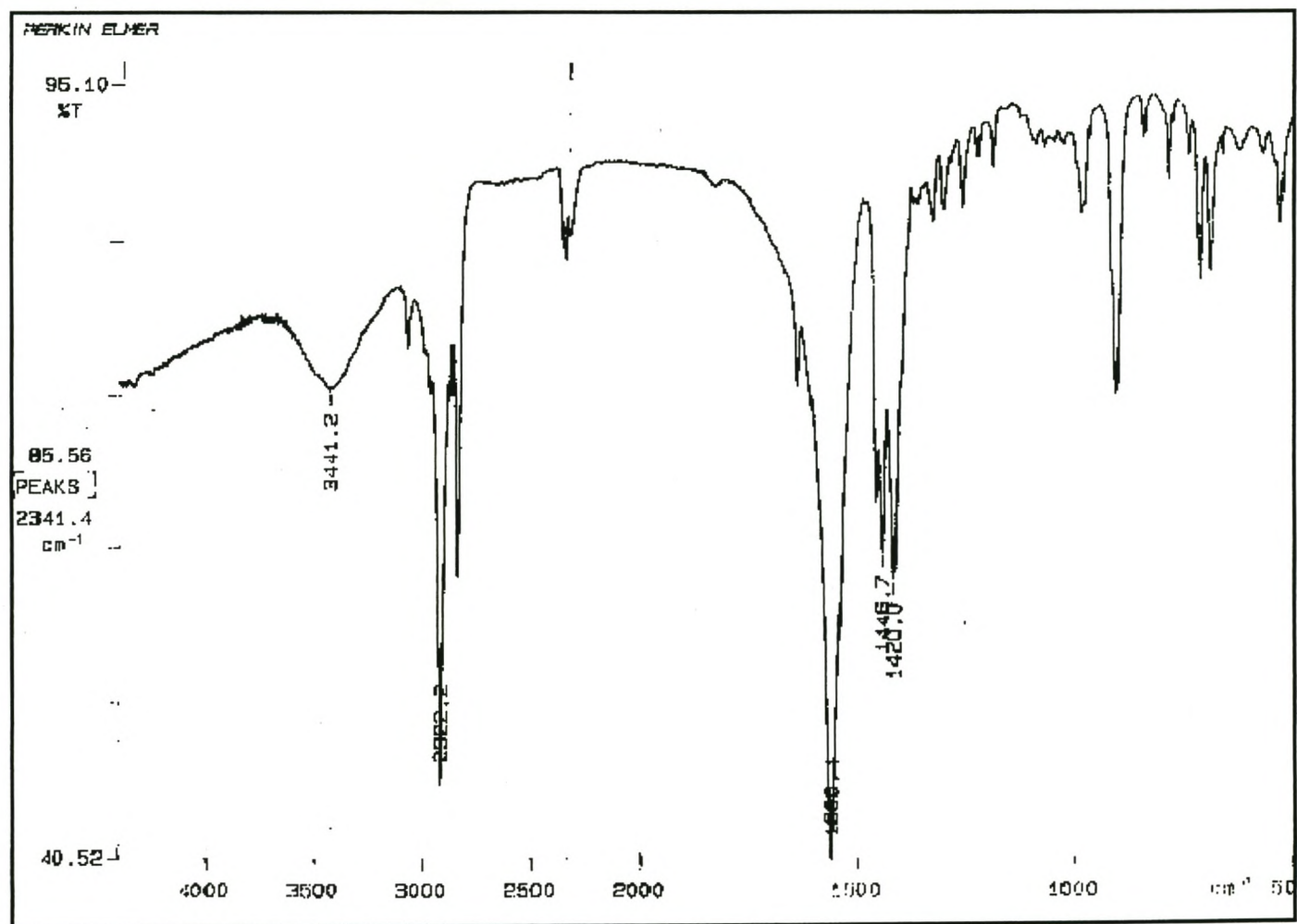
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A FT-IR studies

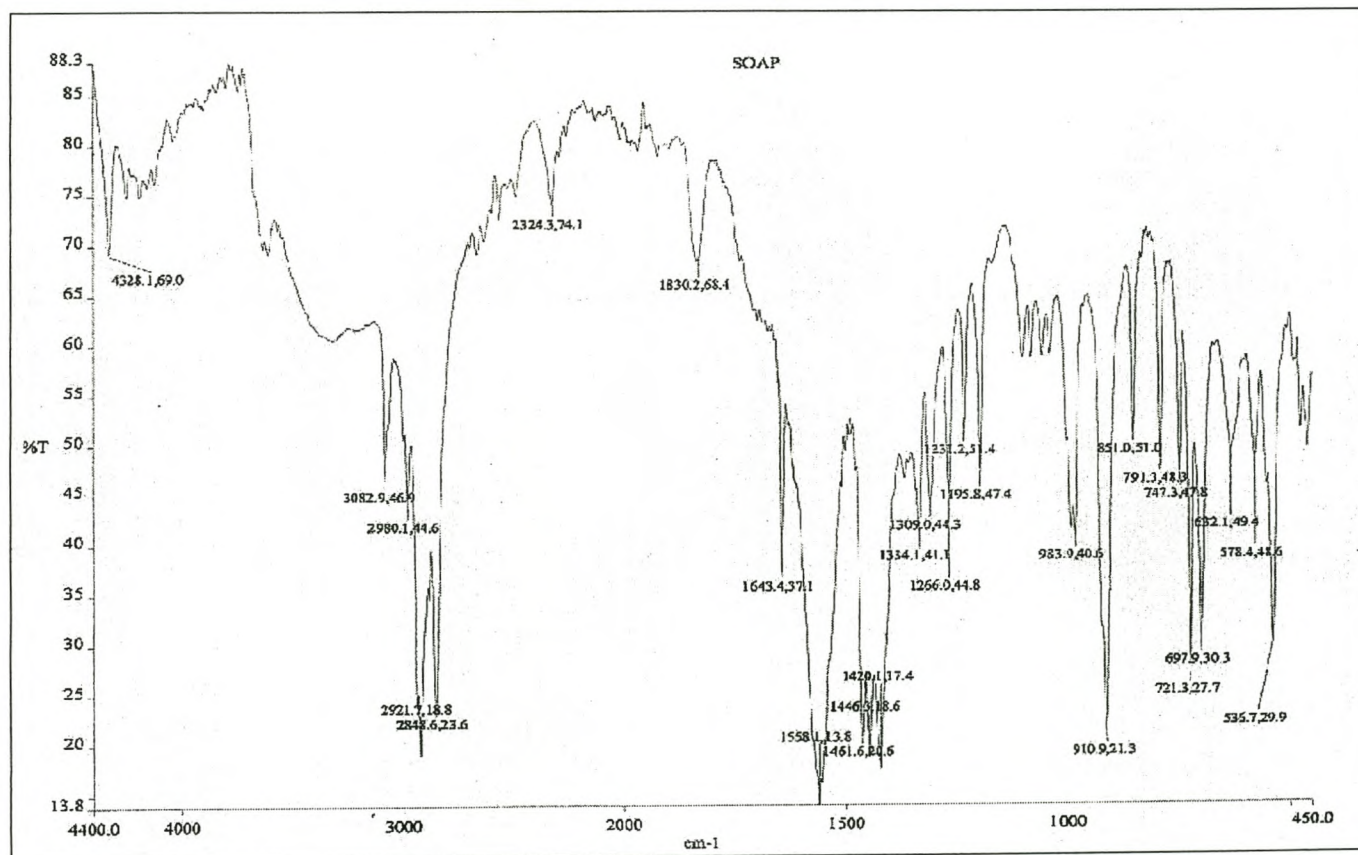
The following FT-IR spectra were recorded:

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6. Gamma irradiation (30 kGy) on std styrene sample see 5.3.1 Sample is polystyrene	viii

1. **FT-IR (Perkin Elmer 1600 FTIR) Sodium 10-undecenoate**

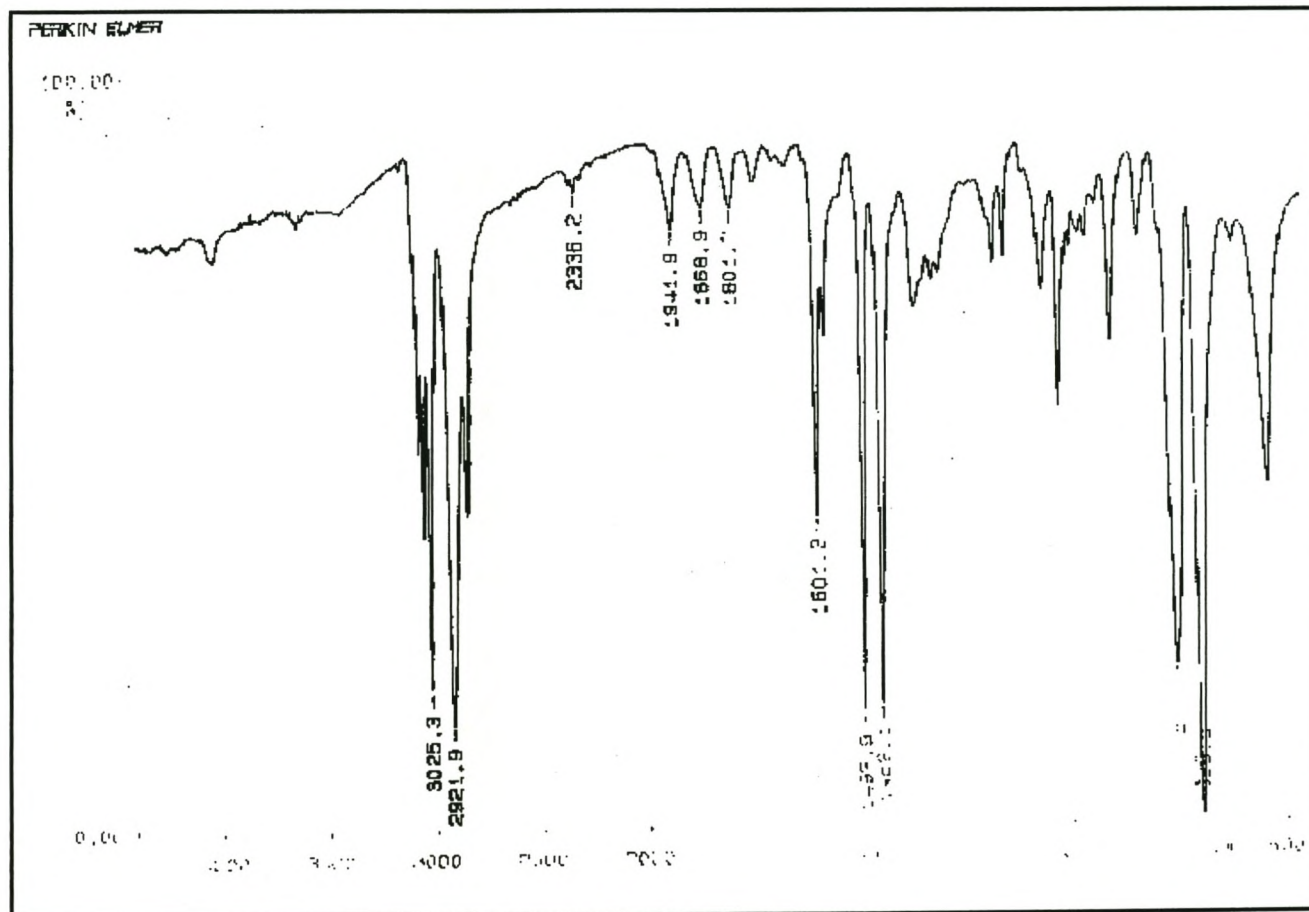


2. FT-IR (Photo-acoustic Spectrum) Sodium 10-undecenoate



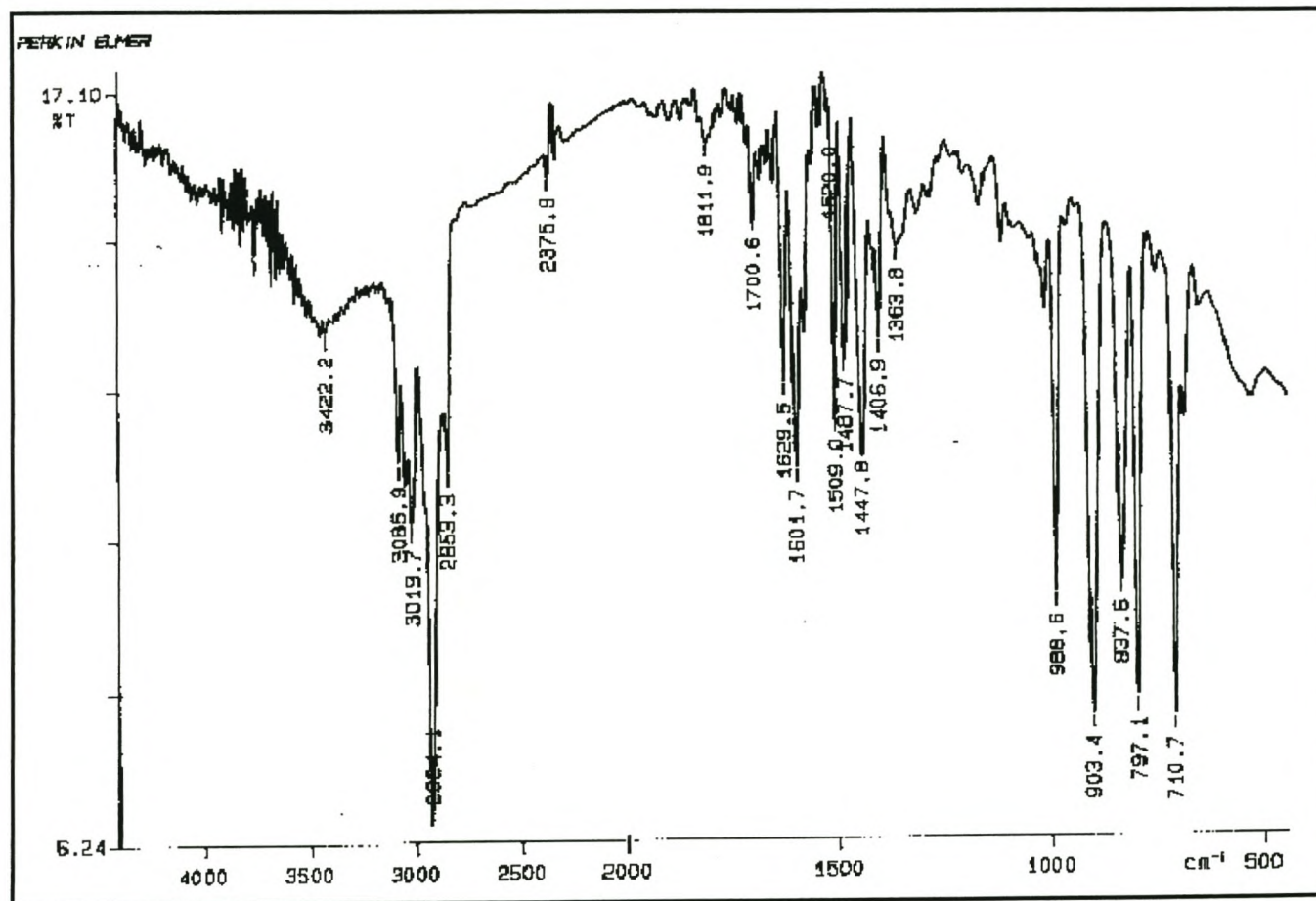
3. Crosslink concentration variation experiment 3.6.1

