Synthesis of acrylate-based polymeric and polymerisable surfactants and their application in the emulsion polymerisation of styrene

by

Lilian M Tichagwa

Dissertation presented for the degree of Doctor of Science

(Polymer Science)

at the

University of Stellenbosch

Promoter: Prof Ronald D Sanderson

Co-promoter: Prof Harald Pasch   **April 2006**

DECLARATION

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

Signature:_____   Date:_____

ABSTRACT

The study described in this dissertation examines the synthesis of mainly acrylate-based surfactants and their subsequent use as emulsifiers/stabilisers in the emulsion polymerisation of styrene. Some acrylamide-based surfactants were also studied, for comparison purposes only. Two major types of surfactants, polymerisable (surfactant monomers or surfmers) and polymeric, were synthesised, characterised and used in emulsion polymerisation reactions. The prepared polymerisable surfactants, 12-acryloyloxydodecanoic acid (12-ADA) and 11-acrylamidoundecanoic acid (11-AAUA), and their sodium salts, had reactive acryloyl functionalities.

As there was a need to control the size of the polymeric surfactants for subsequent use in emulsion polymerisation, the RAFT transfer agents 4-cyano-4-(thiobenzoylthio) pentanoic acid and 4-azobisiso-(thiobenzoylthio) butyronitrile were synthesised and used to prepare the respective polymeric surfactants. The novel RAFT polymerisations of 12-ADA and 11-AAUA produced oligomeric surfactants which could be used in the emulsion polymerisation of styrene.

The effectiveness of all these surfactants as stabilisers or emulsifiers in emulsion polymerisation was compared with that exhibited by the conventional surfactant sodium dodecyl sulphate (SDS).

Polystyrene latices produced by emulsion polymerisation were first purified and then evaluated for stability. The stability tests included subjecting the latices to destabilising conditions such as freeze-thaw cycles, addition of electrolyte, and long-term storage. The surfmers and polymeric surfactants that were synthesised and studied were found to be efficient stabilisers for latices. Some of the surfactants, particularly 12-ADA (both the acid and Na salt forms) and 11-AAUA, were found to produce latices which were remarkably more stable than those stabilised with SDS. It was also found that regardless of whether the surfactants were used in their acid or salt forms they could stabilise the latex. Furthermore, larger latex particles were produced with the polymeric surfactants and the surfmers than with SDS.

OPSOMMING

In hierdie verhandeling word die sintese van hoofsaaklik akrilaat-gebasseerde sepe (Eng. surfactants) en die gebruik daarvan as emulgeerders/stabiliseerders in die emulsiepolimerisasie van stireen ondersoek. Verskeie akrilamied-gebasseerde sepe is ook bestudeer, alleenlik om vergelykings te tref. Twee hooftipes sepe, naamlik polimeriseerbaar sepe (monomere of 'surfmers') en polimeriese sepe is gesintetiseer, gekarakteriseer en in emulsiepolimerisasiereaksies gebruik. Die bereide polimeriseerbare sepe, 12-akrielokisidodekanoësuur (12-ADA) en 11-akrielamidoundekanoësuur (11-AAUA), en die natriumsoute daarvan, het reaktiewe akroliel-funksionaliteit besit.

Aangesien die nodig geag is om die grootte van die polimerieeerbare sepe te kontrolleer, vir latere gebruik daarvan in emulsiepolimerisasiereaksies, is twee RAFT-oordragsverbindings: 4-siano-4-(tiobensoïeltio)pentanoësuur en 4-asobisïso-(tiobensoïeltio)butironitriel gesintetiseer en gebruik om die onderskeie polimerieseerbare sepe te berei. Die nuwe RAFT polimerisasie-reaksies van 12-ADA en 11-AAUA het oligomeriese sepe gelewer, wat later in the emulsiepolimerisasie van strireen gebruik is.

Die doeltreffendheid van al hierdie sepe as stabiliseerders of emulgeerders in emulsiepolimerisasie is vergelyk met die doeltreffendheid wat met die konvensionele seep natriumdodekielsulfaat (SDS) verkry is.

Die polistireen latekse wat d.m.v emulsiepolimerisasie berei is is eers gesuiwer en daarna vir hulle stabiliteit geëvalueer deur blootstelling aan destabiliseringskondisies, b.v. vries-ontdooi siklusse, byvoeging van elektroliet, en lang-termyn opberging. Daar is bepaal dat die sepe en polimeriseerbare sepe wat berei is effektiewe stabiliseerders vir die latekse is. Van die sepe het latekse gelewer wat merkbaar meer stabiel was as dié wat met SDS gestabiliseer is. Daar is ook bepaal dat die sepe in beide hul suur- en sout-vorms effektief is as lateks-stabiliseerders. Verder is groter lateks partikels met hierdie sepe en polimeriese sepe berei, as met SDS.

This thesis is dedicated to you Cornelius

Acknowledgements

Table of Contents

List of Figures

List of Tables

List of Schemes

List of Abbreviations

AA	acrylic acid
11-AAUA	11-acrylamidododecanoic acid
11-AAUA-Na	sodium salt of 11-AAUA
12-ADA	12-acryloyloxydodecanoic acid
12-ADA-Na	sodium salt of 12-ADA
(ADA/AA-1:1)	1:1 copolymer based on 12-ADA and AA monomers
ACP	4,4-azobiscyanopentanoic acid
ACP-RAFT	RAFT reagent based on 4,4-azobiscyanopentanoic acid
AFM	atomic force microscopy
AIBN	2,2'-azobis(isobutyronitrile)
AIBN-RAFT	RAFT reagent based on 2,2-azobis(isobutyronitrile)
ATRP	atom transfer radical polymerisation
BTBS	bis(thiocarbonyl) disulphide
CE	capillary electrophoresis
cmc	critical micelle concentration
copol (ADA/AA)	copolymer based on 12-ADA and AA monomers
CSTR	continuous stirred tank reactors
d	spacing between points of scatter
DLS	dynamic light scattering
DMA	2-dimethyl aminoethyl methacrylate
DSC	differential scanning calorimetry
EA	elemental analysis
ESMS	elecrospray mass spectroscopy
f	efficiency factor
FTIR	Fourier-transform infrared spectroscopy
GPC	gel permeation chromatography
HLB	hydrophilic - lipophilic balance
^{1}H-NMR	proton nuclear magnetic resonance
HUFT	Hansen-Ugelstad-Fitch-Tsai
IA	itaconic acid
K	distribution coefficient

k_d	dissociation rate constant of the initiator
MAA	methyl acrylic acid
MALDI-TOF	matrix-assisted laser desorption/ionisation with time of flight
MEKC	micellar electrokinetic capillary chromatography
M_m	molecular weight of monomer
MMA	methyl methacrylate
Mn	number-average molecular weight
M_{RAFT}	molecular weight of RAFT agent
Mw	weight-average molecular weight
MWD	molecular weight distribution
N	integral number of wavelengths
NMR	nuclear magnetic resonance spectroscopy
PDI	polydispersity index
PEGMA	poly(ethylene glycol) methacrylate
pH	degree of acidity or alkalinity
PMAA	poly(methyl acrylic acid)
PMMA	poly(methyl methacrylate)
Poly (AAUA)	polymer based on 11-AAUA monomer
Poly (ADA)	polymer based on 12-ADA monomer
Poly (ADA-RAFT)	RAFT polymer based on 12-ADA monomer
PS	polystyrene
RAFT	reversible addition-fragmentation chain transfer
rpm	revolutions per minute
SDS	sodium dodecyl sulphate
SEM	scanning electron microscopy
t	time of reaction
TEM	transmission electron microscopy
T_g	glass transition temperature
TGA	thermogravimetric analysis
TLC	thin-layer chromatography
V_A	van der Waals potential energy
VA	vinyl acetate
VE	volume of solution eluted

V_i	volume of liquid within pores
V_O	interstitial volume
V_R	repulsive potential energy
V_t	total potential
WAXS	wide angle X-ray scattering
Z_{ave}	average diameter size measured by DLS
x	fraction of monomer converted
λ	wavelength
$[I]_0$	initial concentration of initiator
$[M]_0$	initial concentration of monomer
$[RAFT]_0$	initial concentration of RAFT agent
$\mu C/cm^2$	microcharge per square centimetre
$Å^2$/charge group	square of Angströms per charge group
2θ	scattering angle

CHAPTER 1

Introduction and Objectives

1.1. Surfactants

Surfactants (surface active agents) are amphiphilic molecules with two components: a hydrophobic (water insoluble) part, such as an alkyl group, and a hydrophilic (water soluble) head group, such as a sulphate or a carboxyl. At low concentrations surfactant molecules organise themselves at the air-water interface with the hydrophobic tails away from the water while the head groups interact with water, resulting in a reduced surface tension. At a certain concentration, the surface tension will remain constant over a wide concentration range. This signifies the critical micelle concentration[1] (cmc) and the molecules organise themselves into small spherical aggregations of molecules, called micelles, which are arranged such that the hydrophobic parts are in the centre and the hydrophilic parts on the outside. At higher concentrations, however, the organisation may become non-spherical and assume other different forms depending on the nature of the surfactant. As amphiphilic molecules, surfactants promote interaction between oil and water phases through the creation of an oil/water interfacial layer.

Polymeric surfactants are those that have high molecular masses in addition to being amphiphilic. When such molecules have few monomeric units and are, therefore, not of high molecular mass, they are sometimes referred to as oligomeric surfactants. Polymerisable surfactants,[2] also called surfactant monomers and abbreviated to *surfmers,* are surfactant molecules which generally carry a reactive group that make them polymerisable.

1.2. Surfactants as emulsifiers and stabilisers

A typical emulsion polymerisation reaction mixture consists of water, a monomer, a water-soluble initiator, and a surfactant which functions as an emulsifier. The role of a surfactant in emulsion polymerisation is important and multi-fold: it influences the

stabilisation of the starting emulsion, it facilitates contact between the oil and water phases, it plays a role in particle nucleation, growth and stabilisation, and in the shelf life of the final latex. By careful choice of the type and quantity of surfactant used, polymer latex properties can be controlled to a large extent.

Recent research efforts in the field of emulsion polymerisation have focused on the development of new, well-defined and tailor-made surfactant molecules, which can be used to prepare stable emulsions for specific applications. Most of the methods used for preparing polymer latices, including emulsion polymerisation, involve the precipitation of polymer from solution during formation. In order to obtain well-formed, distinct particles, some form of stabilisation has to be achieved during particle growth in order to avoid aggregation. The main methods for stabilising dispersions are electrostatic and steric stabilisation. Electrostatic stabilisation relies on coulombic repulsive forces from electric charges while steric stabilisation mainly relies on steric repulsion introduced by lyophilic chains. Both types of stabilisation provide a stabilising layer, which prevents the approach of particles in a range where attractive van der Waals' interactions would otherwise dominate, as illustrated in Figure 1-1.
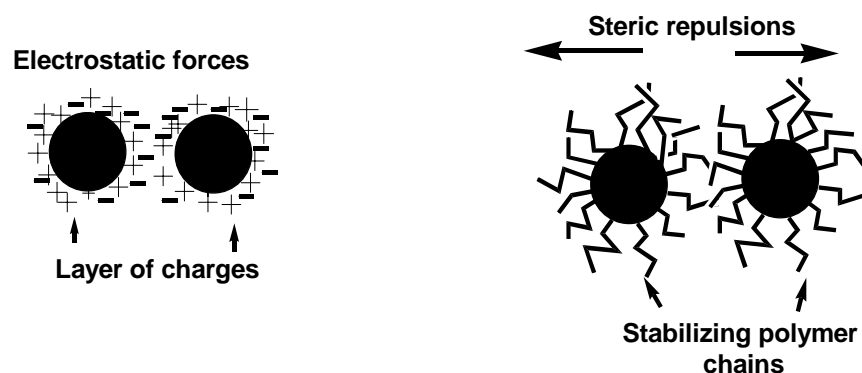
Figure 1-1. Electrostatically-stabilised and sterically-stabilised particles.

2

The Derjaguin, Landau, Verwey and Overbeek (DLVO) theory[3] shows that, particle stabilisation is determined by a balance of Van der Waals' attractive energy and electrical repulsive energy. The theory is described by the following equation:

$$V_T = V_A + V_R \qquad\qquad\qquad\qquad 1\text{-}1.$$

Where,

V_T is the total potential, V_A the van der Waals' potential energy, and V_R the repulsive potential energy, which arises from the repulsion between the electrical double layers on the two particles.

In order to prevent the particles in a liquid dispersion from approaching each other until they overcome the total potential energy barrier, a physical barrier such as an adsorbed layer around the particles is necessary. The thicker the layer, the greater the separation of particles, and hence the more stable the dispersion. This steric effect can be described as steric stabilisation. When charged particles are considered, the electrical double layers that result bring about a repulsive force, which is responsible for electrostatic stabilisation.

The use of surfmers for steric or electrostatic stabilisation allows surfactant incorporation to occur via a chemical reaction, leading to a strong bonding reaction between latex particles and surfactants, so that instead of a physically adsorbed layer, a chemically bonded layer results. Such surfactants are expected to produce stable latex particles with very few chances for surfactant migration. Polymeric surfactants, on the other hand, provide long hydrophobic chains, which show reduced surfactant mobility when compared with shorter ones. This occurs through adsorption onto the particle surface or incorporation into latex particles.

Although surfactants play a very important role in emulsion polymerisation, such as in particle formation and stabilisation of the final latex, they can also have adverse effects on a polymerisation process and on the resulting polymerisation reaction products. Some surfactants can cause foaming[4] and some can migrate to the pigment phase[5] if they are not strongly bound to the latex particles. In some cases, surfactant desorption[6] can occur under conditions such as shear stress and freeze-

thawing cycles, leading to the loss of stabilising moieties. This would result in the coalescence of latex particles. In some plastic films,[7] which are not stable, surfactants may migrate towards the film surface and affect gloss or concentrate in pockets, which could lead to increased water sensitivity and reduced adhesion.

1.3. Motivation and methodology

In this study, the acrylate-based surfmer 12-acryloyloxydodecanoic acid (12-ADA) was to be prepared, converted to its Na salt and polymerised into oligomers. The surfmer, its salt and the oligomers were then to be used respectively as surfactants and stabilisers in the emulsion polymerisation of styrene. A controlled polymerisation method, reversible addition-fragmentation transfer (RAFT)[5] was to be used to prepare the oligomers of 12-ADA in an attempt to control the molecular mass of the polymer. The use of the moderately soluble oligomers, rather than the comparatively insoluble high molecular mass polymers as surfactants was expected to lead to latices with controlled properties, such as molecular mass. Other properties that can be controlled are polydispersity, particle size and particle surface functionality.

-

The choice of surfmer was based on results of preliminary synthetic tests carried out earlier on in this study, which indicated that 12-ADA could be used as a surfactant in its acid form as well as in the Na salt form. The tests involved preparing 12-ADA and its Na salt and using them in the preparation of polystyrene latices. The latices that formed were found to be fairly stable against three freeze-thaw cycles.

The surfmer, its corresponding Na salt and oligomers have not been previously used as surfactants in emulsion polymerisation nor have RAFT oligomers of 12-ADA been synthesised before. In addition, it was considered that 12-ADA would make an interesting case study because it exhibited interesting and unusual properties, such as forming supramolecular structures[6] – indicating a good potential for its application in particle stabilisation.

For further studies, a copolymer of 12-ADA and acrylic acid was to be prepared and analysed and used as a polymeric surfactant in the emulsion polymerisation of

styrene thus providing comparisons between the use of 12-ADA as a surfmer and as a comonomer.

-

The synthesis of 12-ADA was to be carried out according to a reported method.[7] Another surfmer, 11-acrylamidoundecanoic acid (11-AAUA), which is structurally similar to 12-ADA and has been reported to have been used in salt form as an emulsifier,[8] was also to be prepared using a reported method[9] and then studied. The similarity between 12-ADA and the acrylamide 11-AAUA is illustrated in Figure 1-2. The reported use of 11-AAUA as an emulsifier was a strong motivation for its inclusion in this study.

12-acryloyloxydodecanoic acid

11-Acrylamidoundecanoic acid
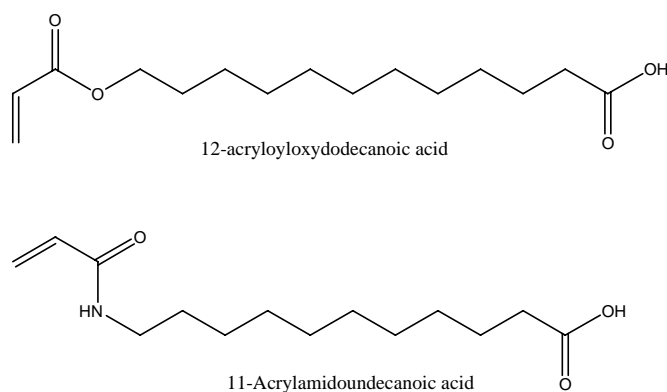
Figure 1-2. Structures of 12-ADA and 11-AAUA.

1.4. Objectives

The overall objective of this study was to prepare, purify and characterise novel polymerisable and polymeric surfactants based on the acrylate functionality, use them as emulsifiers in the emulsion polymerisation of styrene, and evaluate their role as latex stabilisers. This was to be achieved as follows:

- The surfmers 12-ADA and 11-AAUA and their respective sodium salts were to be prepared, and the products purified and analysed.

- RAFT chain transfer agents AIBN-RAFT and ACP-RAFT, which are both dithio-compounds, were to be prepared, purified and analysed.

- The surfmers and the RAFT agents were to be used in RAFT polymerisations to prepare RAFT oligomers, which were then to be purified and characterised.

- Copolymers of 12-ADA and acrylic acid were to be prepared using RAFT reagents, and analysed.

- Formulations for the use of surfmers, SDS, RAFT oligomers and copolymers as surfactants in the emulsion polymerisation of styrene, were to be determined and the respective polymerisations carried out.

- The resultant PS latices were to be purified and characterised.

- The stabilities of the prepared latices were to be evaluated using different methods, and comparisons made.

1.5. Layout of dissertation

Chapter 2 outlines the historical and theoretical background to surfactants and emulsion polymerisation. Properties of surfactant monomers and polymeric surfactants are discussed. The most common methods for cleaning and characterising polymer latices are also mentioned.

In Chapter 3, the synthesis, purification and analysis of the surfmers 12-ADA and 11-AAUA and their sodium salts are described. Analytical results are given and discussed.

In Chapter 4, preparations of the RAFT polymers by the RAFT polymerisation procedure are described. The synthesis and purification of the RAFT reagents 4-cyano-4-(thiobenzoylthio) pentanoic acid and 4-azobisiso(thiobenzoylthio) butyronitrile, and their respective use in the preparation of polymers and copolymers, are also discussed.

In Chapter 5, the synthesis, purification (cleaning) and characterisation of polystyrene latices, prepared using different surfactants, are described. The pre-emulsion tests carried out to determine the extent of emulsification of each polymerisation mixture

are outlined. Characterisation of latices using GPC, MALDI-TOF, WAXS, dynamic light scattering, SEM and TEM is also decribed.

In Chapter 6 the conclusions are presented and recommendations for possible future research are offered.

1.6. References

1.   Mathai K.G., Ottewill R.H., Trans. Faraday Soc. **1966**, 62, 759.
2.   Schoonbrood H.A.S., Asua J.M., Macromolecules **1997**, 30, 6034.
3.   Verwey E.J.W., Overbeek J., Theory of the Stability of Lyophobic Colloids, Elsevier Publishing Co., Amsterdam, **1948**.
4.   Soula O., Guyot A., Williams N., Grade J., Blease T., J. Polym. Sci., A. Polym. Chem. **1999**, 37, 4205.
5.   Hawthorne D.G., Moad G., Rizzardo E., Thang S.H., Macromolecules **1999**, 32, 5457.
6.   Yang J., Marendaz J-L.,Geib S.J., Hamilton A.D., Tetrahedron Lett. **1994**, 35, 3665.
7.   Finkelmann H., Scafheutle M.A., Colloid Polym. Sci. **1986**, 264, 786.
8.   Guillaume J.L., Pichot C., Guillot J.,. Polym. Sci., A. Polym. Chem. **1990**, 28, 137.
9.   Fujimoto C., J. Chromatography A, **2000**, 871, 415.

CHAPTER 2

Historical and Theoretical Background

2.1. Surfactants

Surfactants (surface active agents) are molecules with two major components: a hydrophobic (water insoluble) chain, such as an alkyl group, and a hydrophilic (water-soluble) head group, e.g. a sulphate. At high concentrations they easily organise themselves into small spherical aggregations of surfactant molecules, micelles, with the hydrophilic part on the outside and the hydrophobic part in the centre. At yet higher concentrations they become non-spherical and form long tubes, or 'worm-like' arrangements. Ultimately, they become lamella of organised molecules. Figure 2-1 illustrates some of the organised assemblies into which surfactants can arrange themselves.

micelles   **lamella**
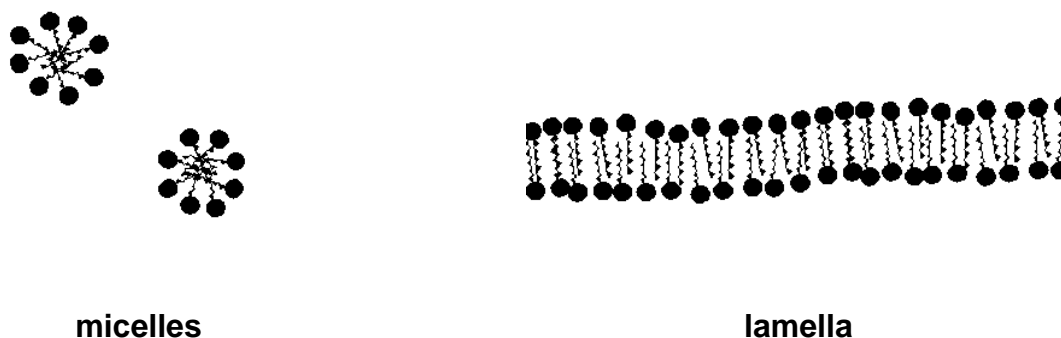
Figure 2-1. Some organised surfactant assemblies.

Polymers often act as surfactants when they bear both hydrophilic and hydrophobic components. Some such polymers have been used as dispersants,[1] thickeners[2] or rheology modifiers.[3] Surfactants stick or adhere to surfaces, leading to a change in the nature of the surface. The surface becomes either hydrophobic or hydrophilic, or it acquires specific properties, depending on the surface created by a particular liquid or substance. Surfactants are used in many industries, processes and products.

They are widely used in detergents, for removing soiling from surfaces. The detergent contains micelles, which adsorb onto the soil, surrounding it. The surfactant is rapidly transferred through water and slowly along the surface, so that the surface tension is rapidly lowered, resulting in the removal of the soil. Different types of surfactants have been synthesised with different end-uses in mind, for example: traditional surfactants, which are relatively short-chain; polymerisable surfactants, which are also known as surfmers, carry polymerisable moieties such as olefinic double bonds; polymeric surfactants, which are obtained by polymerising monomers or surfmers, generally leading to long-chain polymers and also nonionic surfactants which do not dissociate in water. Some examples of nonionic surfactants are poly (ethylene oxide), poly (oxy ethylene) and alkyl polyglycosides as well as some of which are composed of alcohols and fatty acids. They have been used in a variety of applications such as in the reduction of surface tension, to improve herbicide absorption and in miniemulsions.[4]

2.1.1. Polymerisable surfactants

Nowadays, there is a strong need to reduce the use of organic solvents in paints and coatings. This is in accordance with the increasing awareness that good environmental practices include the use of as few toxic chemicals as possible in the chemical and other industries. In the paint industry, this has led to the increasing development and use of water-borne paints in preference to solvent based paints. . Such paints are normally made from a dispersion of latex particles in water and are typically produced by emulsion polymerisation. In such a procedure, surfactants are used to stabilise the particles during the polymerisation process and also during storage. When a water-borne paint is used, the water evaporates and the latex particles form a film. However, as surfactants will be left in the film they may, for example, aggregate and form water-sensitive areas in the film, which can negatively affect the final paint properties in many ways. One solution to this problem caused by such mobile traditional surfactants present in a paint film is to use reactive surfmers instead of conventional surfactants. Surfmers are surfactants that are reactive and act as both monomers and stabilisers. In addition to having a hydrophilic part and a hydrophobic part, like all other surfactants, surfmers additionally possess reactive bonds.