Sample containing 5% crosslinker DVB (polystyrene)



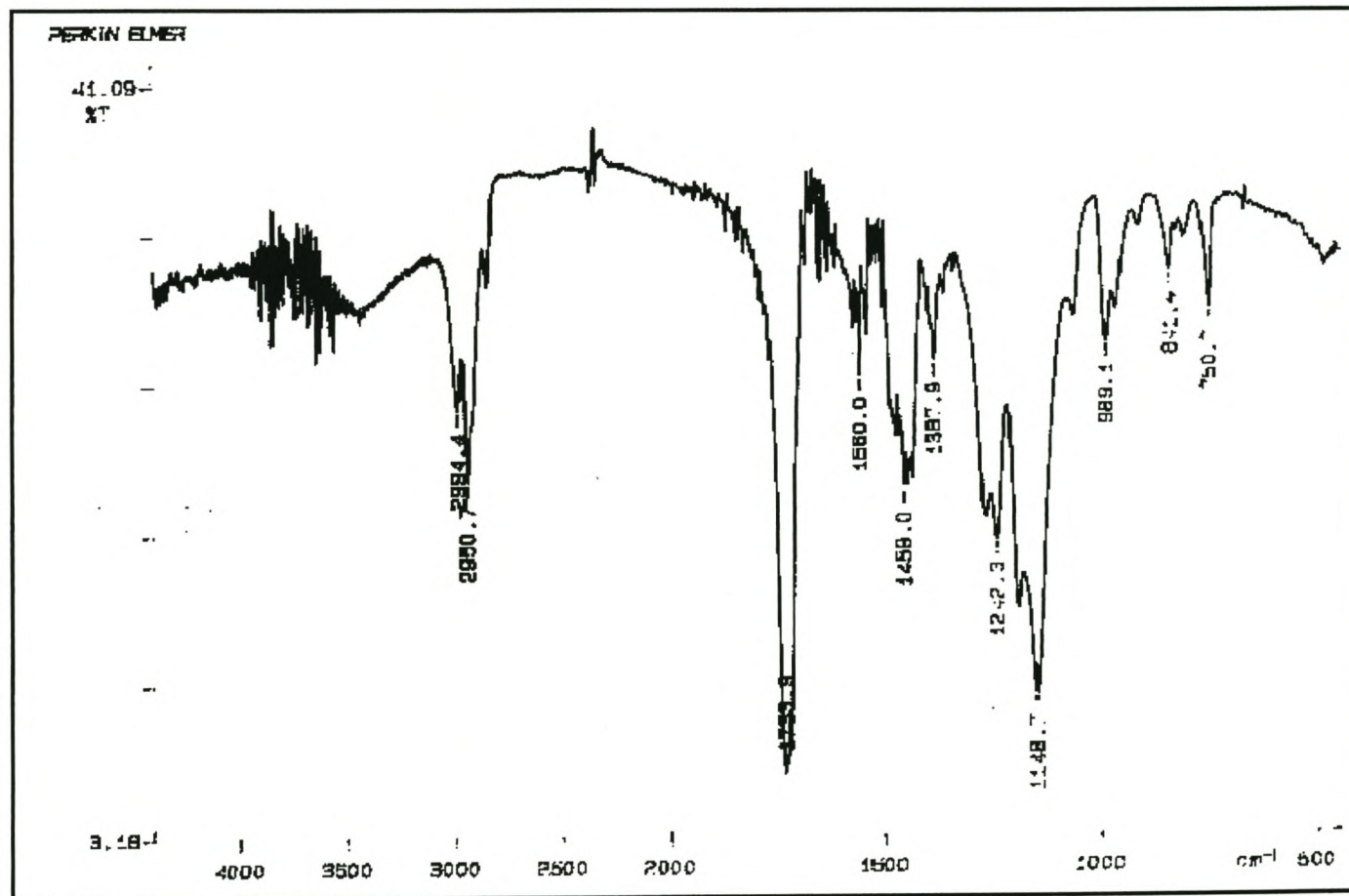
4. Crosslink concentration variation experiment 3.6.1

Sample containing 100% DVB



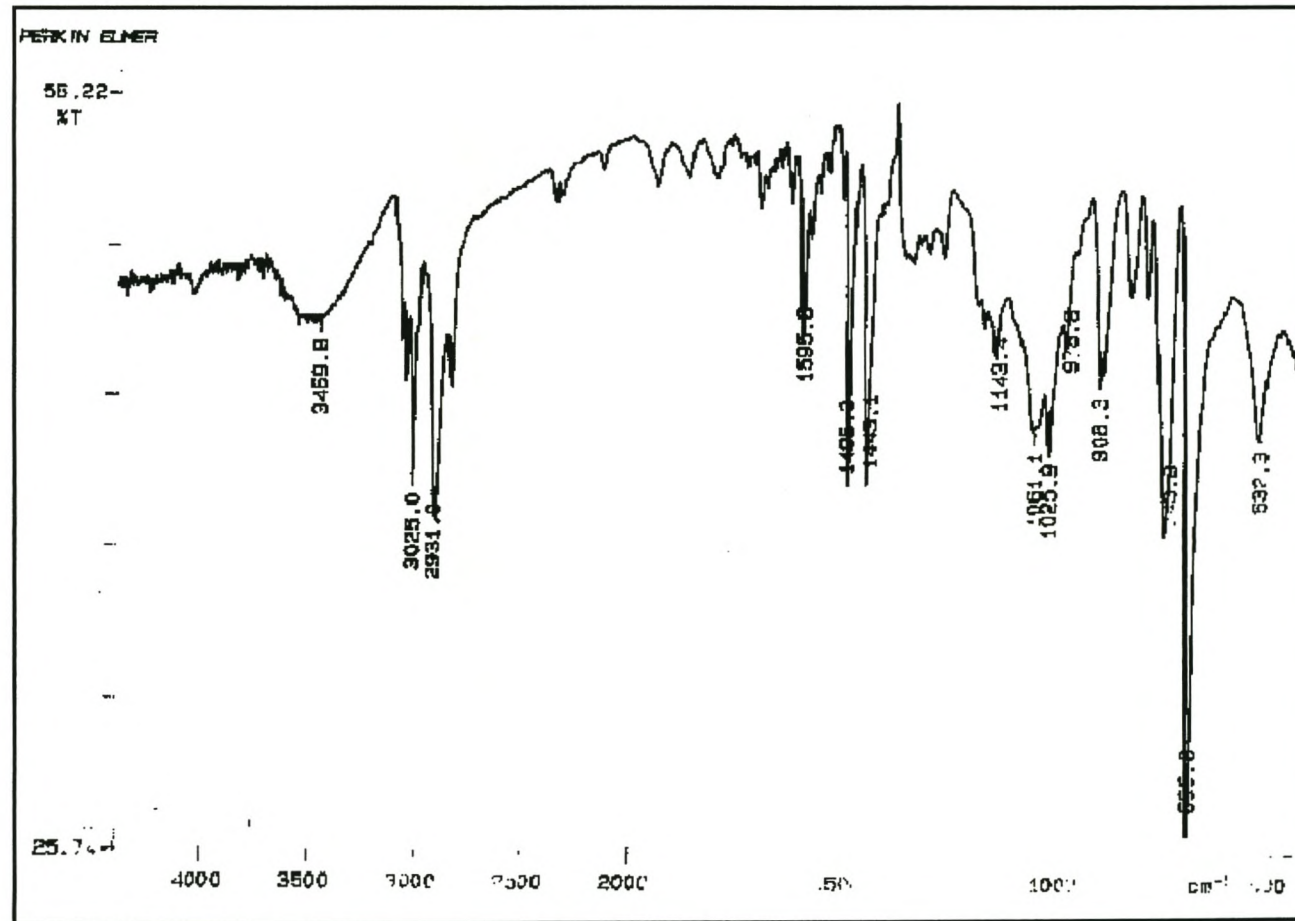
5. Gamma irradiation (30 kGy) on std MMA sample see 5.3.1

Sample is polymethyl methacrylate



6. Gamma irradiation (30 kGy) on std styrene sample see 5.3.1

Sample is polystyrene



B SEM Images

The following SEM images are shown :

Image

Page Number

From literature:

Image from Raj W.R.P ,Sasthav M., and Cheung H.M.

Polymerization of microstructured aqueous systems

formed using methyl methacrylate and potassium

10-undecenoate .Langmuir 1992,8,1931-1936

showing formed structures in a microemulsion containing:

45% methyl methacrylate and 30% potassium 10-undecenoate.

x

Image from Stoffer J.O. and Bone T. polymerization in

water-in-oil microemulsion systems II SEM investigation

of structure J. Dispersion Science and Technology

1980,1,393-412

showing “cold drawing of PMMA in a microemulsion containing:

pentanol, sodium 10-undecenoate, methyl methacrylate

x

Experimental:

1.SEM images acquired using the Topcon ABT60 SEM

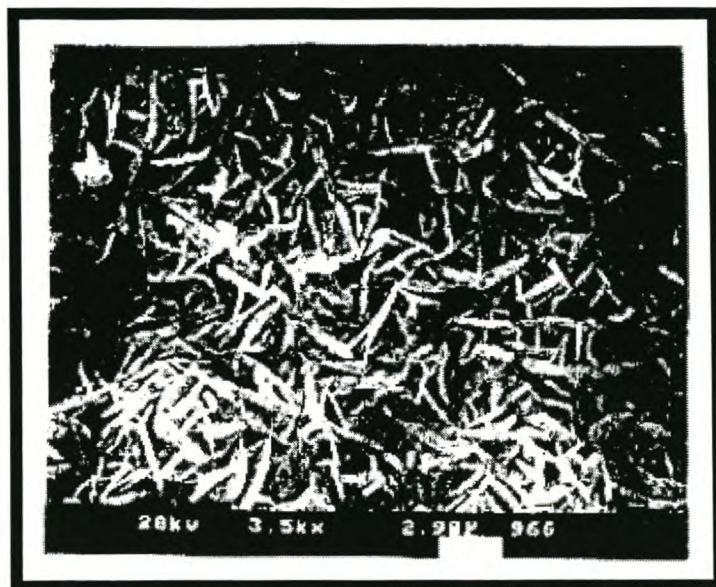
Figure 1.1	Rough particles (spheriodal) found in many samples	xi
Figure 1.2	Filter background for all images	xi
Figure 1.3	Surfactant gel or polymer artifact	xii
Figure 1.4	Surfactant gel artifact closeup	xii
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2.SEM images acquired using the Cambridge Leica S4401

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Figure 2.2	Single star image found among normal stars (2)	xiv
Figure 2.3	Surfactant gel artifact	xv
Figure 2.4	Carbon cement artifact	xv
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3.SEM images acquired using the JEOL 6000FE FESEM

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	Showing leaves.	
Figure 3.2	FESEM image two of alpha 12	xviii
	Showing a tip of a fibre.	
Figure 3.3	FESEM image three of alpha 12	xix
	Showing and enlargement of figure 3.3.	
Figure 3.4	FESEM image four of alpha 12	xix
	Showing separate collections of fibres.	
Figure 3.5	FESEM image five of alpha 12	xx
	An edge enlargement of leaf.	
Figure 3.6	FESEM image six of alpha 12	xx
	The core of a particle.	



Raj et al⁵⁵ formed structures (45% MMA and 30% PUD)

Image showing formed structures in a microemulsion containing: 45% methyl methacrylate and 30% potassium 10-undecenoate.



Stoffer and Bone⁵³ “cold drawing”

Image showing “cold drawing of PMMA” in a microemulsion containing: pentanol, sodium 10-undecenoate, methyl methacrylate.