Polymerisable surfactants have generally been prepared by modifying the structure and function of conventional surfactants or other active reagents through the incorporation of reactive moieties. Some of the ways in which this has been achieved are, through:

- surface-active initiators (inisurfs),[5] in which the polymerisable or reactive moiety is a part of the initiator,
- surface-active monomers (surfmers),[6] where the reactive moiety is part of the monomer, and
- surface-active transfer agents (transurfs),[7] where the reactive moiety is part of a transfer reagent.

2.1.1.1. Surfactant monomers

Surfactant monomers (surfmers) have generated much interest due to their dual nature; they are both surface-active species and polymerisable monomers. As reactive monomers, surfactant monomers have been used in polymerisation reactions, such as emulsion copolymerisation with traditional monomers such as styrene, butyl acrylate and acrylic acid.[8] Surfmers have also been used in heterogeneous polymerisations to replace conventional surfactants, with the aim of improving latex properties.[9]

The relative positions of the three moieties present in a surfmer molecule, i.e. hydrophilic head, hydrophobic tail and polymerisable function, are unrestricted.[10] The reactive polymerisable group can be placed at the end of the hydrophobic tail, in the middle of the hydrophobic tail, or near the hydrophilic head, as illustrated in Figure 2.2.
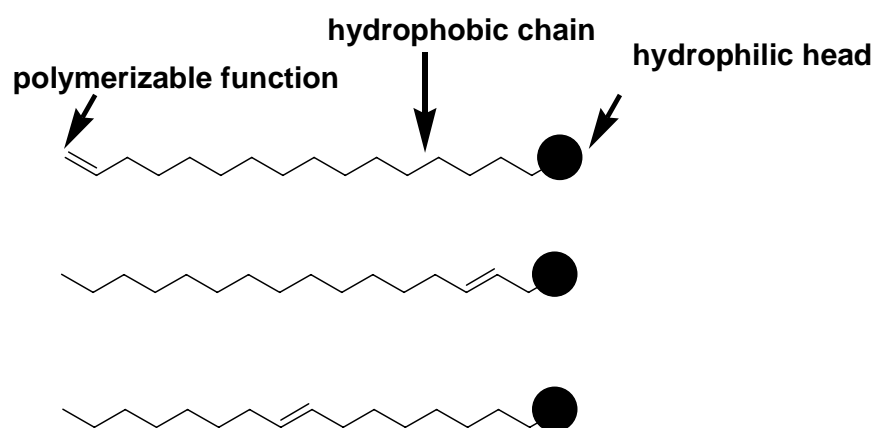
Figure 2-2. Examples of positions of the reactive functionality within a surfmer

The general requirements for a good surfmer in emulsion polymerisations have been summarised by Schoonbrood and Asua[11] and De Le Cal et al[12] as:

- It should be a good surfactant, which should lead to efficient stabilisation of the polymer particles
- it should allow a certain degree of emulsification of the monomer mixture.
- The critical micelle concentration (cmc) of the surfmer should be low so as to limit aqueous-phase polymerisation of the surfmer, so that the production of water-soluble polymeric surfactants (polysoaps) will be reduced. This helps with improving latex stability, because the formation of such polysoaps can lead to "bridging coagulation".[13]
- The surfmer should not react early in the process because, if it does, its mobility will be limited and it can be buried when the particle grows larger.
- If the surfmer remains largely unreacted during the polymerisation, it will be mobile and will remain on the surface of the particle. At the very end of the polymerisation process all of the surfmer should have reacted and should be chemically bound to the surface of the polymer particles.

The above requirements are general recommendations and each surfmer will have its own specific requirements pertaining to a specific application e.g., surfmers which bear a maleic functionality were used in PS latices and found to reduce by a factor of four the amount of surfactant left in water on flocculation by calcium salts.[14] In another study, carboxyl functionality was introduced onto the surface of latex

particles by use of an azo-carboxy initiator with the surfmer sodium acrylamido undecanoate.[15]   Another application was the use of bifunctional surfmers terminated with reactive groups at one end and a polymerisable group on the other which were prepared and used to attach antibodies. This was done by allowing reaction between the polymerisable end and different functional groups on the antibodies.[16]

2.1.1.2. Use of surfmers in emulsion polymerisation

Surfmers have been used to stabilise colloidal particles such as polymer latices.[17] The preparation of polymer latices generally involves the precipitation of the polymer product from solution such as in emulsion polymerisation, which is one of the industrial processes used. It is desirable to obtain distinct particles that make up the polymer latex. Some form of stabilisation is therefore essential to keep polymer particles separated from each other, to avoid them sticking together and leading to coagulation. Stabilisation has to be achieved during particle growth to avoid aggregation and the formation of coagulum. As already described in Chapter 1, the two main phenomena that provide forces that keep particles apart are electrostatic stabilisation, which arises from double layers of charges around particles, and steric stabilisation, which is due to steric repulsions brought about by the hydrophilic bounce-off barrier of the stabilising chains around polymer particles

Most of the surfmers used in emulsion polymerisation have a tail-type stabilisation (see Figure 2.3.). This, in principle, seems to be most appropriate since the reactive function will be positioned in the molecular chain. It has also been found that water-soluble initiators resulted in higher incorporation of surfmer to the particle surface than was achieved with oil-soluble initiators. Once copolymerisation occurs between surfmer and monomer, the surfactant is not expected to easily desorb.[18] Surfmers have therefore been used to prepare stable model latex systems.[19]
The production of polymer latices of high solids content and the control of surface-charge density are other areas of focus. Research into surfmers has been encouraged by findings such as the following: when surfmers are used in place of conventional surfactants in some polymerisations, marked improvements in mechanical stability,[20] tolerance to added electrolyte,[14] water resistance[17] and freeze-thaw stability[21] were reported. Improvements in these properties will therefore lead

to better overall latex properties, such as the paint performance of surface coatings. Current research is largely focused on the improvement of latex stability, and the production of environmentally acceptable and sustainable latices. A new research focus area is to find surfactants that are increasingly efficient. Most surfactants are currently only about 30% efficient because 70% of surfactants are generally buried within the latex particle and do not help in aiding stability.[22,23].

. In one study it was found that the use of surfmers can lead to the preparation of surface coatings with reduced sensitivity to moisture.[24]   Another surfmer, 11-Acryloyloxy undecyl tri methylammonium bromide (AUTMAB) was used to produce nanolatexes which displayed improved gloss when used in paints.[25]

The most common surfmers used in emulsion polymerisation to date have typically contained acrylic, methacrylic, acrylamido, and styrenic polymerisable groups[26]. The amount of surfmer used is an important factor – it needs to be kept below its cmc to discourage the formation of polyelectrolytes. Less reactive functionalities have also been used in emulsion polymerisation.[27] It has been found, however, that allyl surfmers decrease the polymerisation rate of the main monomer. This is attributed to a degenerative chain transfer reaction to the allyl function.[28]

For surfmers, which do not easily homopolymerise at the usual polymerisation temperatures, copolymerisation with other non-homopolymerising monomers, such as maleic anhydride to prepare maleic-based surfactants, has been suggested.[29] When used in the polymerisation of styrene, such copolymers were found to bond to the latex. In one study by Urquiola et al.[30] different reactivity ratios between the surfmer, sodium alkyl allyl sulphosuccinate and vinyl acetate (VA) as the comonomer were made use of. This was found to lead to the reduced polymerisation of VA, while the surfmer acted as a transfer agent. Greene et al[31] used surfmers of sodium 9- and 10- acrylamido stearate to stabilise poly (styrene-butadiene) latex. The initiator used for the in-situ emulsion copolymerisation of the surfmers was potassium persulphate. In these experiments, latex surface coverage by surfactant varied from 20-80%. The latex particles covered with polymerised surfmer at high coverage displayed superior

mechanical stability against added electrolyte compared with latex particles covered with a non-polymerised surfmer at the same degree of coverage.

The amount of solids incorporated in an emulsion system also has a bearing on the coverage of latex with stabilising groups. A carboxyl-based surfmer used by Guillaume and coworkers[15] to prepare high-solid content latices with carboxylic surface groups resulted in a slow polymerisation rate and the latex particles were poorly stabilised because most of the surfmer was found to be adsorbed rather than covalently bonded. The carboxyl surface group coverage was limited to 20-30%, with a large part buried inside the particles when the solids content was high. Chen and Chang[32] used a surfmer with a vinylic end group for the emulsion polymerisation of styrene and found that the polystyrene particles prepared with this surfmer were monodisperse and that their size increased with increasing solids content. They also showed that the number of particles increased with increasing surfmer concentration. Due to the monodipersity of the polymer particles, a homogeneous mechanism was assumed.

In some cases, some surfmers need to be used together with a co-surfactant for the successful stabilisation of latex particles. Fitch and Tsaur[17] used the styrenic surfmer, styrene sodium dodecyl sulphonate ether, together with a classical surfactant, sodium dodecyl sulphate (SDS), in order to form monodisperse latex particles of polystyrene. The surfmer alone was not an adequate latex stabiliser.

Maleate and succinate diester surfactants were used by Montoya-Goni et al.[33] in the emulsion polymerisation of styrene. High conversions of styrene were obtained with maleates, but conversions with succinates varied. Results of tests carried out to determine stability against added electrolyte showed that the succinate-stabilised latices were more stable than the maleate-stabilised ones, even though there was greater chemical bonding with the maleates and more adsorption with the succinates. This implied that while chemical bonding was desirable and should improve some of the properties of latices, e.g. reduced migration of surfactant it may be at the expense of other properties, such as stability against added electrolyte. This suggests that optimum latex properties can only be obtained by varying property

requirements from application to application, in order to attain a delicate balance of properties suitable for a specific application.

2.1.2. Polymeric surfactants

Although less well defined than small-molecule surfactants, polymeric surfactants probably offer greater opportunities in terms of flexibility, diversity and functionality. This is especially true in the light of recent advances in controlled/living radical polymerisation chemistry, such as in atom transfer radical polymerisation (ATRP)[34] and, increasingly, reversible addition-fragmentation chain transfer (RAFT)[35] polymerisation (which was made use of in the current project). This new polymer chemistry is of great interest as it has empowered synthetic polymer chemists to make new tailor-made polymeric surfactants such as well-defined amphiphilic block copolymers, many of which exhibit interesting surfactant behaviour. The size of polymeric amphiphiles, compared to low molecular mass species, allows for much more diverse arrangements of the hydrophobic and hydrophilic segments. The structural similarities of the individual polymer fragments in polymeric surfactants and conventional low molecular mass surfactants make them behave typically with two important properties found in both types of surfactants: the high-solubilisation capacity for hydrophobic molecules and low-viscosities of aqueous solutions due to the hydrophobic aggregation, which reduces the hydrodynamic radii.[36]

Despite these similarities, other properties of polymeric surfactants can differ considerably from those of standard surfactants, e.g., their intramolecular aggregation and the usually low or "missing" critical micelle concentration.[37] Polymeric surfactants have also been found to possess lower diffusion coefficients compared to those of classical low-molecular-mass surfactants such as SDS. Functional groups can be introduced into the molecular structure of polymeric surfactants to produce functionalised polymers, which are capable of undergoing further reaction. The functionalisation generally leads to many properties and applications such as electrical conduction,[38] for the controlled release of drugs,[39] and to block and graft copolymers[40] having varied hydrophobic and hydrophilic sequences. The main advantage of the stabilising layers obtained with the block copolymer surfactants is that the thickness of the hydrophilic layer on the latex

surface can be adjusted as a function of the molecular characteristics (molecular mass, composition, structure) of the block copolymer.

2.1.2.1. Structure of polymeric surfactants

The molecular architecture of polymeric surfactants generally comprises various combinations of polymer and surfactant structures. The most obvious structural segments to be varied are the surfactant fragments, with respect to the hydrophilic head, and the length and branching of the hydrophobic tail. However, polymeric surfactants offer additional variations which are characteristic for polymers but do not exist for "small" surfactants, such as their solubility in water to form micellar polymers. The molecular architecture can be varied in many respects, e.g., with respect to the polymer geometry, the nature of the polymer backbone and the incorporation of spacer groups controlling the distance of the surfactant fragments, from the polymer backbone. Some of the general structures of polymeric surfactants are illustrated in Figure 2-3.

tail-type   **head-type**   **mid-type**
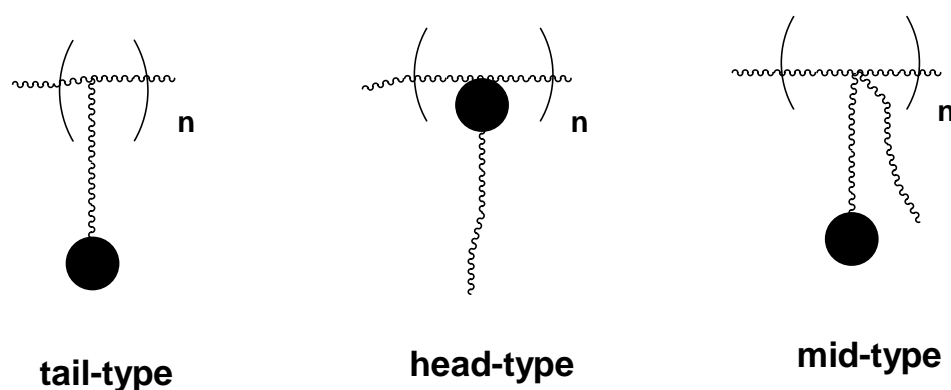
Figure 2-3. Some of the possible molecular arrangements of polymeric surfactants.

Diblock copolymers, with a clear separation of the hydrophilic "head" and the hydrophobic "tail" parts, come closest to the architectures of standard surfactants; and are sometimes referred to as macrosurfactants.[41] Hydrophobic aggregation of chains, generally takes place by intermolecular association. In contrast, amphiphilic star block opolymers[42] and graft polymers preferentially undergo intramolecular aggregation. Amphiphilic dendrimers[43] represent the extreme case, i.e., they can form intramolecular hydrophobic aggregates comprising the whole macromolecule. Micellar polymers are characterised by large, well-separated blocks of hydrophilic

and hydrophobic groups and their amphiphilic character is based on the overall macromolecular architecture. Alternatively, the hydrophilic and hydrophobic groups may be distributed throughout the macromolecule. By attaching the surfactant fragments to the backbone in different ways, various polymer geometries are realised. They include "frontal" attachment at the hydrophilic head group "head type; "terminal" attachment at the end of the hydrophobic tail "tail-end type"; intermediate structures "mid-tail type" and full incorporation into the backbone "main chain type". The aggregation process of polymeric amphiphiles can be improved by the incorporation of flexible side-chain spacer groups. There are many variations in positioning of the surfactant units in polymeric surfactants. Many types of head groups have been used, including: non-ionic, cationic, anionic and zwitterionic ones.

2.1.2.2. Synthesis of polymeric surfactants

The fact that block copolymers have components that can exist in different phases gives them special colloidal properties, such as surface activity. Amphiphilic polymeric surfactants provide chains of stabilising moieties around the surface of polymer particles through adsorption.

There are a number of approaches to the synthesis of polymeric surfactants, which can be used to stabilise colloidal particles. Polysoaps with well-defined structures can be prepared via polyaddition and polycondensation reactions of non-amphiphilic reagents.[44] One other convenient way to prepare polymeric surfactants is by copolymerisation. Polymerisable surfactants are copolymerised with small and often polar hydrophilic comonomers, creating well-defined surfactant fragments in the polymers.[45] Polymeric surfactants offer more possibilities than low molecular weight ones in the tailoring of properties of colloidal materials because more monomers such as in copolymers may be used in their synthesis. For example, diblock copolymers of 4-vinyl pyridine and sodium methacrylate have been used as effective stabilizers for aqueous dispersions.[46] Amphiphilic polymeric surfactants many of which are block copolymers contain hydrophobic segments which may strongly adsorb onto hydrophobic surfaces such as those of polymer latices.[47-49]

Other polymeric surfactants can also be prepared by first preparing hydrophilic polymers and then modifying the preformed hydrophilic polymers with hydrophobic reagents.[50]

The hydrophilic-lipophilic balance (HLB)[51] is one factor that has to be considered when preparing polymeric surfactants. The HLB is a number, which can be assigned to an emulsifier and represents the balance of hydrophilic and lipophilic groups in the molecule. Hydrophilic groups increase HLB and lipophilic groups decrease HLB. The HLB number has an arbitrary range of 1-40 with the most commonly used emulsifiers in the range between 1 and 20. A generalised equation for HLB is:

HLB for a mixture A+B = (HLB of A X fraction of A) + (HLB of B X fraction of B)

Polysoaps are expected to have an appropriate hydrophilic-hydrophobic balance to allow for water solubility on the one hand (not just dispersion), and sufficient hydrophobic parts to enable aggregation on the other. A good emulsifier will sit at the interface, producing a low interfacial tension. An optimum balance of lipophilic and hydrophilic groups in the molecule is required for a good surfactant and the optimum balance needed will depend on the type of emulsion and system. General guidelines follow Bancroft's Rule,[52] which states that: "the phase in which the emulsifier is preferentially soluble will become the continuous phase of the emulsion". The relative sizes of the hydrophilic and lipophilic groups determine the preferred curvature of the interface and thus determine the different phases.

Many methods for the synthesis of polysoaps have been established[53-55] covering a wide range of preparative polymer chemistry, to meet practical needs. The method used for the work-up leading to the final polysoap has to be taken into account when selecting a synthesis pathway, as the amphiphilic character of the polysoap can lead to practical difficulties e.g. purification of latex from residual reagents and by-products.

Most systematic investigations of the surfactant fragments in polymeric surfactants have been restricted to the influence of the length of the alkyl tails, in analogy to

homologous surfactant series. It has been shown that the minimum length of the hydrocarbon tail required to produce polysoap properties is about C_8.[53] There may be some polysoap behaviour observed for some shorter chains, but additional hydrophobic units need to be present in the backbone. It has also been found that hydrophobic counter-ions, such as alkyltrimethylammonium[54] ions, induce hydrophobic aggregation for short chain "polysoaps," although it has been disputable whether the amphiphilic ions favour the hydrophobic aggregation of the polymer, or rather the polymer favours the aggregation of the "counter-ions". There are some indications of an optimum length of about C_{18}, beyond which the hydrophobic chains are "crystallised" and the hydrophobic aggregates are no longer deemed to be fluid-like.[55] Within these limits, the effects of length variations generally agree well with the known effect of similar variations on low molecular mass surfactants. If the length of the alkyl tails is increased or if fluorocarbon tails are used in place of hydrocarbon ones, then the hydrophobic association of the polysoaps is promoted.

2.1.2.3. Applications of polymeric surfactants

Some polymeric surfactants are used in medical applications, examples of which are given in the work of Gabizon;[56] polymeric micelle-forming surfactants such as poly (ethylene-glycol)-phosphatidyl ethanolamine (PEG-PE) were used as drug carriers. Such surfactants are illustrated in Figure 2-4.[56] Similar polymeric surfactants were also used in pharmaceutical applications such as in formulations of insoluble drugs[57] and in catalytic systems such as in the work of Levashov[58] who found that some polymeric micelles could be used as enzyme-activity regulators.

In colloidal applications, polymeric surfactants are most frequently used as dispersants or emulsifiers.[59-61] Although several studies have been carried out on the use of polymerisable surfactants, which are in fact the precursors of polymeric surfactants, the use of polymeric surfactants in emulsion polymerisation is still uncommon. In colloidal applications, improved latex stability and improved resistance of film-formed latices to moisture are still the desired goals.
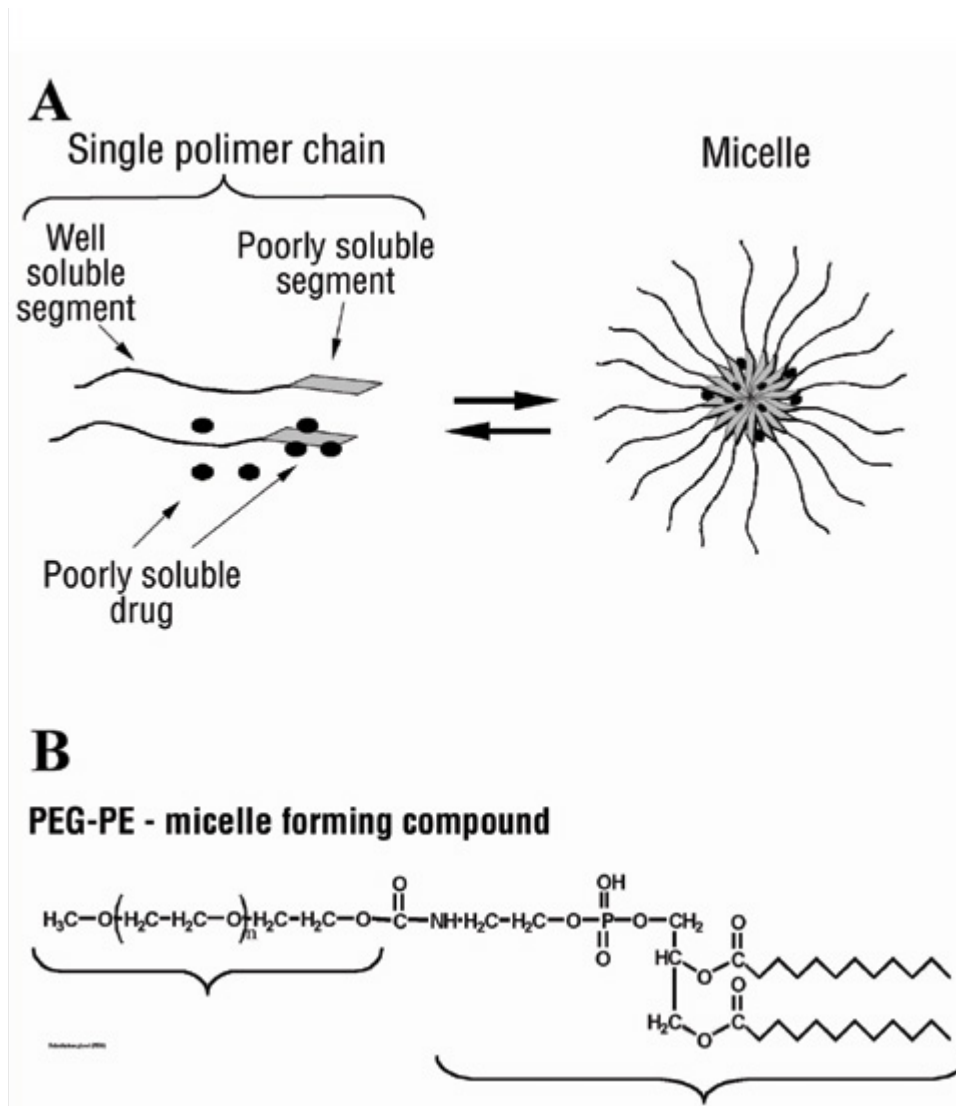
Figure 2-4. An illustration of the solubilisation of an insoluble drug (A) and an example of a polymeric surfactant (B).[56]