1. SEM images acquired using the Topcon ABT60 SEM

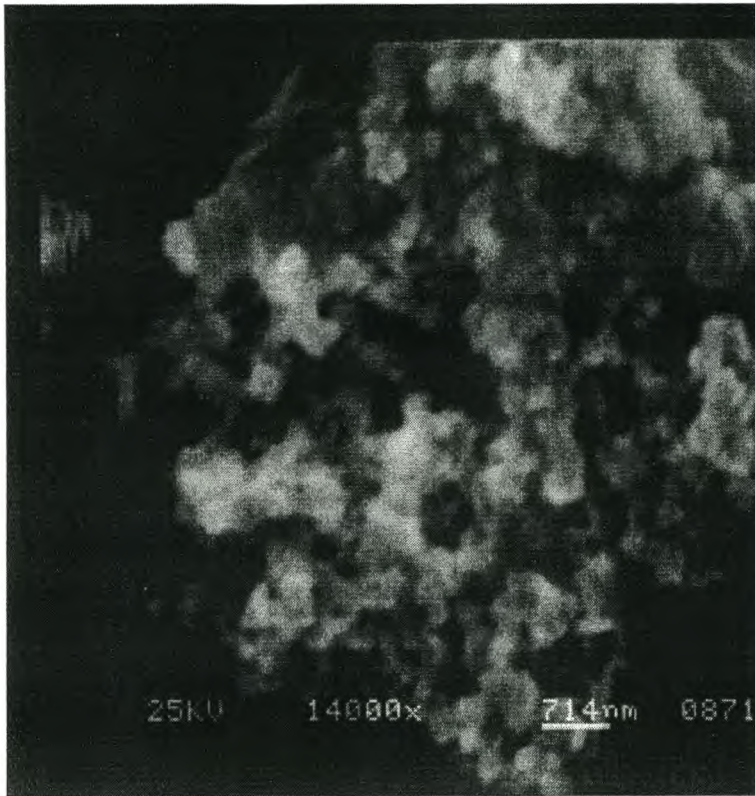


Figure 1.1 Rough particles (spheroidal) found in many samples

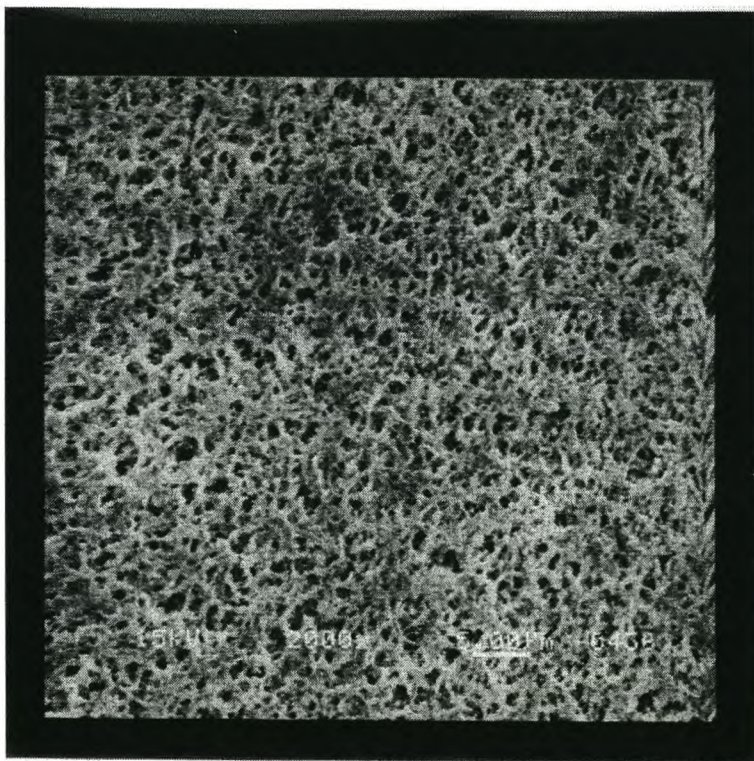


Figure 1.2 Filter background for all images



Figure 1.3 Surfactant gel artifact



Figure 1.4 Surfactant gel artifact closeup



Figure 1.5 Typical image of high star-like particle concentration

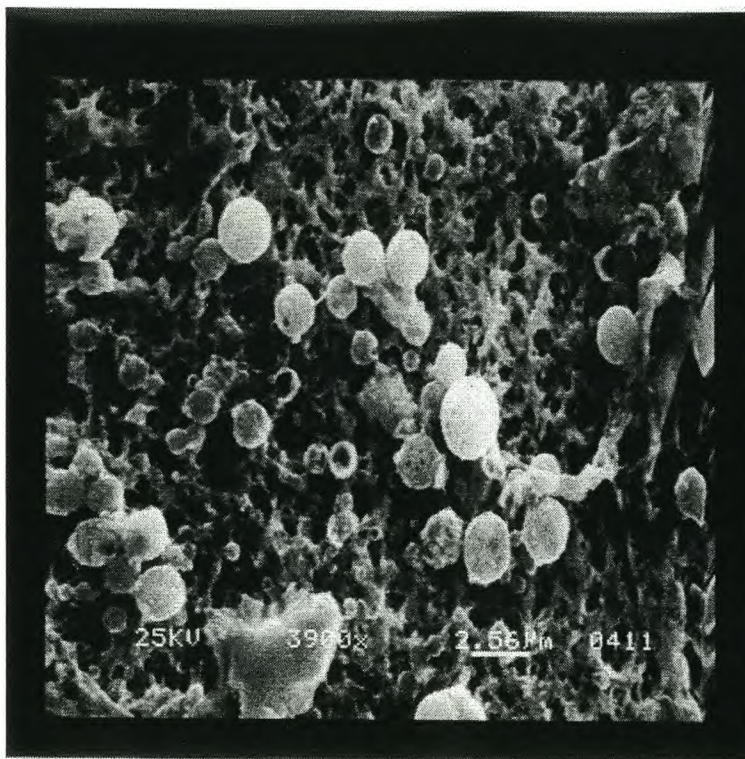


Figure 1.6 Typical image of spheroidal particles

2. SEM images acquired using the Cambridge leica S4401

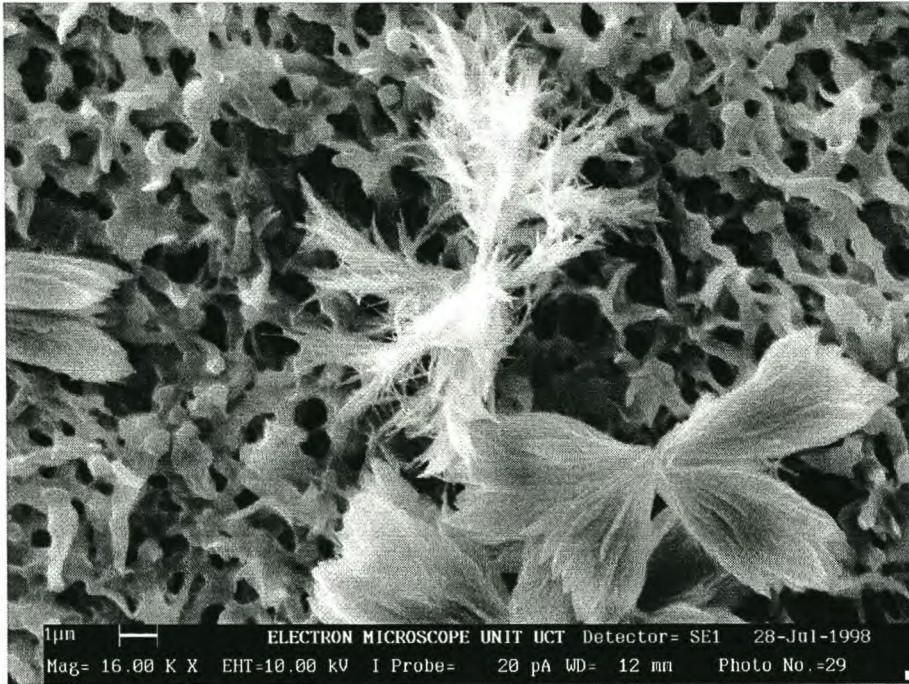


Figure 2.1 Single star image found among normal stars (1)

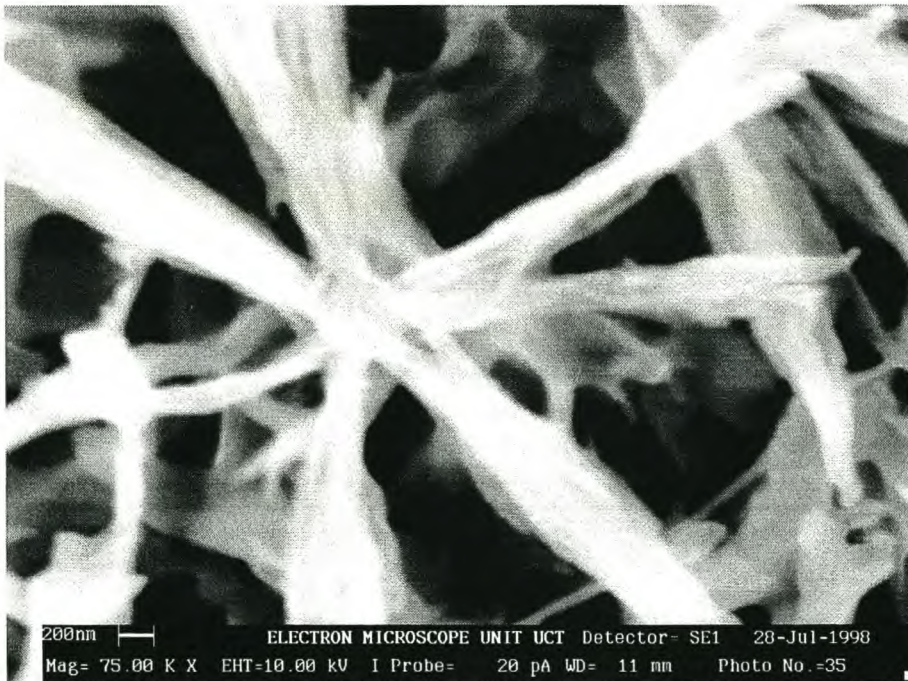


Figure 2.2 Single star image found among normal stars (2)

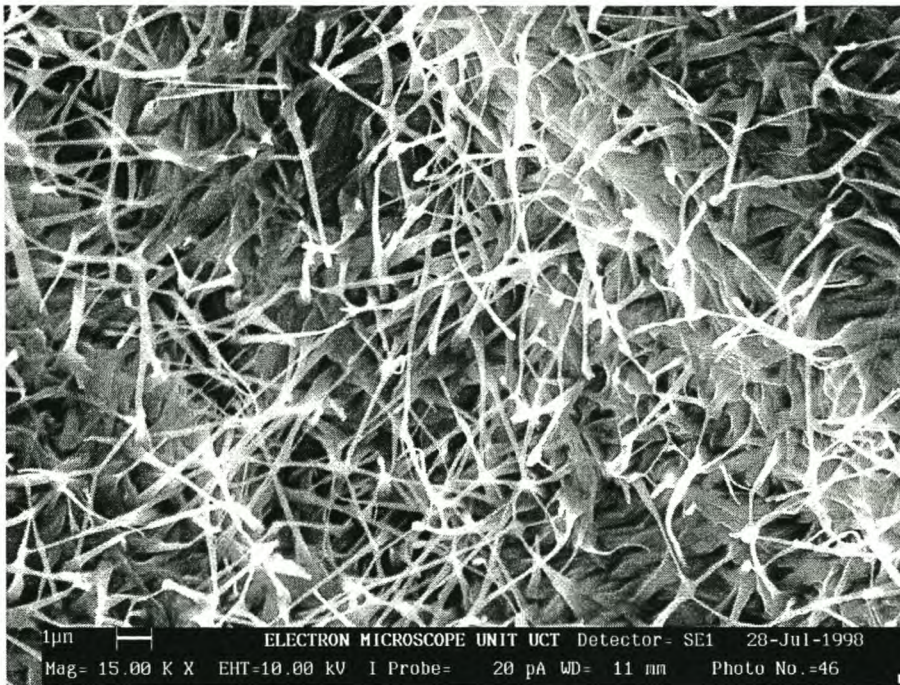


Figure 2.3 Surfactant gel artifact

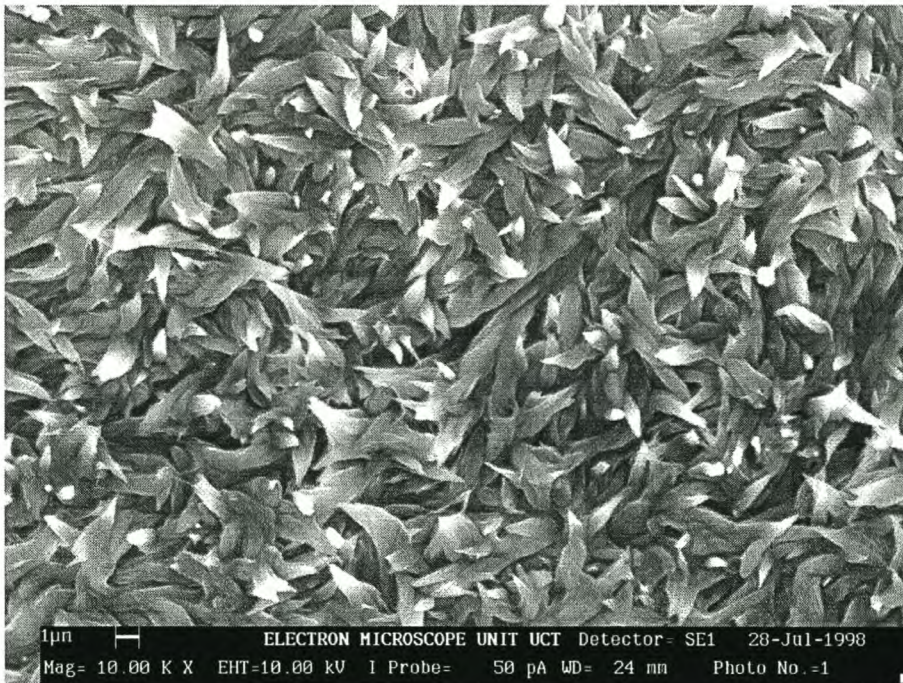


Figure 2.4 Carbon cement artifact

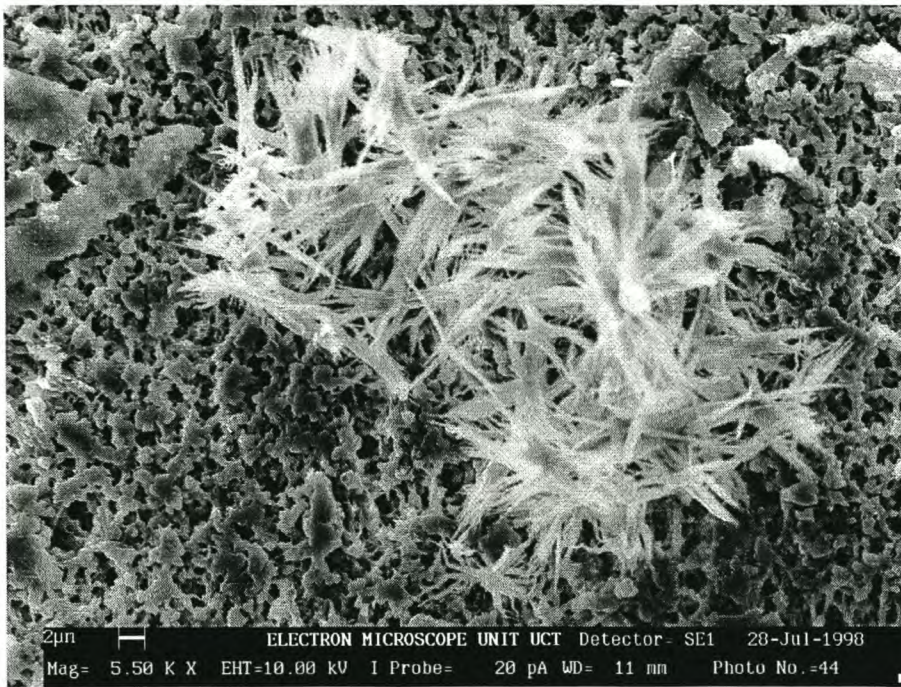


Figure 2.5 Fibrous structures



Figure 2.6 Spiral surfactant growth



Figure 2.7 High concentration of starlike particles



Figure 2.8 Surfactant gel showing “cold drawing”