Although polymeric surfactants are used to stabilise latices, the opposite use for flocculation has also been evaluated in wastewater treatment, as described by Yeoh and coworkers.[62] The researchers reported the successful use of synthetic polyelectrolytes in water and wastewater treatment. Coagulation implies aggregation caused by compression of the electrical double layers surrounding colloidal particles, whereas flocculation arises from bridging colloidal particles by long-chain polymer molecules. The aggregation of the colloidal particles into larger flocculants is necessary for successful cleaning by sedimentation. This involves destabilisation of the colloidal particles by addition of inorganic electrolytes and polyelectrolytes. The

polyelectrolyte molecules may first serve as a coagulant to reduce the opposite charges of colloidal particles, and then as a flocculant to bridge adjacent particles via extended segments of adsorbed polymer molecules. Some examples of synthetic anionic polyelectrolytes, which are the most widely used, are based on polyacrylamide[63] and its copolymers.[64]

2.1.2.4. Copolymeric surfactants

Most of the work done on polymeric surfactants to date has been with hydrophilic-hydrophobic diblock copolymers, where the hydrophobic block is permanently hydrophobic. There has also been some interesting work done on hydrophilic-hydrophilic diblocks, in which the less hydrophilic block can be altered to become hydrophobic by changing the external solution conditions, such as solution pH, temperature or electrolyte concentration, such as reported by Liu and Armes.[65] This type of work has been extended to include 'schizophrenic' AB diblock copolymers, which can form both micelles with the A block in the micelle core and also reverse micelles with the B block in the micelle core in aqueous solution, as described by Bütün et al. who investigated tertiary amine methacrylate-based diblock copolymers.[66] Figure 2-5 illustrates such polymers.
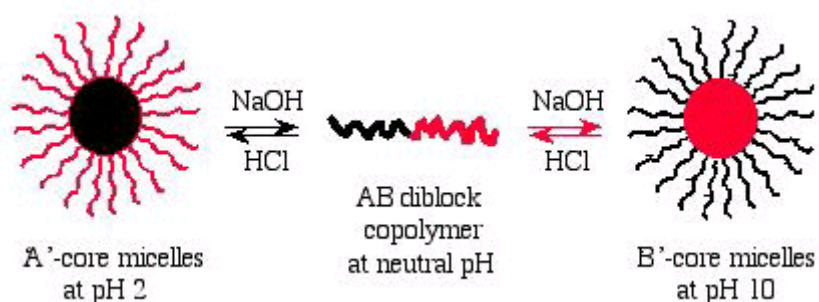
Figure 2-5. Reverse micelles of AB diblock copolymer.[66]

Other novel polymeric surfactants that have been used in latex synthesis include statistical comb copolymers comprising octadecyl side chains and carboxylic acid-based backbones, produced via conventional free radical copolymerisation. These were used as effective emulsifiers and steric stabilisers in the mini-emulsion

polymerisation of styrene, such as reported by Baska and co-workers.[67] Diblock copolymers, which were amphiphilic were prepared by Burguire and others.[68] In this work they used both ATRP and/or nitroxide-mediated polymerisation and investigated the efficacy of using the block copolymers as polymeric stabilisers in the emulsion polymerisation of styrene.

Emulsifiers, which are sensitive to pH have been prepared by the statistical copolymerisation of MAA and poly (ethylene glycol) methacrylate (PEGMA) in the work done by Drescher and others.[69] The polymers were found to behave like conventional polyelectrolytes at neutral pH and like amphiphilic surfactants at low pH. Furthermore, the pH-dependent surface activity was found to be completely reversible.

Banez et al.[70] reported on the synthesis of well-defined AB diblock copolymers where the A block was low molecular mass PDMS and the B block was made up of residues of 2-(dimethylamino) ethyl methacrylate (DMA), and used the copolymers as siloxane-based polymeric surfactants. The copolymers were found to undergo self-assembly in solvents, which were good solvents for the A block, but still formed micelles in water as expected. Li et al.[71] prepared a PDMS-based 'ambidextrous' ABC triblock copolymer composed of PMAA-PMMA-PDMS blocks, which was subsequently used in preparing PMMA latex in supercritical carbon dioxide (sometimes referred to as a "green solvent"). The PDMS chains provided the stabilising moieties while both the neutral MMA and acid MAA were strongly adsorbed onto the latex surface due to their solubilities in the supercritical carbon dioxide. Remarkably, on venting the CO_2, it was found that the latices could be redispersed in water at up to a 40%-solids content.

2.1.2.5. Self-assembly

Spontaneous self-assembly in aqueous solution or THF/water mixtures of some amphiphilic, multiblock copolymers based on near-monodisperse poly (ethylene oxide) and polydisperse poly (methylphenylsilane), have been reported by Sommerdijk and others.[72] There has been growing interest in the production of colloidal cross-linked nanostructures via polymeric surfactants. Wooley and coworkers[73] studied the stabilisation of self-assemblies of polymeric surfactants while

Zhang[74] reported on work done on the preparation of hollow structures, "nanocages," based on cross-linked poly (acrylic acid) from cross-linked micelles.

2.1.2.6. Use of polymeric surfactants in electrokinetic capillary chromatography

Polymeric surfactants have reportedly been used as pseudo-stationary phases in micellar electrokinetic capillary chromatography (MEKC) by Fujimoto and coworkers.[75] The researchers examined the use of polymers of poly (Na 11-AAUA) with a very high molecular mass ($>10^6$) as a pseudo-stationary phase. This mode of capillary electrophoresis (CE) is based on the differential distribution of solutes between a running buffer phase and a pseudo-stationary phase, allowing the separation of uncharged analytes under the influence of an electric field.

2.2. Heterophase polymerisations

There are a number of heterophase polymerisation processes that are used to prepare polymers industrially. These include suspension, precipitation, dispersion, miniemulsion, macro- and micro-emulsion and inverse emulsion polymerisation processes.

Emulsion polymerisation is one of the most important of the heterophase polymerisation processes. Here, the monomer or a mixture of monomers emulsified in water is polymerised, generally using a water-soluble initiator. The simplest composition of an emulsion polymerisation includes water, surfactant, a water-insoluble monomer and a water-soluble initiator. The product of the reaction comprises a colloidal dispersion of polymer particles in an aqueous medium, also known as the latex.

Suspension polymerisation is a polymerisation in an aqueous system with monomer as a dispersed phase. Generally, an oil-soluble initiator is used and the locus of the polymerisation is in the monomer droplets. These droplets subsequently change into the polymer phase through polymerisation.

In precipitation polymerisation, the polymer is insoluble in the monomer or solvent (whichever is the continuous phase). The locus of the polymerisation is generally in the precipitated polymerisation droplets.

In dispersion polymerisation, the monomer is partially soluble in the dispersion medium, while the polymer formed is insoluble. Polymer forms in the dispersed droplets or in the continuous phase and adds to the dispersed phase, i.e. the stabilised particle, where polymerisation continues. Here, the stabilising agent is normally steric, e.g. poly (vinyl alcohol).

In microemulsions, a monomer and a water-soluble initiator are two of the starting materials, in addition to water, monomer and surfactant. Very small particles are prepared, containing the polymer. The mechanism of microemulsion polymerisation is well described by Gilbert.[76]

A miniemulsion polymerisation can be considered to be a special case of emulsion polymerisation. Co-stabilisers and surfactants are generally used to allow small, semi-stable emulsion droplets to be formed initially, in the early stages of polymerisation, and particles are formed by the entry of a radical into a droplet, which provides the locus of polymerisation. [77-80] In a study by Anderson et al.[81] the influence of surfactant packing was shown to be dependent on particle and surfactant sizes.

2.3. Emulsion polymerisation

2.3.1. The development of emulsion polymerisation

Since the early development of the emulsion polymerisation process, in the early 1930s, the process has received increasing industrial interest. This interest has been mainly driven by the numerous advantages offered by the process compared to other modes of polymerisations. Initially developed for the synthesis of synthetic rubber, emulsion polymerisation is nowadays an economically important process that is applicable to a wide variety of monomers, to produce elastomers, thermoplastics, and numerous specialty polymers. A good account of the historical development of emulsion polymerisation is given by Gilbert,[76] in which the technical history is divided

into three periods, which he terms: the "Heroic Age", "Age of Exploration" and "Age of Enlightenment".

The "Heroic Age", which was the period around 1930, is reported as the time when emulsion polymers were first produced. This involved the study of natural rubber latex and attempts to produce synthetic rubber. It was during this period that the synthesis of rubber was attempted by DuPont and resulted in the discovery of neoprene. The first attempts at emulsion polymerisation led to products, which had limited applications as they lacked the necessary good latex properties such as robustness and good film-forming properties.

The "Age of Exploration" covered the period from the 1950s to the 1980s. During this time there was a rapid growth in the range of emulsion polymerisation products, and there was a concerted research effort towards the production of better quality products. Although some basic principles about emulsion polymerisation were established, the process could not be developed fully because industrial research was mainly carried out via trial-and-error methods, with minimal use of mechanistic principles. This led to an extensive range of formulations, which were usually kept secret by the founding industrial companies.

In the "Age of Enlightenment", new physical techniques for investigation were developed, and this subsequently led to a better understanding of the fundamental mechanisms that govern the emulsion polymerisation process. This subsequently resulted in the development of knowledge-based, well-formulated products with enhanced performance.

The focus of the future is thus on the improvement of existing technologies to develop a better understanding of the emulsion polymerisation process while seeking ways to further improve the industrial process and produce more value-added materials.

2.3.2. Advantages of emulsion polymerisation

Emulsion polymerisation generally proceeds at low viscosities, allowing adequate heat dissipation, hence avoiding overheating in reactors. High monomer conversions

are generally realised and thus problems associated with residual monomers are reduced. Generally, high molar mass polymers are produced without using modifiers, suggesting that the addition of chain transfer agents (such as in RAFT or ATRP processes) can be used to control the molar mass fairly easily. The use of water and the absence of organic solvents are advantages in which water constitutes an inert and harmless continuous phase. This helps to maintain a relatively low viscosity of the end products and provides for adequate heat transfer. The polymerisation actually takes place in the latex particles that act as numerous micro reactors for bulk polymerisation. The use of functional monomers is possible and these are usually used together with other monomers to improve latex properties or to create sites for surface modification, or to tailor-make polymer latex for a specific application. This offers a possibility for the development of a new materials and applications for emulsion polymerisation products.

2.3.3. Disadvantages of emulsion polymerisation

A major disadvantage of emulsion polymerisation is related to the compartmentalisation[82] of the reaction. This is when polymerisation occurs simultaneously with other processes and in different phases of the same system. Furthermore, the heterophase reaction mixtures generally contain several additives, such as surfactants and initiator fragments, which may prove difficult to remove, and subsequently affect the quality of the final product. There are a great variety of reactants and procedures used in polymerisation recipes and in emulsion polymerisation. While this may lead to a wide and exciting range of products, it can also make mechanistic studies of reactions complex, due to the heterogeneous nature of the process, reactants, intermediates and products. Removal of the aqueous continuous phase, which may be necessary after polymerisation, to isolate the polymer, might be difficult to achieve industrially and can result in a significant increase in production costs.

2.3.4. Emulsion polymerisation conditions

The most common methods for preparing polymer latices by emulsion polymerisation are: batch wise, in continuous stirred tank reactors (CSTR), and by starved feed conditions. In single-batch polymerisation, all the polymerisation reagents are added, mixed and stirred at the appropriate temperature and the products are then recovered after the polymerisation. In a semi-batch process, a portion of the

reactants are added to a reactor at the beginning of the process and the rest of the reactants are added during the reaction in a controlled manner, allowing some flexibility in process design and operation. In this mode, variables such as temperature, polymer composition and particle size distribution can be adjusted by controlling feed inputs. Most commercial emulsion products are produced in semi-batch processes. In the continuous reactor system, reactants are added throughout the process while products are continuously removed. This system operates in a steady-state condition and allows optimisation of production rates. In some of these cases, pre-formed latex particles are added to the reactor to replace removed particles, to maintain steady-state conditions. In a starved-feed process, the polymer composition is fixed by adding a pre-determined ratio of monomers that allows the monomer feed to be the rate-determining step in particle growth.

2.3.5. Theory and mechanism of emulsion polymerisation

Emulsion polymerisation is a mechanistically complex process, and it presents many scientific challenges in addition to industrial interest. Harkins[83] has given a qualitative description of emulsion polymerisation processes, while Smith and Ewart[84] have developed a corresponding mathematical model. Extensive work has subsequently been carried out to better understand and quantitatively describe the mechanisms involved during the process. The key issues are the control of the polymerisation reaction and design of emulsion polymers. Piirma[85] and Gilbert[76] have given good overviews on emulsion polymerisation in the literature.

A batch emulsion polymerisation process can commonly be divided into three, time-separated intervals. The reaction mixture initially consists of monomer droplets and monomer-swollen surfactant micelles dispersed in a continuous aqueous phase. At the start of the polymerisation process the monomers are dispersed into small droplets that are stabilised by surfactants, and most of the remaining surfactant molecules gather as micelles in the water phase, as illustrated in Figure 2-6.
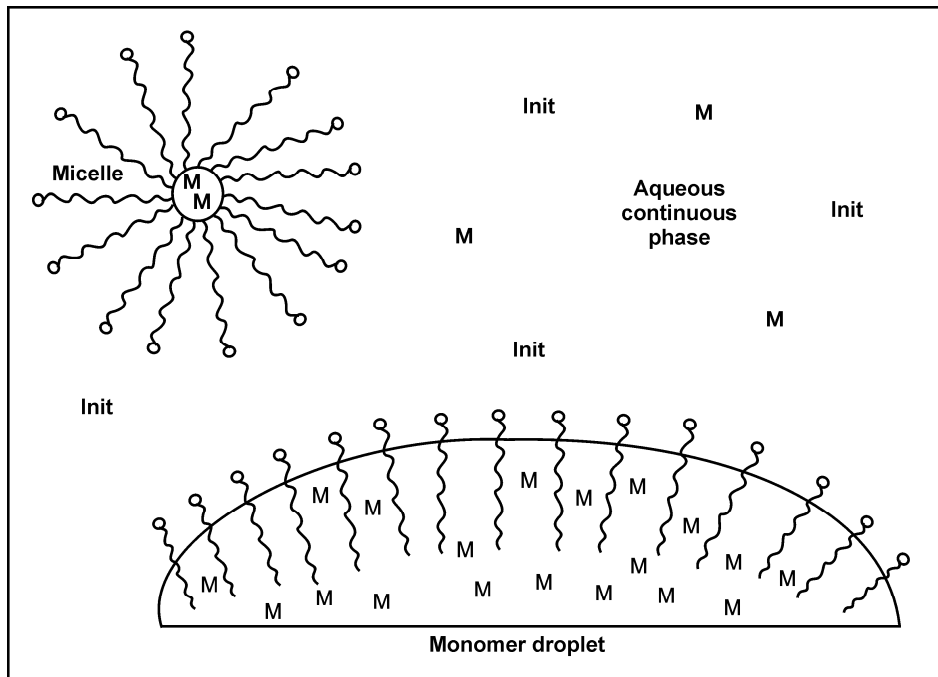
Figure 2-6. Events that occur at the start of a batch emulsion polymerisation.

The micelles are very small compared to the monomer droplets. Three different stages of emulsion polymerisation can be distinguished. In the first stage, called the nucleation step or Interval I, the initial formation of polymer particles occurs and monomer-swollen micelles disappear and nascent polymer particles appear. The stage ends when all the micelles have disappeared. After nucleation, the next stage, Interval II, commences and the polymer particles grow at the expense of the monomer droplets which decrease in size and it ends when the supply of monomer is stopped. Interval III starts only when even the monomer droplets have disappeared. Polymerisation continues in Interval III until the monomer present in the particles or dissolved in the aqueous phase is depleted. The polymerisation rate in this interval decreases gradually. These events are illustrated in Figure 2-7.
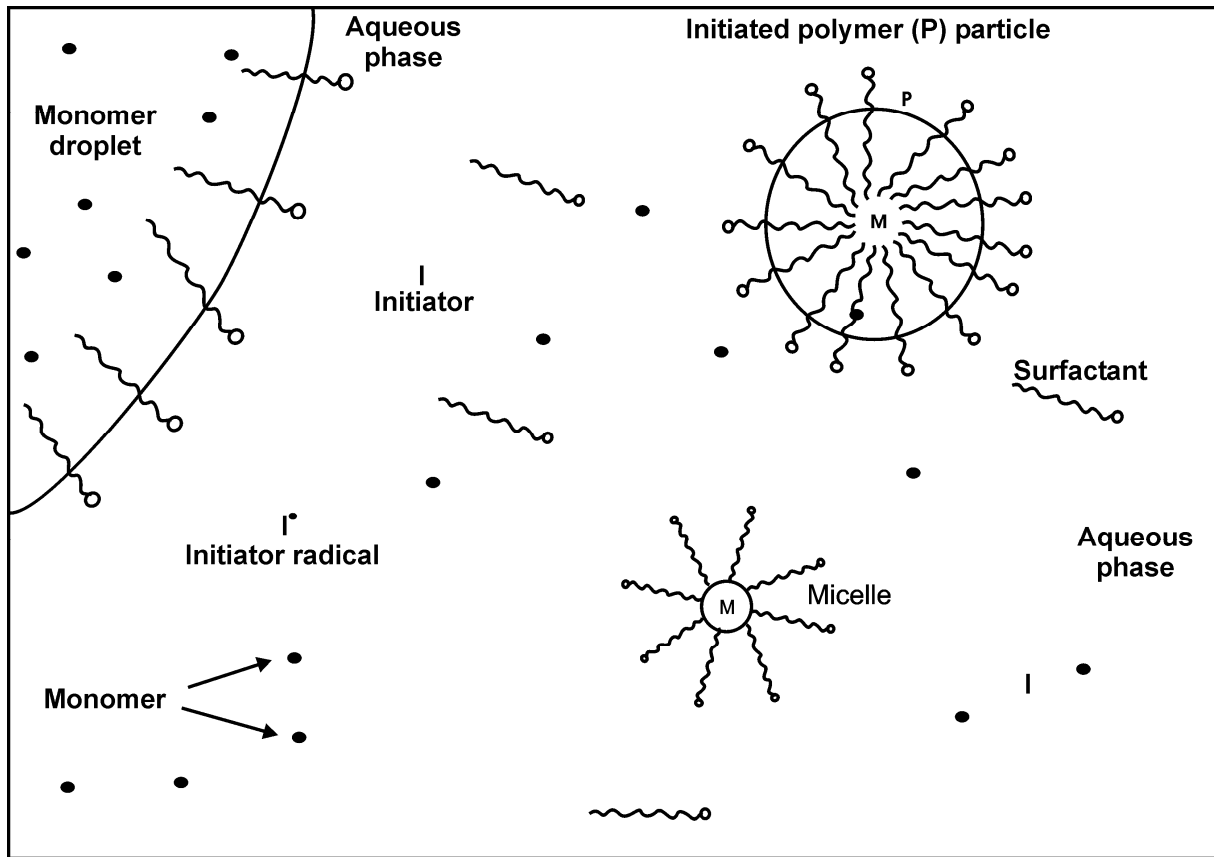
Figure 2-7. The various species present during emulsion polymerisation.

2.3.5.1. Generation of free radical oligomers

An important step preceding nucleation is the generation of free radical species. This process remains an important issue throughout the course of emulsion polymerisation reactions. The initiator introduced in the recipe is usually water-soluble, e.g. a persulphate, and dissociates in the aqueous phase to form free radical species, as indicated in equation 2-1.

$$S_2O_8^{2-} \longrightarrow 2SO_4^{-} {}^{\bullet} \qquad\qquad 2.1$$
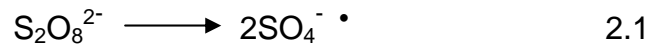
Where,

$SO_4^{-}{}^{\bullet}$ represents a sulphate radical which forms a sulphate end group

M   a monomer unit and

${}^{\bullet}$ a radical species.

29

The monomers, on the other hand, are sparingly water-soluble, although a sufficient amount of monomer is dissolved in the continuous phase to react with the formed radical species, as indicated in equation 2-2.

$$SO_4^{-\bullet} + M \longrightarrow SO_4^- M^{\bullet} \qquad 2.2$$

This results in "monomeric" radicals as shown above, which undergo free-radical polymerisation or even participate in transfer reactions. Due to the heterogeneous nature of emulsion polymerisation, processes such as the mass-transfer phenomenon between the continuous aqueous phase and the dispersed organic phase can also occur. The small oligomeric radicals may enter surfactant micelles and monomer droplets, accounting for particle nucleation. The entry of radicals in the particle phase or into already existing polymer particles is one of the key factors that leading to latex particle growth and controls emulsion polymerisation kinetics. The degree of water solubility and surface activity of the oligomeric radicals play important roles with regard to mass-transfer phenomena. The incorporation of monomer units into oligomeric radicals growing in the aqueous phase is limited by a critical degree of polymerisation, above which the polymer chains become surface active and irreversible entry occurs. Surface activity is dependent on the nature of the monomers available for polymerisation in water. Since a dynamic equilibrium between the aqueous phase and the dispersed organic phase probably exists, each oligomeric radical will be characterised by its own partition coefficient.

2.3.5.2. Particle formation

Nucleation, described as Interval I of emulsion polymerisation, is the period during which latex particles are formed. Goodall[86] suggests a nucleation mechanism dominated by micellar nucleation, where entry of oligomeric radicals occurs in surfactant micelles. However, this model is not obeyed by a wide range of monomers especially those that are significantly water-soluble. One of the first researchers to propose a homogeneous nucleation mechanism was Priest.[87] This mechanism was later quantitatively treated by Fitch and Tsai,[88] and Ugelstad and Hansen,[89] and developed into the HUFT theory (Hansen-Ugelstad-Fitch-Tsai

theory).[90] According to this model, radicals add monomer units in the aqueous phase until they exceed their water solubility, leading to precipitation, the absorption of solvent, and the formation of a precursor polymer particle. The monomer diffuses from the droplet phase to swell the newly formed latex particles and polymerisation proceeds further. Surfactant, originating from solution and from micelles, contributes to the colloidal stability of the newly nucleated particles.

A coagulative nucleation mechanism, which is just an extension of the homogeneous nucleation model, was proposed by Napper[91] and others. According to this mechanism, the precursor particles formed by homogeneous nucleation are not colloidally stable and therefore aggregate or coagulate to form mature stable latex particles which may grow further from monomer absorption and eventually surfactant adsorption. Nucleation is thus a very complex but important part of the emulsion polymerisation process. Actually, all mechanisms described above may occur simultaneously. The parameters determining which mechanism may dominate the others are the monomer solubility, the surfactant concentrations and the quality of monomer emulsification. For instance, homogeneous nucleation is considered to be the primary mechanism for monomers with high water-solubilities and/or low surfactant levels. Seeded emulsion polymerisation[92] generally follows heterogeneous nucleation since pre-formed latex is introduced to the reaction mixture right at the start of polymerisation.