3. SEM images acquired using the JEOL 6000FE FESEM

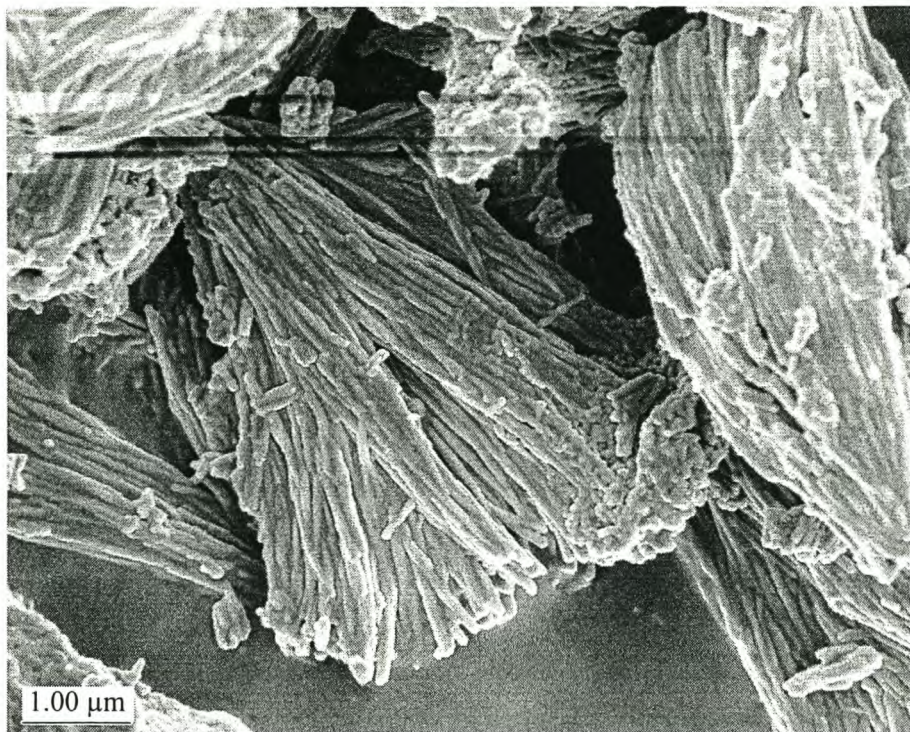


Figure 3.1 FESEM image one of alpha 12

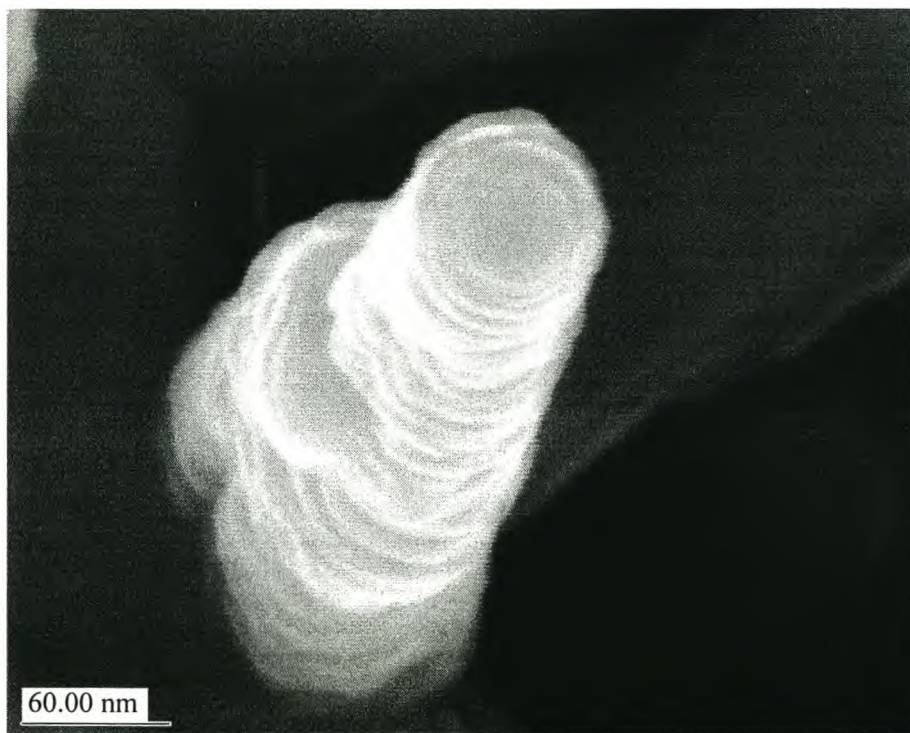


Figure 3.2 FESEM image two of alpha 12

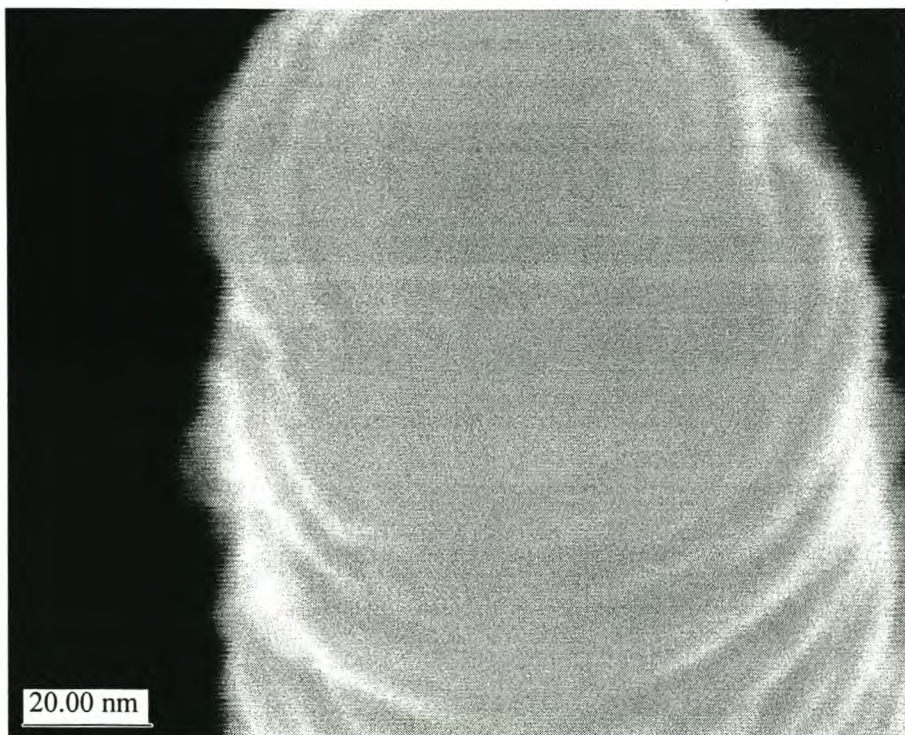


Figure 3.3 FESEM image three of alpha 12

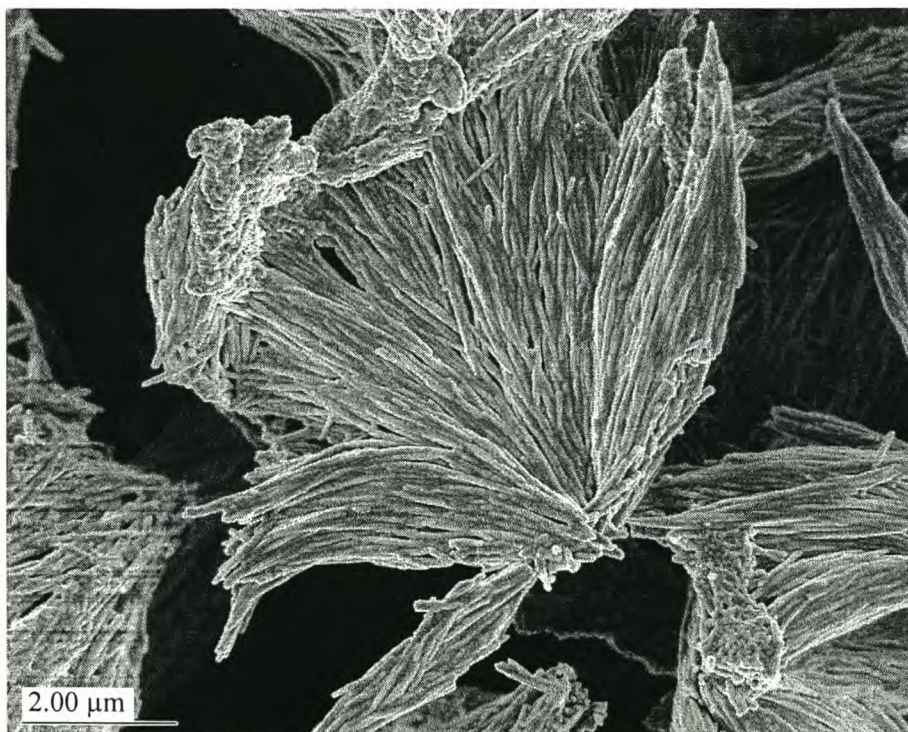


Figure 3.4 FESEM image four of alpha 12

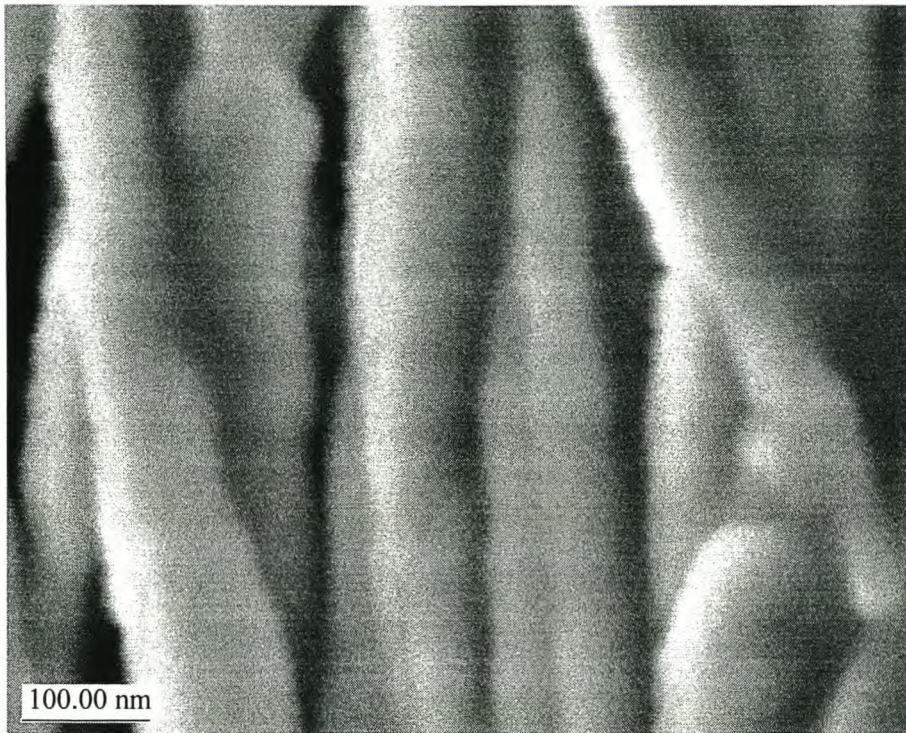


Figure 3.5 FESEM image five of alpha 12

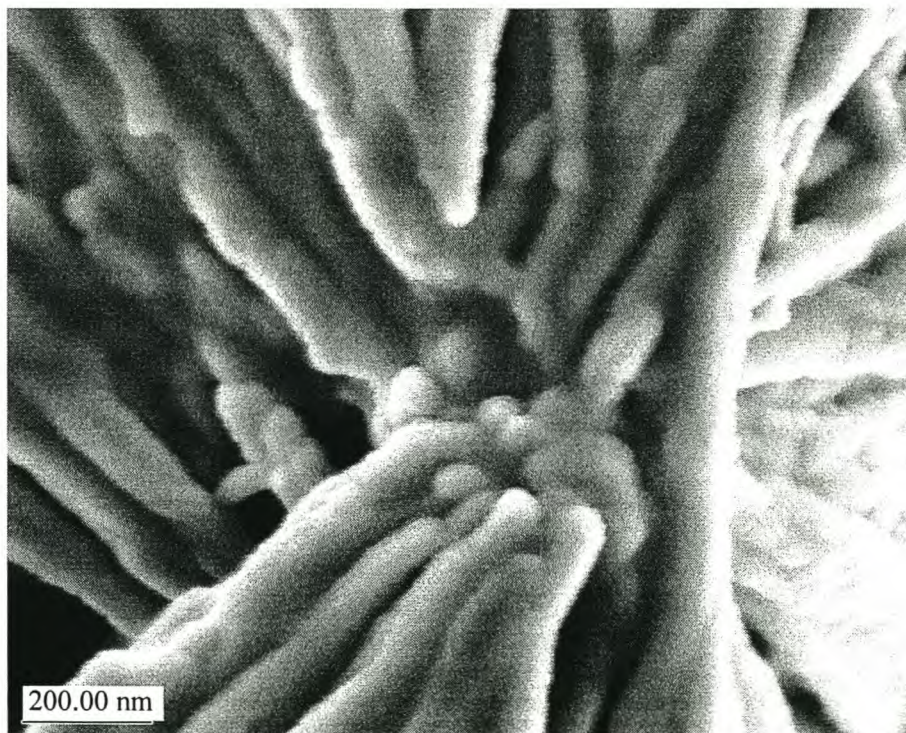


Figure 3.6 FESEM image six of alpha 12

C Miscellaneous Spectra

This section contains the following spectra:

<u>Spectra</u>	<u>Page number</u>
----------------	--------------------

Malvern zetasizer particle size analysis

From std MMA sample (10 kGy) (section 5.3.1)

- | | | |
|----|----------------------------|------|
| 1. | As a function of intensity | xxiv |
| 2. | As a function of number | xxv |
| 3. | Data analysis | xxvi |

From polymerization of monomeric surfactant (section 2.2.1)

- | | | |
|----|----------------------------|--------|
| 4. | As a function of intensity | xxvii |
| 5. | Data analysis | xxviii |
| 6. | Monomodal scans | xxix |

Differential scanning calorimetry

- | | | |
|-----|-----------------------------------------------|-----|
| 9. | DSC scan of sodium 10-undecenoate | xxx |
| 10. | DSC scan of "poly(sodium 10-undecenoate)/PMMA | |

(Ethanol precipitation of UV irradiated sample

45% surfactant 10% monomer 5% crosslinker 0.5% initiator)

SEM analysis which showed amorphous product. xxxi

Nuclear magnetic resonance spectroscopy

11. Solid state NMR scan of PMMA

Formed by a sample that precipitated PMMA under UV

irradiation similar setup to batch X 12 see section 3.6.3 xxxii

Electrospray mass spectrometry

12. ESMS scan comparison of sample E1 at 150kGy

and unirradiated surfactant (See chapter five) xxxiii

13. ESMS scan comparison of sample E1 at 50,100,150 kGy xxxiv

14. ESMS scan comparison of std MMA at 50,100,150 kGy xxxv

Atomic force microscopy

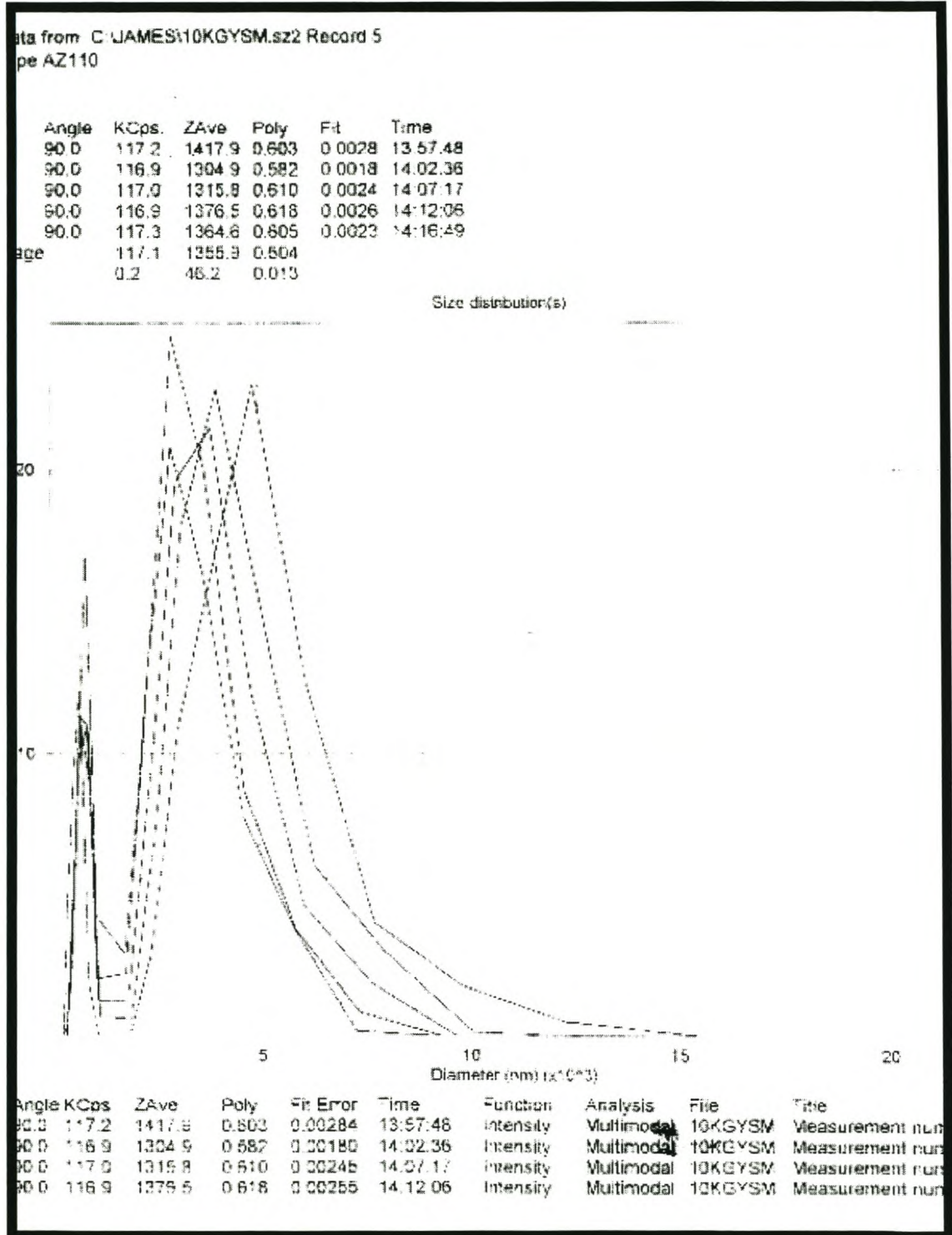
15. AFM image of sample alpha 12 10 x 10 μm xxxvi