2.3.5.3. Particle growth

Once the particles have been formed, the new polymer phase offers a destination for the monomer so that it partitions itself among the monomer droplets, the aqueous phase and the polymer particles. Particle growth occurs during the Intervals II and III defined in section 2.3.5. In these intervals nucleation would have ceased and the number of particles would be constant as they were at the end of Interval I. Each particle then behaves as a micro-reactor. During the polymerisation the particles are swollen with monomer at a rate, which is usually fast compared with the rate of consumption of monomer by polymerisation. The rate of swelling will depend upon diffusion of monomer from the emulsified monomer droplets through the aqueous phase into the polymer particles. At some stage of the polymerisation all the monomer droplets will have been consumed and the concentration of monomer in

the polymer particles decreases. This will be accompanied by a decrease in the rate of polymerisation.

2.3.5.4. Termination

Termination can often be quite complex, with several reactions occurring simultaneously in different loci. In one case, radical exit can occur through chain transfer to monomer. This occurs when the propagating free radical abstracts a hydrogen atom from the monomer, terminating its own growth and producing a monomeric radical as follows:

$$\text{Mp}^{\bullet} + \text{MH} \longrightarrow \text{Pp} + \text{M1p}^{\bullet} \qquad\qquad 2.3$$
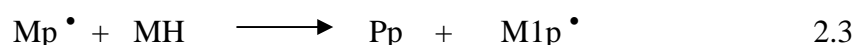
Where,

Mp • is the propagating oligomeric radical

MH the monomer showing the H abstracted

Pp the polymer formed and

M1p • is the new monomeric radical.

The product M1p• can easily diffuse out of the particle and into the aqueous phase, where it can undergo termination. Termination can also occur when a second radical enters a growing particle.

2.4. Control of the radical polymerisation process

Controlled radical polymerisation leads to the synthesis of polymers with tailor-made molecular masses and molecular mass distributions.[93] This type of polymerisation also leads to the synthesis of polymers with controlled polymer architecture such as block copolymers and branched and even star structures. Control of the polymerisation can be achieved through "living" polymerisation processes. For a polymerisation to be termed "living," radical-radical termination as normally occurs in free radical polymerisation should be negligible. Polymerisation conditions are thus selected so as to encourage chain transfer during polymerisation. Most methods for achieving "living" radical polymerisation can be used in the synthesis of block

copolymers and other structures of complex architecture. The use of these methods has however been limited by the fact that the processes are not always compatible with all monomers or reaction conditions.

In atom transfer radical polymerisation the use of conventional surfactants such as SDS results in high molecular mass and broad distributions.[94] Semi-batch conditions or mini-emulsions have been proposed to try to overcome some of the problems associated with the broad distributions.

2.4.1. Reversible Addition-Fragmentation Transfer (RAFT) agents

RAFT, as one of the methods for controlling radical polymerisation, offers versatility in providing polymers of predetermined molecular mass and very narrow polydispersities.[95] This is achieved by performing the polymerisation in the presence of chain transfer agents such as dithio compounds[96] which act as RAFT chain transfer agents to provide the polymerisation with living characteristics.   Unlike ATRP, which has limitations with monomers or initiators containing acid functionalities the RAFT method can be used with a wide range of monomers to prepare narrow-polydispersity block copolymers.   Some of the monomers that have been successfully RAFT polymerized are:

Acrylics such as Acrylic acid and methyl methacrylate,

Acrylamides such as N,N-dimethylacrylamide and acylamide,

Vinyl acetate and styrenes.

RAFT is also tolerant to monomers with functionalities such as –OH, -COOH and –NR$_2$.   It has can also be used in aqueous media. However, to obtain control of molecular weight with RAFT agents, the exchange between growing and dormant chains should be highly efficient.[97] Although RAFT polymerisation has been found to be very versatile in terms of suitable monomers, the process is rather slow. This is because the rate of transfer is much greater than the rate of propagation and only one monomer unit can be added per addition-fragmentation cycle. In conversional emulsion polymerisation inhibition periods in which little monomer is consumed have been reported.[98,99] Colloidal destabilisation of monomer droplets or latex particles early in the reaction has been reported in water dispersion systems.[100]   It has also

been reported that in water-borne dispersions, RAFT reactions reach a limiting conversion before suddenly ceasing polymerisation. [101]

The RAFT technique relies on a sequence of addition-fragmentation chain transfer reactions, as illustrated in Scheme 2-1.[102]
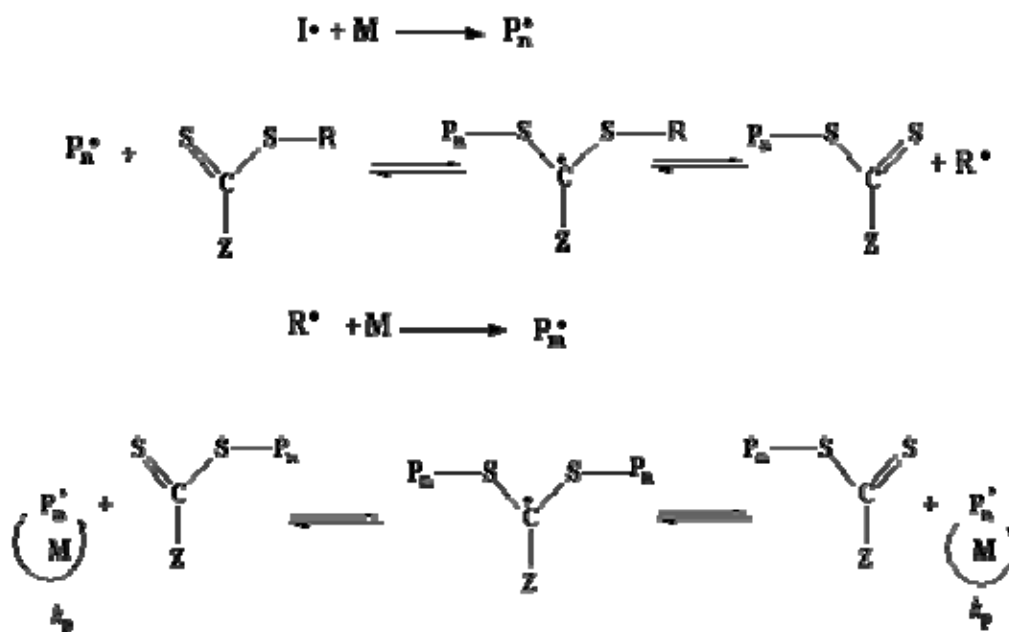
Scheme 2-1. Suggested mechanism for RAFT polymerisation.

Using a suitable initiator, an active species $P_n\bullet$ is produced and added to the RAFT agent, which in turn undergoes fragmentation, resulting in an oligomeric dithio compound, which then releases a radical $R\bullet$ and reinitiates polymerisation to give a new active species $P_m\bullet$. The active species adds to the oligomeric species and fragmentation follows, resulting in a new propagating radical $P_n\bullet$. The reversible addition-fragmentation sequence allows transfer between dormant and active chains and maintains the "living" character of the polymerisation as there is a large ratio of dormant to active chains. The majority of chains in the product polymer possess the RAFT moiety via which polymerisation can be continued in the presence of a second monomer, to give a block copolymer. A requirement for forming a narrow polydispersity AB block copolymer in a batch polymerisation is that the first-formed

polymeric dithio compound should have a high transfer constant in the subsequent polymerisation step, to give the B block.[103-104]

The amounts of RAFT agent and initiator are calculated as proposed by Rizzardo et al.[105] in the following equation:

$$M_n = M_{RAFT} + \frac{[M]_0 \cdot x \cdot M_m}{[RAFT]_0 + 2f[I]_0 \cdot \left(1 - e^{-k_d \cdot t}\right)}$$
2-4

where,

M_n is the target molecular mass of the polymer / oligomer [g/mol]

M_{RAFT} is the molecular mass of RAFT agent [g/mol]

$[M]_0$ is the initial concentration of monomer [mol/l]

M_m is the molecular mass of monomer [g/mol]

x is the fractional conversion of monomer

$[RAFT]_0$ is the initial concentration of RAFT agent [mol/l]

f   is the efficiency factor (fraction of initiator radicals that will form polymers)

$[I]_0$ is the initial concentration of the initiator [mol/l]

k_d is the dissociation rate constant of the initiator (dependent on the solvent and temperature) [s^{-1}]

t   is the time of reaction [s].

If the ratio of $[RAFT]_0$ to $[I]_0$ is chosen as 100:1, and $[I]_0$ in Equation 2.4 is substituted with $100 \cdot [RAFT]_0$, and if the initiator efficiency for AIBN is chosen with an efficiency factor f of 0,7, then Equation 2.4 can be written as Equation 2.5:

$M_n = M_{RAFT} + \{[M]_0 \cdot x \cdot M_m\} / \{[RAFT]_0 + (2 \times 0{,}7) \times 100 [RAFT]_0 \cdot (1 - e^{-k_d \cdot t})\}$ 2-5

If $[RAFT]_0$ is made the subject of Equation 2-5 to calculate the initial concentration of the RAFT agent, Equation 2-6 results.

$[RAFT]_0 = \{[M]_0 \cdot x \cdot M_m\} / \{M_n - M_{RAFT}\} + \{1 + (2 \times 0{,}7) \times 100 [RAFT]_0 (1 - e^{-k_d \cdot t})\}$ 2-6

From this, the amount of RAFT agent and thus the initiator concentration can be calculated.

2.5. Functionalised polymer latices

Functionalised latices are those that have chemical moieties incorporated in them. The extent of the functionalisation generally differs from polymer molecule to polymer molecule although a random distribution of functional groups is generally aimed for. One way of achieving this is by selecting reaction conditions that allow the desired functional group to be copolymerised with other monomer units in a random manner. In emulsion polymerisation, monomer units bearing such functional groups do not always enter the polymer in a random manner as required because of the following constraints:

- functionalising monomer may be withheld until nearly the end of the polymerisation reaction, during which time it may enter the polymer, and
- reaction conditions may be such that the functionalising monomer may partition strongly in favour of the dispersion medium rather than the reaction loci and will tend to homopolymerise in that medium, if it does at all.

This phenomenon has been reported with aqueous carboxylated latices in alkaline conditions.[106]

2.5.1. Carboxylated latices

The most important chemical grouping used to functionalise polymer latices is the carboxylic acid moiety, which is generally incorporated to give carboxylated latices. Other functional groups that have been used include sulphonates, hydroxyl moieties and amino moieties. The study of functionalised latices has been encouraged by the realisation that, besides such polymers offering interesting latex properties, modifications of the functional groups are also possible, and this can be made use of in a wide range of reactions.

2.5.1.1. Mechanism of carboxylated latex formation

Most monomers usually partition between the continuous aqueous phase, the monomer droplets and the latex particles. However, due to the hydrophilic nature of carboxylic monomers and polymers, initiation takes place in the aqueous phase

where the monomer concentration is higher than in conventional systems. In some cases, monomer concentration influences the polymerisation rate through interaction of the monomer with the initiator itself or with the initiator-derived radicals trapped in a "solvent cage" [107]. This behaviour can be expected to have a significant influence on the rate of free radical generation. Carboxylic monomers are generally used as functional comonomers in the emulsion polymerisation of monomers with low water solubility. The polymerisation scheme in the aqueous phase is therefore complicated by the presence of more than one monomer and by the relatively high overall monomer concentration in the continuous phase. As described in Sections 2.1.2 and 2.1.3, the water solubility and the surface activity of the oligomeric radicals formed in the aqueous phase play very important roles in the nucleation process and in the radical transfer from the aqueous phase to the particle phase. However, aqueous phase polymerisation is difficult to study in emulsion polymerisation due to the presence of the discontinuous particle phase and the partitioning of all (oligomeric) species between the phases involved. Further, the relatively low concentrations of oligomeric species hamper a detailed mechanistic study because these species cannot be isolated and characterised. Therefore mechanistic information about the aqueous phase in emulsion polymerisation processes can generally not be directly obtained. There are still problems in trying to attain high carboxylic group contents in emulsion systems, as it is difficult to maintain emulsion stability with high acid content.