16. AFM image of sample alpha 12 5 x 5 μm xxxvii

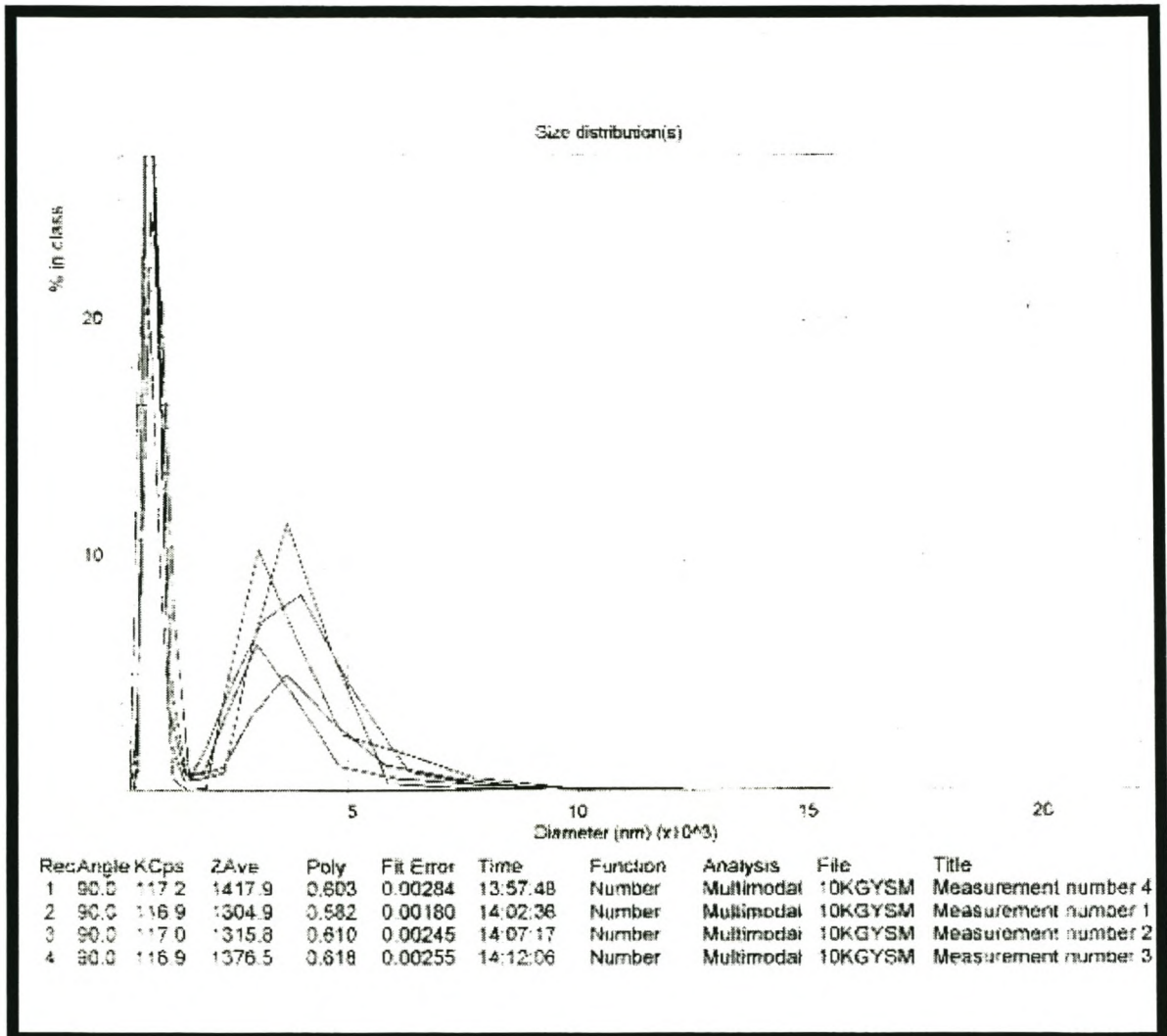
Malvern zetasizer particle size analysis

From std MMA sample (10 kGy) see 5.3.1

1 As a function of intensity



2 As a function of number



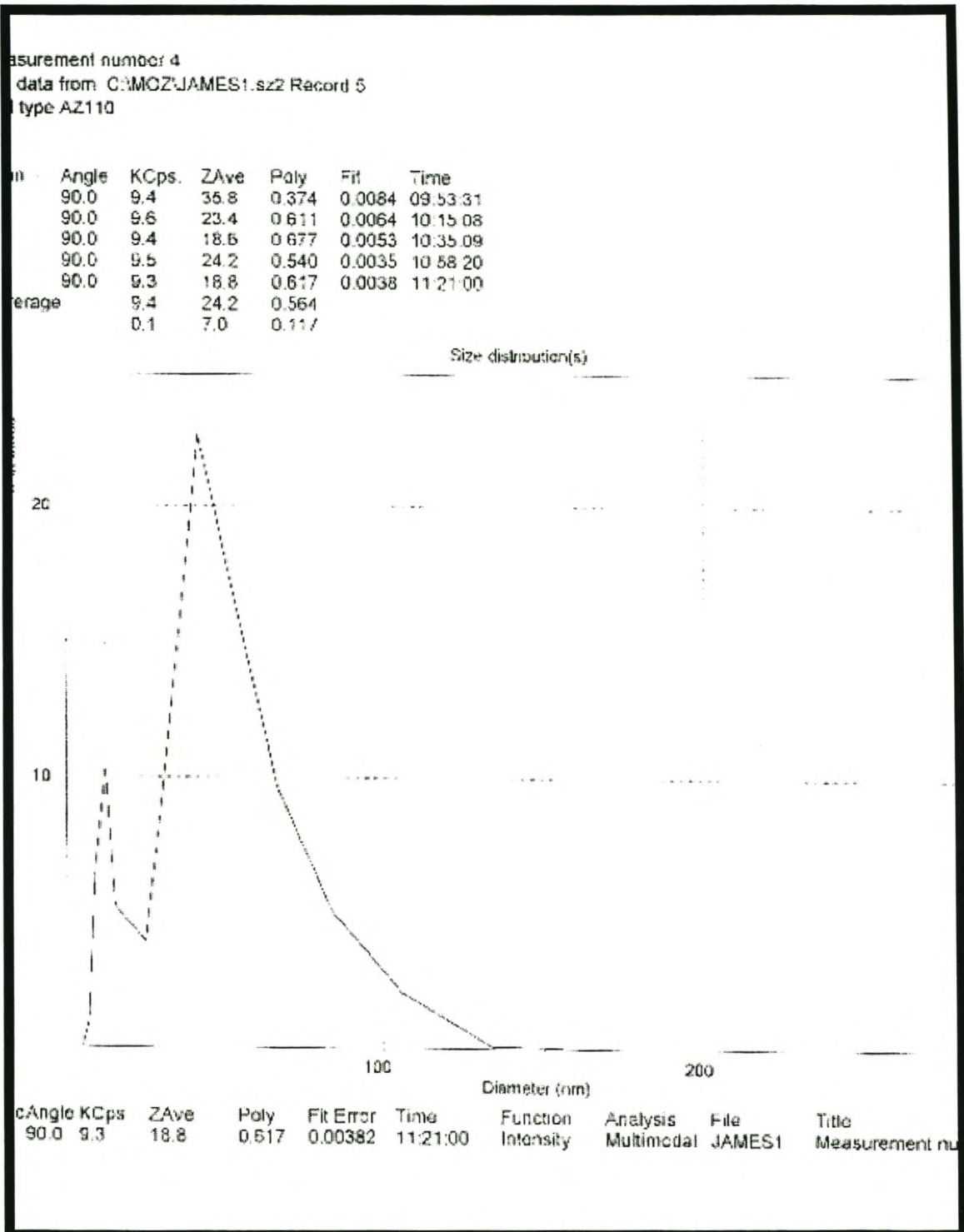
3 Data analysis

Measurement number 4
 File data from C:\JAMES\10KGYSM.sz2 Record 5
 Cell type AZ110

Size(nm)	Intensity	Volume	Number	Peak Analysis by intensity			
96.5	0.0	0.0	0.0	Peak	Area	Mean	Width
121.5	0.0	0.0	0.0	1	28.1	834.7	468.2
153.0	0.0	0.0	0.0	2	71.9	3740.2	2552.7
192.6	0.0	0.0	0.0	Peak Analysis by volume			
242.5	0.0	0.0	0.0	Peak	Area	Mean	Width
305.3	0.0	0.0	0.0	1	4.9	884.0	489.5
384.4	0.0	0.0	0.7	2	58.6	3483.4	1372.3
483.9	0.3	0.1	4.1	3	36.5	6553.2	2916.0
609.3	4.6	0.9	19.4	Peak Analysis by number			
767.1	11.4	2.0	33.4	Peak	Area	Mean	Width
966.9	10.9	1.6	21.4	1	63.3	792.5	447.5
1216.1	1.3	0.5	4.3	2	18.7	3304.5	1761.1
1531.1	1.3	0.3	0.6				
1927.8	1.3	0.9	0.8				
2427.2	9.2	10.6	3.4				
3055.9	19.7	23.1	6.2				
3847.6	21.5	19.1	3.9				
4844.3	12.1	11.8	1.0				
6099.3	4.6	13.3	0.5				
7679.3	1.9	11.7	0.3				
9668.7	0.0	4.2	0.1				
12173.4	0.0	0.0	0.0				
15327.0	0.0	0.0	0.0				
19297.6	0.0	0.0	0.0				

From polymerization of monomeric micelles see 2.2.1

1 As a function of intensity



2 Data analysis

Measurement number 4

File data from C:\MOZJAMES1.sz2 Record 5

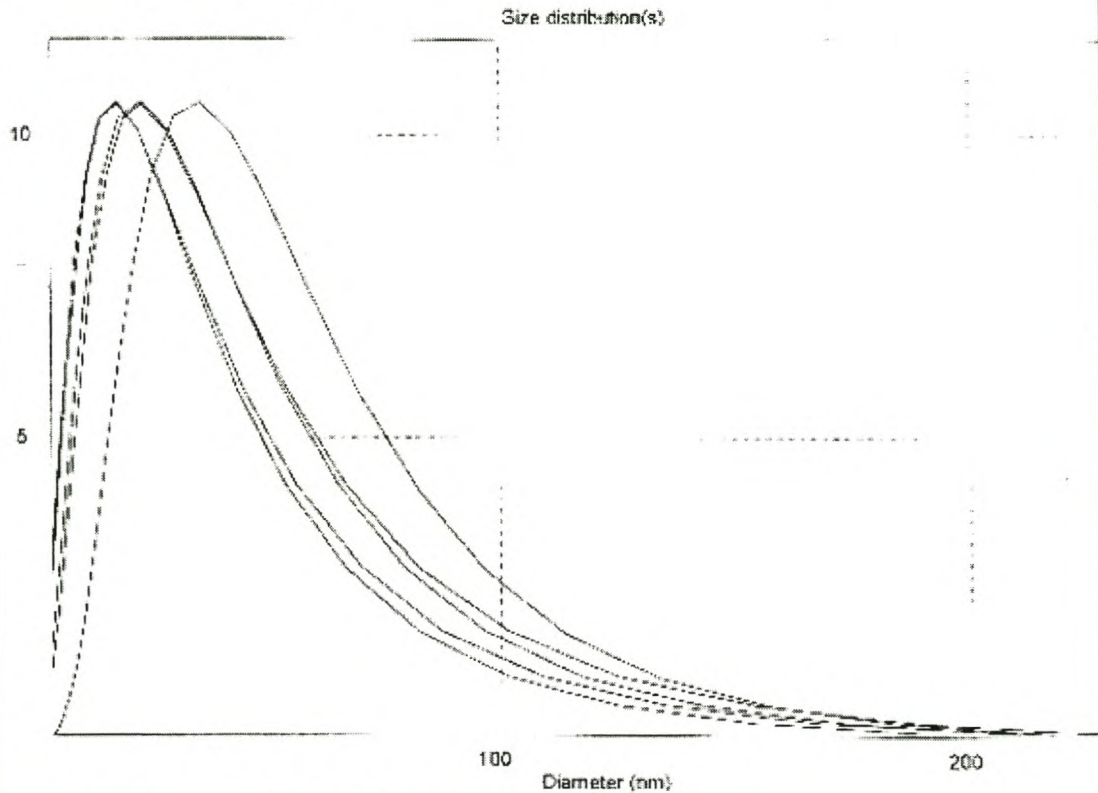
Cell type AZ110

Size(nm)	Intensity	Volume	Number	Peak Analysis by intensity			
1.3	0.0	0.0	0.0	Peak	Area	Mean	Width
1.7	0.0	0.0	0.0	1	30.4	15.9	7.5
2.1	0.0	0.0	0.0	2	69.6	50.4	30.8
2.7	0.0	0.0	0.0	Peak Analysis by volume			
3.3	0.0	0.0	0.0	Peak	Area	Mean	Width
4.2	0.0	0.0	0.0	1	100.0	14.2	7.8
5.3	0.0	0.0	0.0	Peak Analysis by number			
6.7	0.0	2.8	7.1	Peak	Area	Mean	Width
8.4	1.0	15.6	26.5	1	100.0	10.9	6.5
10.6	6.6	30.3	35.5				
13.3	10.3	27.2	22.5				
16.8	5.2	12.5	5.2				
21.1	4.6	4.1	0.9				
26.6	3.9	2.2	0.2				
33.5	12.3	2.1	0.1				
42.1	22.6	1.9	0.0				
53.0	16.7	1.0	0.0				
66.8	9.5	0.3	0.0				
84.1	5.0	0.1	0.0				
105.8	2.1	0.0	0.0				
133.3	0.1	0.0	0.0				
167.8	0.0	0.0	0.0				
211.3	0.0	0.0	0.0				
256.0	0.0	0.0	0.0				

8. Monomodal scans

Measurement number 4
 data from C:\MOZJAMES1.sz2 Record 5
 type AZ110

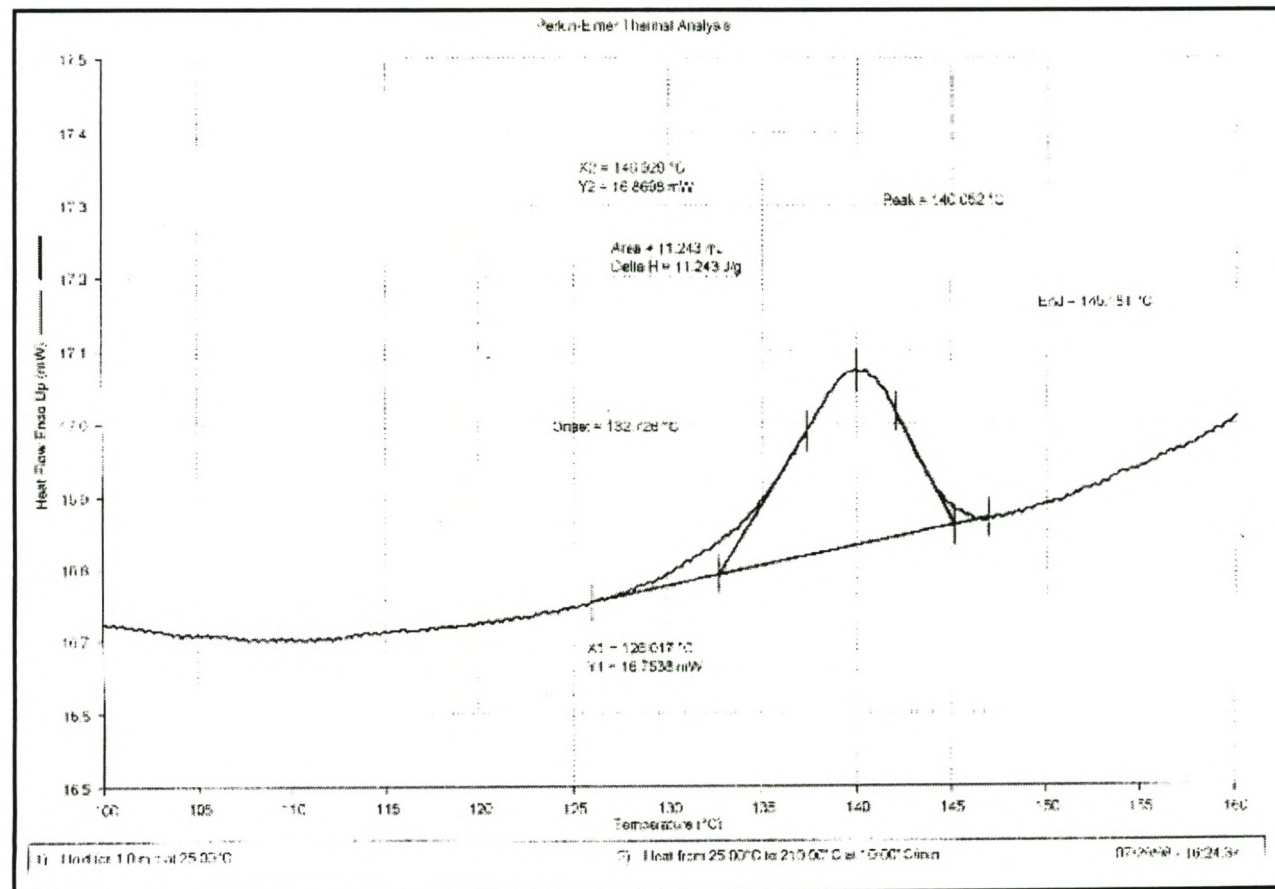
Angle	KCps.	ZAve	Poly	Fit	Time
90.0	9.4	35.8	0.374	0.0106	09:53:31
90.0	9.6	23.4	0.611	0.0043	10:15:08
90.0	9.4	18.6	0.677	0.0048	10:35:09
90.0	9.5	24.2	0.540	0.0048	10:58:20
90.0	9.3	18.8	0.617	0.0045	11:21:00
Average	9.4	24.2	0.564		
	0.1	7.0	0.117		



Angle	KCps	ZAve	Poly	Fit Error	Time	Function	Analysis	File	Title
90.0	9.4	35.8	0.374	0.01062	09:53:31	Intensity	Monomodal	JAMES1	Measurement nu
90.0	9.6	23.4	0.611	0.00428	10:15:08	Intensity	Monomodal	JAMES1	Measurement nu
90.0	9.4	18.6	0.677	0.00477	10:35:09	Intensity	Monomodal	JAMES1	Measurement nu
90.0	9.5	24.2	0.540	0.00477	10:58:20	Intensity	Monomodal	JAMES1	Measurement nu

Differential scanning calorimetry

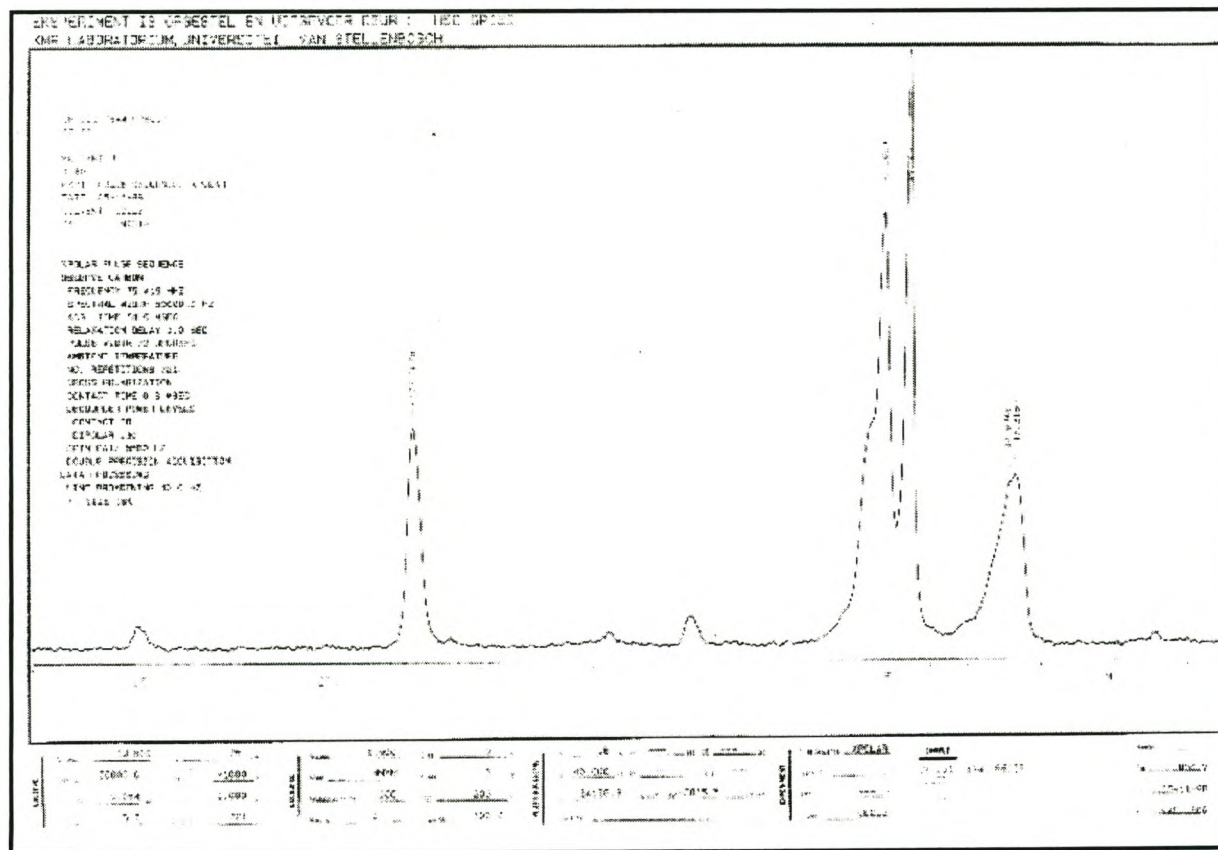
9. DSC scan of sodium 10-undecenoate



Nuclear magnetic resonance spectroscopy

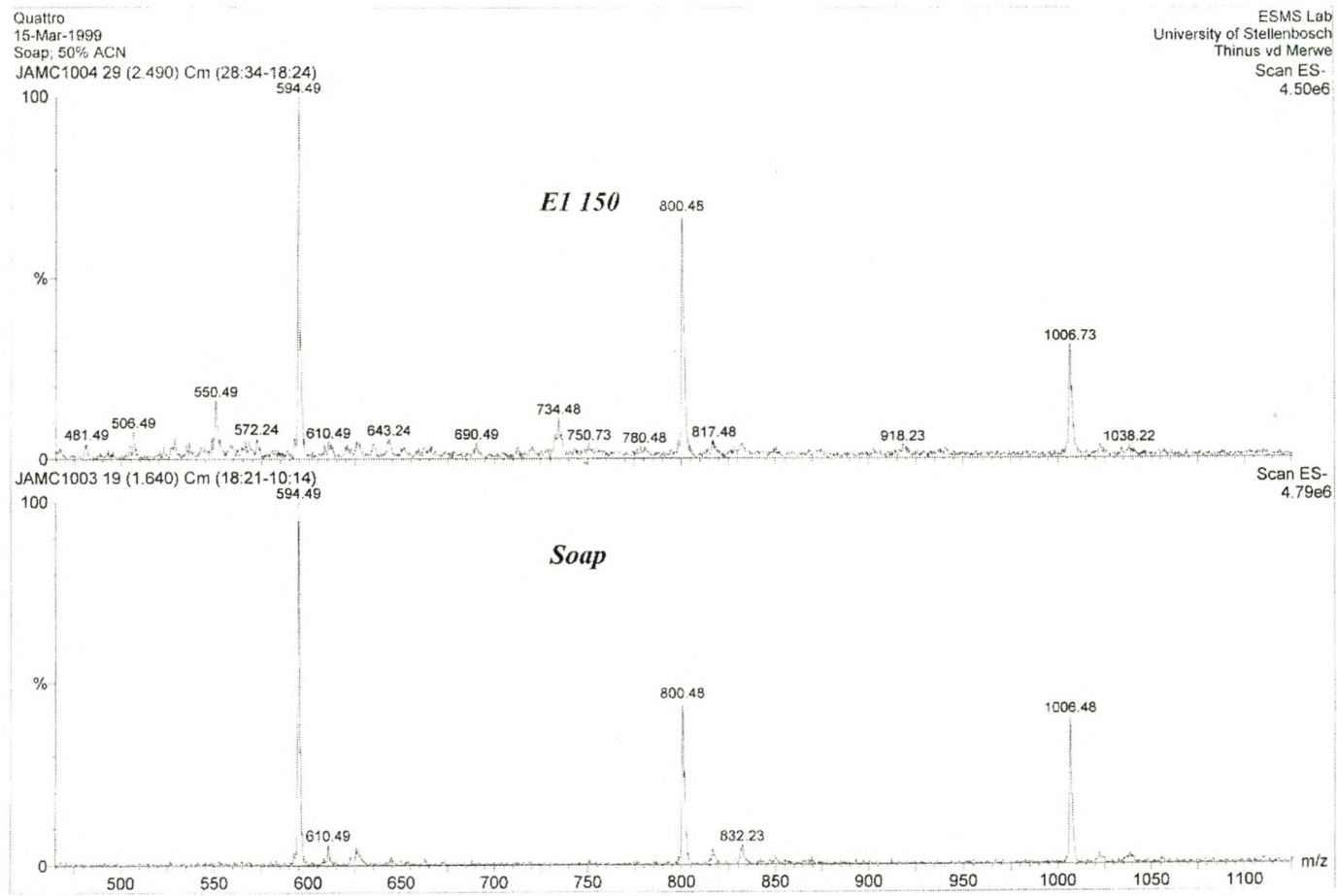
11. Solid state NMR scan of PMMA

Formed by a sample that precipitated PMMA under UV irradiation similar setup to batch X 12 see section 3.6.3

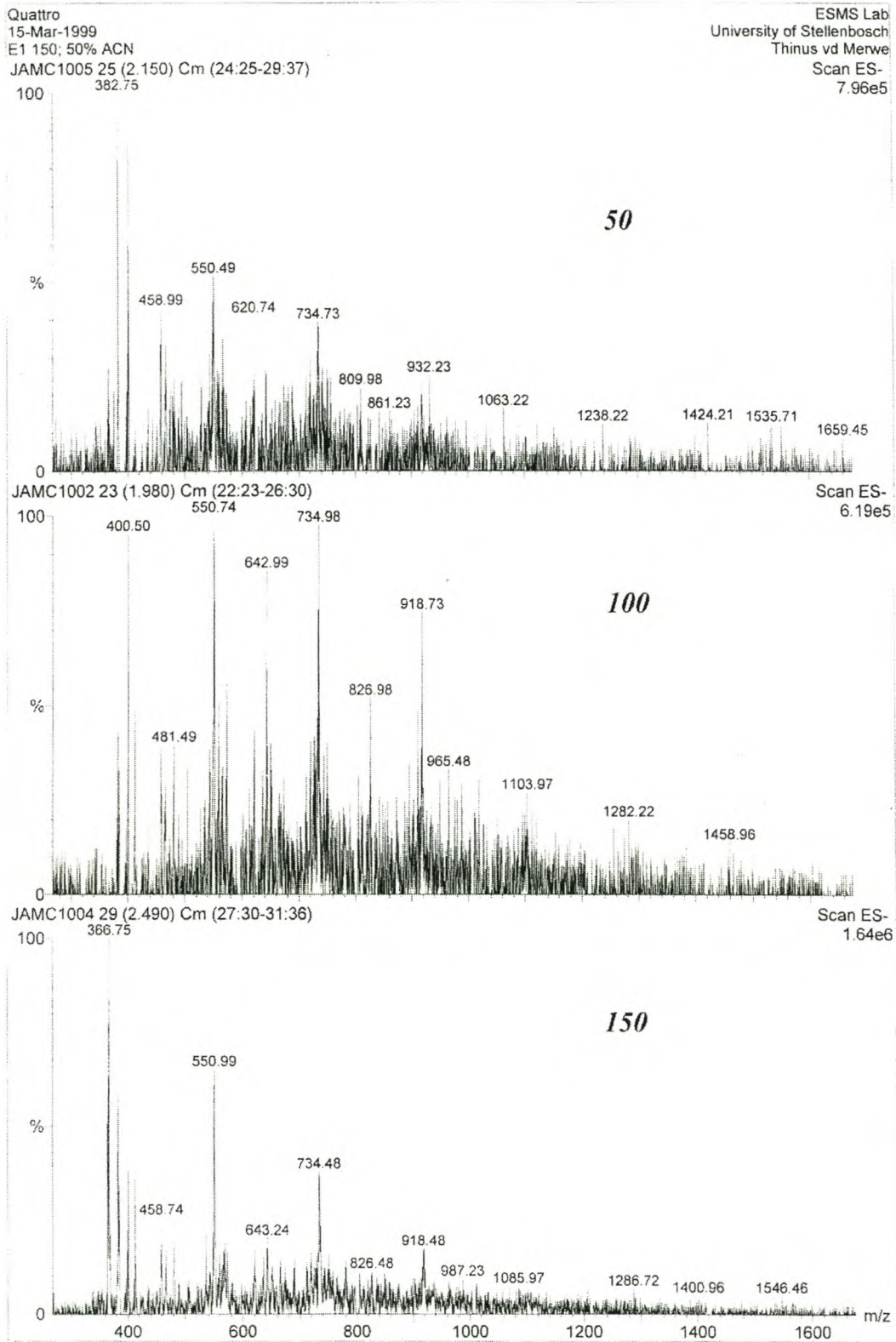


Electrospray mass spectrometry

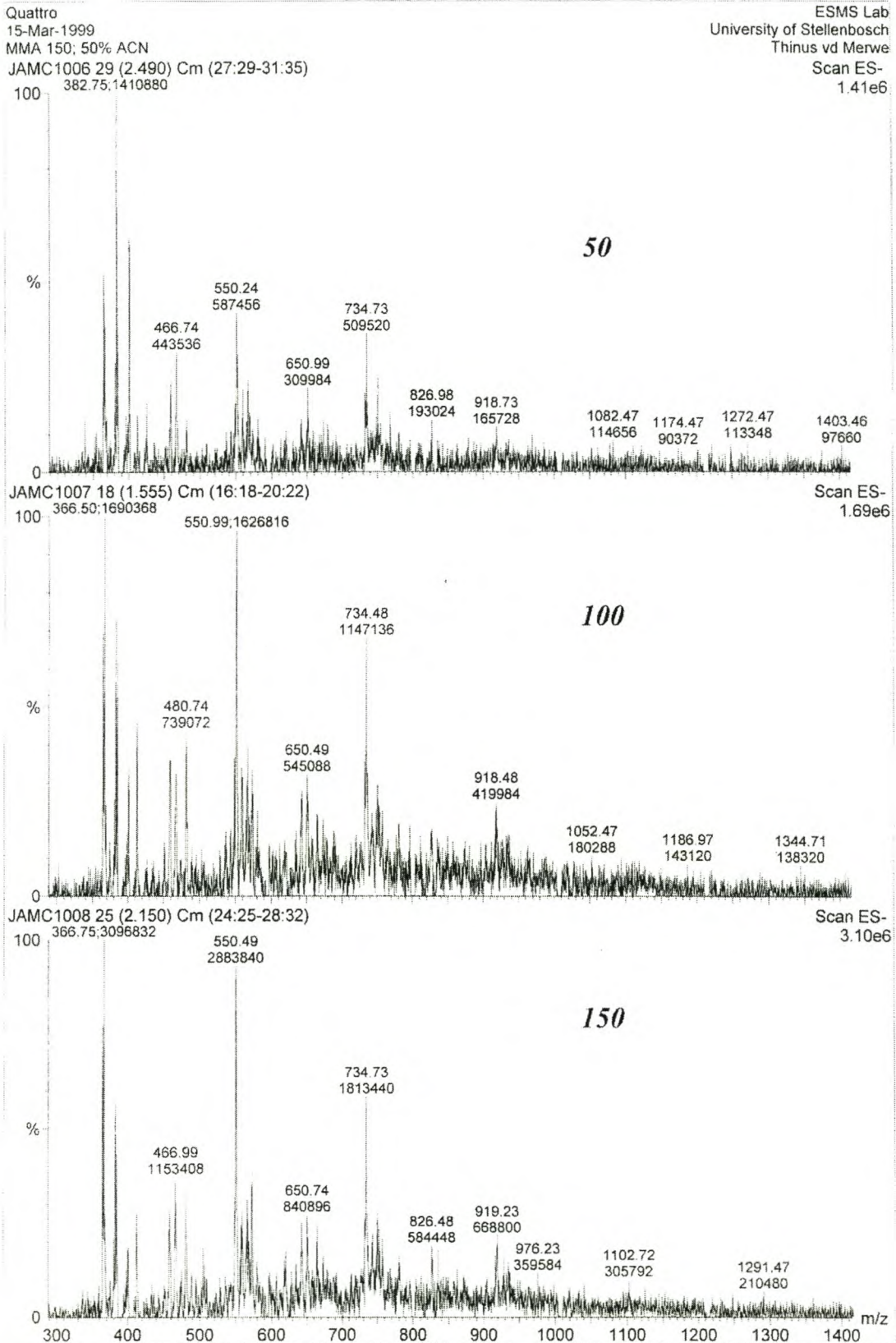
12. ESMS scan comparison of sample E1 at 150kGy and unirradiated surfactant (See chapter five)



13. ESMS scan comparison of sample E1 at 50,100,150 kGy

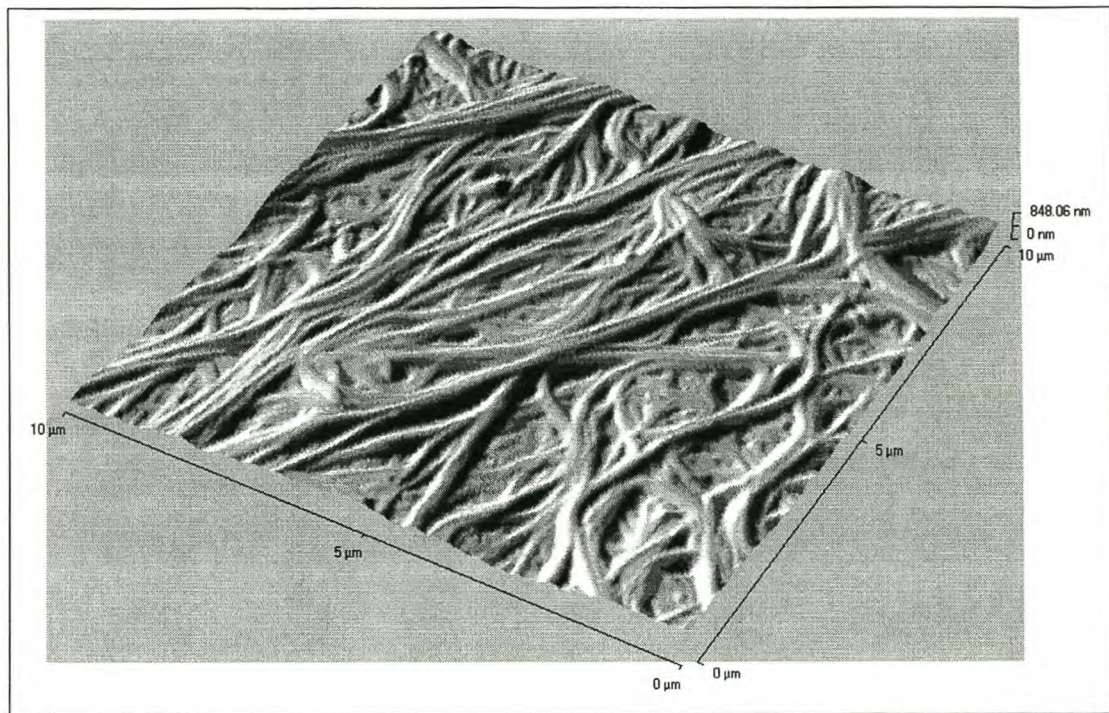


14. ESMS scan comparison of std MMA at 50,100,150 kGy

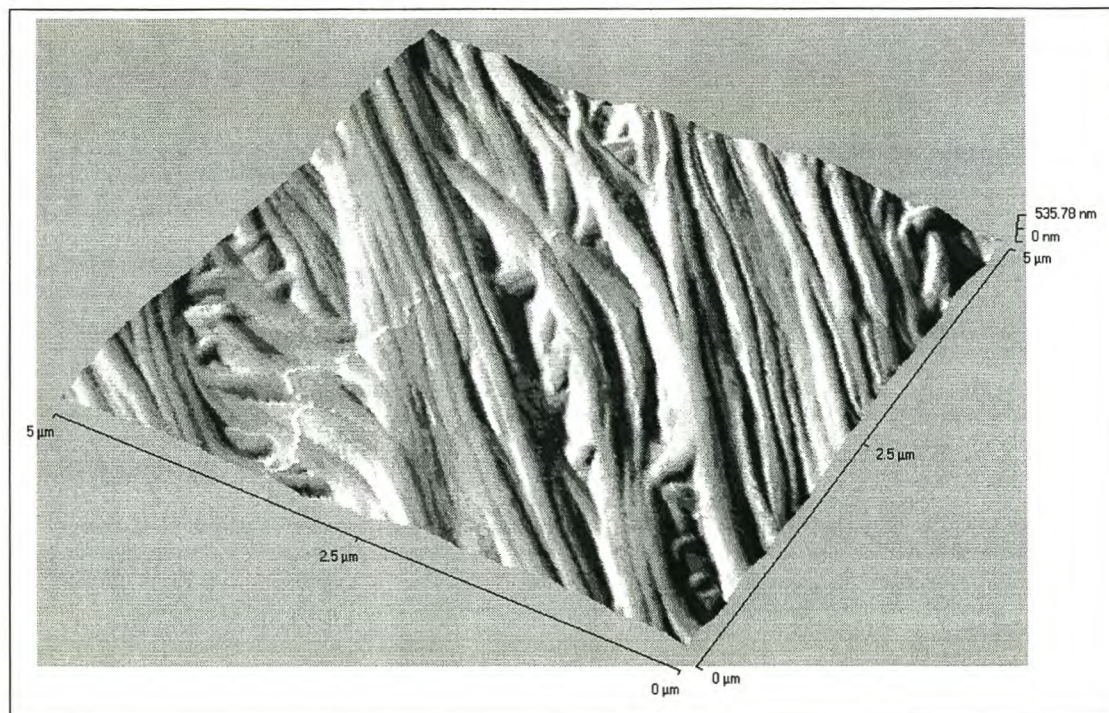


AFM images

15 AFM image of sample alpha 12 10 x 10 μm



16 AFM image of sample alpha 12 5 x 5 μm



D Sample Identification Tables

The following tables are the compositions of the samples that were prepared in chapter four:

<u>Table</u>	<u>Page Number</u>
Table 1 <u>SDS setup</u>	xxxix
This is the table for section 4.4.1	
Table 2 <u>Sodium 10-undecenoate setup experiment one</u>	xxl
This is the table for section 4.5.1	
Table 3 <u>Sodium 10-undecenoate setup experiment two</u>	xli
This is the table for section 4.5.2	
Table 4 <u>Sodium 10-undecenoate setup experiment three</u>	xlii
This is the table for section 4.5.3	
Table 5 <u>Sodium 10-undecenoate setup experiment four</u>	xliii
This is the table for section 4.5.4	
Table 6 <u>Sodium 10-undecenoate setup experiment five</u>	xliv
This is the table for section 4.5.5	
Table 7 <u>Sodium 10-undecenoate setup experiment six</u>	xlvi
This is the table for section 4.5.6	
Table 8 <u>Sodium 10-undecenoate setup Batch X</u>	xlvi
Table is the table for section 4.6.3	

Table 1 SDS setup (This is the table for section 4.4.1)

30%sol(SDS)	1/solconc	%	SDS(g)	ml	Sample no	in%	Styrene(g)	ml	Initiator(0.05%)	divinylbenzen	total(g)	ml(0.907)	DDIwater in ml	Total(ml)
d=0.907	3.333333	10%	1.5	5	1	1%	0.15	0.13605	0.000075	0.0075	0.157575	0.142921	9.857079475	15
	3.333333		1.5	5	2	2%	0.3	0.2721	0.00015	0.015	0.31515	0.285841	9.71415895	15
	3.333333		1.5	5	3	5%	0.75	0.68025	0.000375	0.0375	0.787875	0.714603	9.285397375	15
	3.333333		1.5	5	4	10%	1.5	1.3605	0.00075	0.075	1.57575	1.429205	8.57079475	15
	3.333333	15%	2.25	7.5	5	1%	0.15	0.13605	0.000075	0.0075	0.157575	0.142921	7.357079475	15
	3.333333		2.25	7.5	6	2%	0.3	0.2721	0.00015	0.015	0.31515	0.285841	7.21415895	15
	3.333333		2.25	7.5	7	5%	0.75	0.68025	0.000375	0.0375	0.787875	0.714603	6.785397375	15
	3.333333		2.25	7.5	8	10%	1.5	1.3605	0.00075	0.075	1.57575	1.429205	6.07079475	15
	3.333333	25%	3.75	12.5	9	1%	0.15	0.13605	0.000075	0.0075	0.157575	0.142921	2.357079475	15
	3.333333		3.75	12.5	10	2%	0.3	0.2721	0.00015	0.015	0.31515	0.285841	2.21415895	15
	3.333333		3.75	12.5	11	5%	0.75	0.68025	0.000375	0.0375	0.787875	0.714603	1.785397375	15
	3.333333		3.75	12.5	12	10%	1.5	1.3605	0.00075	0.075	1.57575	1.429205	1.07079475	15
				100			8.1		0.00405	0.405	8.50905	7.717708	72.28229165	

Table 2 Sodium 10-undecenoate setup experiment 1(This is the table for section 4.5.1)

60%stock	1/solconc	%	So Undec(g)	ml		sty%	Styrene(g)	ml				Samples
d(st)=0.907	1.666667	30%	4.5	7.5		5%	0.75	0.68025				1
	1.666667	35%	5.25	8.75		5%	0.75	0.68025				2
	1.666667	40%	6	10		5%	0.75	0.68025				3
	1.666667	45%	6.75	11.25		5%	0.75	0.68025				4
	1.666667	50%	7.5	12.5		5%	0.75	0.68025				5
			30	50	150		3.75	3.40125	10.20375			
Initiator(0.25%)	ml		divinylbenzene 5%	ml	total(g)	ml(0.907)		DDIwater in ml		Total(ml)		
0.001875			0.0375		0.789375	0.716		6.7840		15		1
0.001875			0.0375		0.789375	0.716		5.5340		15		2
0.001875			0.0375		0.789375	0.716		4.2840		15		3
0.001875			0.0375		0.789375	0.716		3.0340		15		4
0.001875			0.0375		0.789375	0.716		1.7840		15		5
0.009375			0.1875		3.946875	3.580	10.73944688	21.4202	64.26055			

40	2	0.1
styrene	divinylbenzene	initiator

Table 3 Sodium 10-undecenoate setup experiment 2(This is the table for section 4.5.2)

40	4	0.2
styrene	divinylben	initiator

		blank 10	blank 20	blank 30	blank 40	1%Monom	2% Mono	5%Monom	10% Mono	10	20	30	40	
amount	standard	1	2	3	4	5	6	7	8	9	10	11	12	total
50%stock(1:2)	9	3	6	9	12	9	9	9	9.0000	3	6	9	12	96
styrene(g)	5%	0	0	0	0	0.15	0.3	0.75	1.5000	0.75	0.75	0.75	0.75	5.7
styrene(ml)		0	0	0	0	0.165375	0.33075	0.826875	1.65375	0.826875	0.826875	0.826875	0.826875	6.28425
initiator(g)	0.5%of s	0	0	0	0	0.00075	0.0015	0.00375	0.0075	0.00375	0.00375	0.00375	0.00375	0.0285
initiator														
divinyl benzene(g)	10%of S	0	0	0	0	0.015	0.03	0.075	0.15	0.075	0.075	0.075	0.075	0.57
divinyl benzene(ml)														
total(g)		0	0	0	0	0.16575	0.3315	0.82875	1.6575	0.82875	0.82875	0.82875	0.82875	6.2985
total(ml)d=0.907		0	0	0	0	0.182739	0.365479	0.913697	1.827394	0.913697	0.913697	0.913697	0.913697	6.944096
DDI water(ml)	6	12	9	6	3	5.817261	5.634521	5.086303	4.172606	11.0863	8.086303	5.086303	2.086303	77.0559
total vol	15	15	15	15	15	15	15	15	15	15	15	15	15	180

Table 4 Sodium 10-undecenoate/SDS experiment 3 (This is the table for section 4.5.3)

40	2	0.2
styrene	divinylben	initiator

amount	standard	1	2	3	4	5	6	7	8	9	10	11	12	total
total soap		25	30	35	40	25	25	40	40	40	40	40	45	
sds		25	25	25	25	20	15	20	15	10	5	0	0	
un		0	5	10	15	5	10	20	25	30	35	40	45	
50%stock(1:2) und	0%	0	1.5	3	4.5	1.5	3	6	7.5	9	10.5	12	13.5	72
40%stock(2:5) SDS	25%	9.375	9.375	9.375	9.375	7.5	5.625	7.5	5.625	3.75	1.875	0	0	69.375
styrene(g)	5%	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	9
styrene(ml)		0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	9.9225
initiator(g)	0.5%of s	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.045
initiator														
divinyl benzene(g)	5% of S	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.45
divinyl benzene(ml)														
total(g)		0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	9.495
total(ml)d=0.907		0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	10.46824
DDI water(ml)	15	4.752647	3.252647	1.752647	0.252647	5.127647	5.502647	0.627647	1.002647	1.377647	1.752647	2.127647	0.627647	28.15676
total vol	15	15	15	15	15	15	15	15	15	15	15	15	15	180

Table 5 Sodium 10-undecenoate Setup Experiment 4(This is the table for section 4.5.4)

40	2	0.2
styrene	divinylben	initiator

amount	standard	1	2	3	4	5	6	7	8	9	10	11	12	total
total soap		25	30	35	40	25	25	40	40	40	40	40	45	5
sds		25	25	25	25	20	15	20	15	10	5	0	0	1.666s
un		0	5	10	15	5	10	20	25	30	35	40	45	
60%stock(1:2) und	0%	0	1.25	2.5	3.75	1.25	2.5	5	6.25	7.5	8.75	10	11.25	60
45%stock(2:5) SDS	25%	8.33	8.33	8.33	8.33	6.664	4.998	6.664	4.998	3.332	1.666	0	0	61.642
styrene(g)	5%	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	9
styrene(ml)		0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	9.9225
initiator(g)	0.5%of s	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.045
initiator														
divinyl benzene(g)	5% of S	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.45
divinyl benzene(ml)														
total(g)		0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	9.495
total(ml)d=0.907		0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	10.46824
DDI water(ml)	15	5.797647	4.547647	3.297647	2.047647	6.213647	6.629647	2.463647	2.879647	3.295647	3.711647	4.127647	2.877647	47.88976
total vol	15	15	15	15	15	15	15	15	15	15	15	15	15	180

amount	standard	13	14	15	16	17	18	19	20	21	22	23	24	total
total soap		25	20	15	?	20	25	30	35	40	45	50	55	5
sds		25	20	15	?	0	0	0	0	0	0	0	0	0
un		0	0	0	?	20	25	30	35	40	45	50	55	1.25u
60%stock(1:2) und	0%	0	0	0	15	5	6.25	7.5	8.75	10	11.25	12.5	13.75	90
45%stock(2:5) SDS	25%	8.33	6.664	4.998	0	0	0	0	0	0	0	0	0	19.992
styrene(g)	5%	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	9
styrene(ml)		0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	9.9225
initiator(g)	0.5%of s	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.045
initiator														
divinyl benzene(g)	5% of S	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.45
divinyl benzene(ml)														
total(g)		0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	9.495
total(ml)d=0.907		0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	10.46824
DDI water(ml)	15	5.797647	7.463647	9.129647	0	9.127647	7.877647	6.627647	5.377647	4.127647	2.877647	1.627647	0.377647	60.41212
total vol	15	15	15	15	15.87235	15	15	15	15	15	15	15	15	180.8724

Table 6 Sodium 10-undecenoate Setup Experiment 5 (This is the table for section 4.5.5)

40	2	0.2
styrene	divinylben	initiator

amount	standard	1	2	3	4	5	6	7	8	9	10	11	12	total
total soap		30	35	40	45	50	55	60	35	40	45	50	55	5
														1.666s
un		30	35	40	45	20	25	30	35	40	45	50	55	
66%undec sol		6.75	7.875	9	10.125	4.5	5.625	6.75	7.875	9	10.125	11.25	12.375	101.25
		5%							10%					0.15
styrene(g)		0.75	0.75	0.75	0.75	0.75	0.75	0.75	1.5	1.5	1.5	1.5	1.5	12.75
styrene(ml)		0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	0.826875	1.65375	1.65375	1.65375	1.65375	1.65375	14.05688
initiator(g)	0.5%of s	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.00375	0.0075	0.0075	0.0075	0.0075	0.0075	0.06375
initiator														
divinyl benzene(g)	5% of S	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.0375	0.075	0.075	0.075	0.075	0.075	0.6375
divinyl benzene(ml)														
total(g)		0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	0.79125	1.5825	1.5825	1.5825	1.5825	1.5825	13.45125
total(ml)d=0.907		0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	0.872353	1.744706	1.744706	1.744706	1.744706	1.744706	14.83
DDI water(ml)	15	7.327647	6.252647	5.127647	4.002647	9.627647	8.502647	7.377647	5.280294	4.255294	3.130294	2.005294	0.880294	63.77
total vol	15	15	15	15	15	15	15	15	15	15	15	15	15	180

amount	standard	13	14	15	16	17	18	19	20	21	22	23	24	total
total soap		60	65	40	45	50	55	60	65	70	50	50	50	5
un		60	65	40	45	50	55	60	65	70	50	50	50	
66%undec sol	0%	13.5	14.625	9	10.125	11.25	12.375	13.5	14.625	15.75	11.25	11.25	11.25	148.5
		10%		0%					10%		15%	20%	25%	0.8
styrene(g)		1.5	1.5	0	0	0	0	0	0	0	2.25	3	3.75	12
styrene(ml)		1.65375	1.65375	0	0	0	0	0	0	0	2.480625	3.3075	4.134375	13.23
initiator(g)	0.5%of s	0.0075	0.0075	0	0	0	0	0	0	0	0.01125	0.015	0.01875	0.06
initiator														
divinyl benzene(g)	5% of S	0.075	0.075	0	0	0	0	0	0	0	0.1125	0.15	0.1875	0.6
divinyl benzene(ml)														
total(g)		1.5825	1.5825	0	0	0	0	0	0	0	2.37375	3.165	3.95625	12.66
total(ml)d=0.907		1.744706	1.744706	0	0	0	0	0	0	0	2.617059	3.489413	4.361766	13.95765
DDI water(ml)	15	-0.344706	-1.369706	6	4.875	3.75	2.625	1.5	0.275	-0.75	0.982941	0.060588	-0.861766	16.74235
total vol	15	15	15	15	15	15	15	15	15	15	15	15	15	180

Table 7 Sodium 10-undecenoate Setup Experiment 6(This is the table for section 4.5.6)

40	2	0.2
styrene	divinylben	initiator

amount	standard	1	2	3	4	5	6	7	8	9	10	11	12	total
total soap		30	35	40	45	50	55	35	40	45	50	55	25	5
														1.666s
un		30	35	40	45	50	55	35	40	45	50	55	25	
66%undec sol		3.375	3.9375	4.5	5.0625	5.625	6.1875	3.9375	4.5	5.0625	5.625	6.1875	2.8125	56.8125
		5%						10%					2.5	2.65
styrene(g)		0.375	0.375	0.375	0.375	0.375	0.375	0.75	0.75	0.75	0.75	0.75	0.1875	6.1875
styrene(ml)		0.413438	0.413438	0.413438	0.413438	0.413438	0.413438	0.826875	0.826875	0.826875	0.826875	0.826875	0.206719	6.821719
initiator(g)	0.5%of s	0.001875	0.001875	0.001875	0.001875	0.001875	0.001875	0.00375	0.00375	0.00375	0.00375	0.00375	0.000938	0.030938
initiator														
divinyl benzene(g)	5% of S	0.01875	0.01875	0.01875	0.01875	0.01875	0.01875	0.0375	0.0375	0.0375	0.0375	0.0375	0.009375	0.309375
divinyl benzene(ml)														
total(g)		0.395625	0.395625	0.395625	0.395625	0.395625	0.395625	0.79125	0.79125	0.79125	0.79125	0.79125	0.197813	6.527813
total(ml)d=0.907		0.436177	0.436177	0.436177	0.436177	0.436177	0.436177	0.872353	0.872353	0.872353	0.872353	0.872353	0.218088	7.196913
DDI water(ml)	15	3.638823	3.126323	2.563823	2.001323	1.438823	0.876323	2.590147	2.127647	1.565147	1.002647	0.440147	1.969412	23.34059
total vol	15	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	90

amount	standard	13	14	15	16	17	18	19	20	21	22	23	24	total
total soap		30	35	40	45	50	55	30	35	40	45	50	55	5
un		30	35	40	45	50	55	30	35	40	45	50	55	
66%undec sol	0%	3.375	3.9375	4.5	5.0625	5.625	6.1875	3.375	3.9375	4.5	5.0625	5.625	6.1875	57.375
								1%						
styrene(g)		0.1875	0.1875	0.1875	0.1875	0.1875	0.1875	0.09375	0.09375	0.09375	0.09375	0.09375	0.09375	1.6875
styrene(ml)		0.206719	0.206719	0.206719	0.206719	0.206719	0.206719	0.103359	0.103359	0.103359	0.103359	0.103359	0.103359	1.860469
initiator(g)	0.5%of s	0.000938	0.000938	0.000938	0.000938	0.000938	0.000938	0.000469	0.000469	0.000469	0.000469	0.000469	0.000469	0.008438
initiator														
divinyl benzene(g)	5% of S	0.009375	0.009375	0.009375	0.009375	0.009375	0.009375	0.004688	0.004688	0.004688	0.004688	0.004688	0.004688	0.084375
divinyl benzene(ml)														
total(g)		0.197813	0.197813	0.197813	0.197813	0.197813	0.197813	0.098906	0.098906	0.098906	0.098906	0.098906	0.098906	1.780313
total(ml)d=0.907		0.218088	0.218088	0.218088	0.218088	0.218088	0.218088	0.109044	0.109044	0.109044	0.109044	0.109044	0.109044	1.962795
DDI water(ml)	15	3.906912	3.344412	2.781912	2.219412	1.656912	1.094412	4.003456	3.453456	2.890956	2.328456	1.765956	1.203456	30.64971
total vol	15	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	90

Table 8 Sodium 10-undecenoate setup Batch X (this is the table for section 4.6.3)

amount	standard	1	2	3	4	5	6	7	8	9	10	11	12	total
total soap		30	35	40	45	50	55	35	40	45	50	55	25	5
un		30	35	40	45	50	55	35	40	45	50	55	25	1.666s
66%undec sol		3.375	3.9375	4.5	5.0625	5.625	6.1875	3.9375	4.5	5.0625	5.625	6.1875	2.8125	56.8125
		5%						10%					2.5	2.65
styrene(g)		0.375	0.375	0.375	0.375	0.375	0.375	0.75	0.75	0.75	0.75	0.75	0.1875	6.1875
styrene(ml)		0.413438	0.413438	0.413438	0.413438	0.413438	0.413438	0.826875	0.826875	0.826875	0.826875	0.826875	0.206719	6.821719
initiator(g)	0.5%of s	0.001875	0.001875	0.001875	0.001875	0.001875	0.001875	0.00375	0.00375	0.00375	0.00375	0.00375	0.000938	0.030938
initiator														
divinyl benzene(g)	5% of S	0.01875	0.01875	0.01875	0.01875	0.01875	0.01875	0.0375	0.0375	0.0375	0.0375	0.0375	0.009375	0.309375
divinyl benzene(ml)														
total(g)		0.395625	0.395625	0.395625	0.395625	0.395625	0.395625	0.79125	0.79125	0.79125	0.79125	0.79125	0.197813	6.527813
total(ml)d=0.907		0.436177	0.436177	0.436177	0.436177	0.436177	0.436177	0.872353	0.872353	0.872353	0.872353	0.872353	0.218088	7.196913
DDI water(ml)	15	3.638823	3.126323	2.563823	2.001323	1.438823	0.876323	2.590147	2.127647	1.565147	1.002647	0.440147	1.969412	23.34059
total vol	15	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	90

amount	standard	13	14	15	16	17	18	19	20	21	22	23	24	total
total soap		30	35	40	45	50	55	30	35	40	45	50	55	5
un		30	35	40	45	50	55	30	35	40	45	50	55	
66%undec sol	0%	3.375	3.9375	4.5	5.0625	5.625	6.1875	3.375	3.9375	4.5	5.0625	5.625	6.1875	57.375
								1%						
styrene(g)		0.1875	0.1875	0.1875	0.1875	0.1875	0.1875	0.09375	0.09375	0.09375	0.09375	0.09375	0.09375	1.6875
styrene(ml)		0.206719	0.206719	0.206719	0.206719	0.206719	0.206719	0.103359	0.103359	0.103359	0.103359	0.103359	0.103359	1.860469
initiator(g)	0.5%of s	0.000938	0.000938	0.000938	0.000938	0.000938	0.000938	0.000469	0.000469	0.000469	0.000469	0.000469	0.000469	0.008438
initiator														
divinyl benzene(g)	5% of S	0.009375	0.009375	0.009375	0.009375	0.009375	0.009375	0.004688	0.004688	0.004688	0.004688	0.004688	0.004688	0.084375
divinyl benzene(ml)														
total(g)		0.197813	0.197813	0.197813	0.197813	0.197813	0.197813	0.098906	0.098906	0.098906	0.098906	0.098906	0.098906	1.780313
total(ml)d=0.907		0.218088	0.218088	0.218088	0.218088	0.218088	0.218088	0.109044	0.109044	0.109044	0.109044	0.109044	0.109044	1.962795
DDI water(ml)	15	3.906912	3.344412	2.781912	2.219412	1.656912	1.094412	4.003456	3.453456	2.890956	2.328456	1.765956	1.203456	30.64971
total vol	15	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	90

amount	standard	25	26	27	28	229	30	31	32	33	34	35	36	total
total soap		30	35	40	45	50	55	60	65	66.666	30	35	30	
un		30	35	40	45	50	55	60	65	66.666	30	35	30	
66%undec sol	0%	3.375	3.9375	4.5	5.0625	5.625	6.1875	6.75	7.3125	7.499925	3.375	3.9375	3.375	60.93743
		0%												0
styrene(g)		0	0	0	0	0	0	0	0	0	1.125	1.125	1.5	3.75
styrene(ml)		0	0	0	0	0	0	0	0	0	1.240313	1.240313	1.65375	4.134375
initiator(g)	0.5%of s	0	0	0	0	0	0	0	0	0	0.005625	0.005625	0.0075	0.01875
initiator														
divinyl benzene(g)	5% of S	0	0	0	0	0	0	0	0	0	0.05625	0.05625	0.075	0.1875
divinyl benzene(ml)														
total(g)		0	0	0	0	0	0	0	0	0	1.186875	1.186875	1.5825	3.95625
total(ml)d=0.907		0	0	0	0	0	0	0	0	0	1.30853	1.30853	1.744706	4.361766
DDI water(ml)	15	4.125	3.5625	3	2.4375	1.875	1.3125	0.75	0.1875	7.5E-05	2.81647	2.25397	2.380294	24.70081
total vol	15	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	90