2.5.1.2. Acid group distribution

Acid groups can be present in latex products as follows:
- incorporated into copolymer chains inside the polymer particles, i.e. buried,
- in copolymer chains but residing in the outer shell of the polymer particles, i.e. at or near the particle surface,
- in surface active copolymer chains physically adsorbed onto the polymer particle surface, i.e. acting as adsorbed surfactant molecules,
- in water-soluble copolymer chains with a low surface activity, i.e. dissolved in the aqueous phase, or
- homopolymerised in the aqueous phase.

The final distribution of acid groups in latex products is however controlled by several factors, the most important of which are:

- the reactivities of the monomers, the hydrophilicity of the carboxylic acid monomer and its partitioning behaviour,
- the pH of the reaction mixture, and
- the manner in which the monomers, and more particularly the functional carboxylic ones, are supplied to the reaction mixture.

Useful mechanistic information can be obtained from the determination of the acid group distribution. Effective entry of acid-rich oligomeric radicals will mainly result in the incorporation of acid groups chemically bound to the polymer molecules in the latex particles. Monomer units partitioned into the latex particles will copolymerise and remain buried inside the particles. After transfer or termination in the aqueous phase, oligomeric radicals will remain dissolved in the aqueous phase or will adsorb onto the surface of the latex particles, depending on their surface activity, and therefore on their chemical composition.

2.6. Cleaning of latices

A number of experimental techniques have been used in the study of carboxylated latices. These include the procedures used in the synthesis and purification of carboxylated latices and those used in the characterisation of the latices. Due to the heterogeneous nature of emulsion polymerisation reactions, the products have to be cleaned before any characterisation is undertaken. The products may contain undesirable species such as initiator fragments, oligomeric species, polyelectrolytes and added buffers, which make characterisation difficult. Some of the methods for cleaning latices have been described in the literature.[108]

2.6.1. Use of ion-exchange resins to clean latices

Most polymer colloids carry charges generated by ionic functional groups introduced during polymerisation. A mixed-bed, ion-exchange resin removes all electrolyte (polymeric and small ions) from the products and it exchanges all the counterions for H^+ in the case of anionic particles and OH^- in the case of cationic particles. The removal of ionic surfactant from the latex during ion exchange may induce

coagulation if the residual surface charge density is low and particle size is small. These two effects can:

- reduce the solids content, which, if not measured after ionic exchange, will lead to gross errors, and
- lead to errors in particle size distributions for systems which are not monodisperse.

2.6.2. Use of dialysis and serum replacement to clean latices

One way of cleaning latices is by dialysis through a semi-permeable membrane. The membrane is expected to be permeable to small molecules, ions and oligomers, but not to colloids. The water in which the dialysis tube is placed is replaced periodically and the conductivity of the dialysate recorded. It usually takes weeks to obtain clean latices. Latices are considered clean when the water conductivity remains constantly low.

In serum replacement, pure water is added to latex to dilute the serum, which is then continuously forced out through the membrane. Measurement of the surfactant concentration is done conductometrically. Clean latex is indicated by low conductivities, as close to that of deionised water as possible.

2.6.3. Use of centrifugation to clean latices

In some cases, even dialysis and the use of ion-exchange resins may not be sufficient to remove contamination from latex, hence the use of ultracentrifugation is also considered. This technique involves the use of an ultracentrifuge in which the latex is spun down to a pellet. The supernatant serum is then decanted and the particles redispersed with ultrasound into clean deionised water. This is repeated until a constant titre is obtained with a suitable titrant. The major disadvantage associated with the use of this cleaning method is that adsorbed stabilisers might be removed. The method is therefore useful only for latices of high stability.

2.7. Surface functionality

The control and characterisation of the surface properties of latex are often required in efforts to better understand the properties of the latex. Properties of latices

influence their behavior and dictate how they should be handled in manufacturing processes, for their prospective uses, for example, the formation of films, as coatings, or for use as model colloids. Because of the small size of a latex particle, the high surface area/volume ratio means that a particle's properties are largely influenced by its surface characteristics. The complete characterisation of latex requires the determination of the surface charge density and identification of the source of that charge because this plays such an important function in the colloidal properties of the latex and its stability, as reported by Zhao et al.[109] and Ottewill.[110] Much care needs to be taken with characterising polymer latices because the surface chemistry may be changed by the cleaning method employed, or simply from prolonged storage.

Surface functionality can be introduced by means of the addition of a functional monomer in a reaction recipe, or by using techniques such as copolymerisation or "shot growth"-type addition, as reported by Sakota et al.[111] In Fitch's review of polymer colloids,[88] it is suggested that in order to bring about functionality at the particle surface, the comonomer should be surface active and insoluble in both the polymer and in water. A study by Vijayendran[112] looked at the carboxylation of polystyrene. In the study the effect of hydrophobicity in a number of carboxylated acidic monomers, e.g. itaconic acid (IA, $CH_2=C(COOH)CH_2COOH$), acrylic and methacrylic acids (i.e., AA and MAA, respectively) was investigated. It was found that the more hydrophobic acid (and thus the most soluble in styrene) concentrated at the particle core during the polymerisation in the order MAA > AA > IA. The ease of diffusion of the MAA into the styrene was cited as the reason, also noting the lower reactivity of the IA. In a study by Hoy[113] and co-workers carried out to investigate the way a carboxylated monomer was added in an industrial set-up, the results showed that the method of addition had little effect on where the carboxyl groups would be finally located.

Post-polymerisation reactions may also be used to modify surface functionality. One important reaction of this type is the oxidation of hydroxyl end-groups to carboxyl groups[114], which is made use of in latex surface characterisation. In addition to being steric stabilisers, surfactants and emulsifiers can also contribute to stabilising surface charge density due to hydrophilic end groups. Surface species may also be grafted

onto the particles, thus increasing the surface charge density as reported by Ryan[115] and Pelton[116].

In a study conducted by Stone-Masui and Watillon[117], latices prepared in the presence of sodium alkyl sulphate or sulphonate surfactants were shown, after cleaning by ion exchange, to contain only strong acid groups. When the same latices were prepared in the presence of potassium stearate or sodium laurate however, they were found to contain weak acid groups in addition to the strong acid groups. This may suggest that not all latices can be cleaned by some methods and tests may need to be carried out before one subjects a large quantity of latex to an untried cleaning method. In a study by Fitch and MacCarvill[118], analysis of surface groups of latex particles showed that sodium dodecyl sulphate and sodium dodecyl sulphonate contributed considerably to the number of chemically bound sulphate and sulphonate groups respectively.

2.8. Characterisation of a polymer latex

2.8.1. Surface charge density

The most common methods used to determine charge density of polymer latex are conductometric titrations with acid or base[119]. The slopes of the titration curves obtained can provide information regarding the nature of the surface groups and the purity of the latex. The equivalence point is readily obtained by extrapolation of the linear points of the titration curves. Experimental data from the procedure are used to calculate the charge density on the surface of a latex particle. A sharp end-point is characteristic of strong acid groups.

2.8.2. Light scattering

Polymer latices can be characterised by their effect on collimated light rays.[120] As the refractive index of the disperse phase is different from that of the medium, latex will display the Tyndall effect, which occurs when the size of particles that cause scatter are larger than the wavelength of the radiation that is scattered, resulting in the latex showing a bluish colour. Static and dynamic light scattering can be used for the characterisation of latex particles, especially in determining particle size and polydispersity. The mean diameter of the particle population and the percentage

coefficient of variation in the diameter of the particles are based on measurements of about 500 particles or until further counting does not change the distribution. The measurements also indicate whether the particle population is monodisperse. Neutron scattering[121] can also be used to determine the dimensions of a surface such as the lyophilic layer, which serves as a steric stabiliser for latex particles.

2.8.3. Microscope analysis

As latex particles are about 10 nm to 1000 nm in size, transmission electron miscroscopy (TEM) can be used to investigate the morphology and composition of latex particles. Scanning electron microscopy (SEM) is used to investigate the surface of the particles. TEM can also be used to determine the size of latex particles. Sample preparation for TEM involves microtomy and staining, whereas no special sample preparation is necessary for SEM. Atomic force microscopy (AFM) can also be used to examine film surfaces.

2.8.4. Nuclear magnetic resonance spectroscopy (NMR)

NMR spectroscopy has been used to investigate the composition of latices by looking at chemical shift patterns. Signals are observed only when the polymer is in solution.

2.8.5. Gel permeation chromatography (GPC) analysis

Gel permeation chromatography has been successfully used as a method to determine molecular mass and molecular mass distributions of polymers. GPC is a form of liquid chromatography in which molecules are separated into their respective molecular sizes. In this process, a dilute solution of a polymer is injected into a continuous flow of solvent passing through a column containing microporous gel particles. Larger molecules cannot permeate within the porous beads of the column as readily as the small ones, so that the larger molecules cannot pass through small pores and are thus eluted first, while small molecules need higher elution times. It is important to make a suitable selection of packings for the different columns. Different molecular fractions have different elution volumes V_E, which is the volume of solution eluted and is related empirically to the interstitial volume V_O and to the volume of liquid within the pores V_i as shown in equation 2-7:

$$V_E = V_O + k\,V_i \qquad\qquad 2.7$$

Where, k is a distribution coefficient, which indicates the relative ease with which solute molecules penetrate into the pores of the gel.

Although GPC is generally used for most of the molecular mass and MWD measurements, the results are not entirely accurate because it is not an absolute method. The method needs to be calibrated using standards such as PS or PMMA of low polydispersity, which differ chemically, and therefore have different hydrodynamic volumes in the eluent than the sample being measured. Thus unless a universal calibration is used, results are relative.

2.8.6. Stability of emulsions

The stability of latices is measured by the extent of the response of latex to agents of instability, such as the addition of electrolytes, freeze-thaw cycles, ultracentrifugation, pH changes, temperature changes and even ageing.

Current research is still centred on investigating optimum conditions for the production of stable latices using sustainable and environmentally friendly materials.

2.9. References

1. Kawaguchi S., Winnik M.A., Ito K., Macromolecules **1995**, 28, 1159.
2. Fonnum G., Bakke J., Hansen F.H., Colloid Polym. Sci. **1993**, 271, 280.
3. Schulz D.N., Glass J.E., "Polymers as Rheology Modifiers" ACS. Symp. **1991**, 462, 18.
4. Landfester K., Bechthold N., Tiarks F., Antonietti M., Macromolecules **1999**, 32, 2679.
5. Guyot A., Tauer K., Asua J.M., Van Es S., Gauthier C., Hellgren A.C., Sherrington D.C., Montoya-Goni A., Sjoberg M., Sindt O., Vidal F., Unzue M.J., Schoonbrood H.A.S., Shipper E., Lacroix-Desmazes P., Acta Polym. **1999**, 50, 57.
6. Schoonbrood H.A.S., Asua J.M., Macromolecules **1997**, 30, 6034.
7. Vidal F., Guillot J., Guyot A., Colloid Polym. Sci. **1995**, 273, 999.
8. Schoonbrood H.A.S., Unzue M.J., Ole-Jacob B., Asua J.M., Macromolecules **1997**, 30, 6024.

9.   Greene B.W., Saunders F.L. J., Colloid Interface Sci. **1970**, 33, 393.

10.   Anton P., Koberle P. L., Laschewsky A., Makromol Chem. **1993,**194,1.

11.   Asua J.M., Schoonbrood H.A.S., Macromolecules **1997**, 30, 6034.

12.   De La Cal J.C., Asua J.M., J. Polym. Sci., A, Polym Chem. **2001**, 39, 585.

13.   Takahashi K., Nagai K., Polymer **1996**, 37, 1257.

14.   Guyot A., Goux A. J. Appl. Polym Sci. **1997**, 65, 2289.

15.   Guillaume J.L., Pichot C., Guillot J. Polym. Sci. Polym. Chem. Ed. **1990**, 28, 137.

16.   Charleux B., Pichot C. Polymer **1993**, 34, 195.

17.   Tsaur S.L., Fitch R.M., J. Colloid Interface Sci. **1987**, 115, 450.

18.   Soula O., Guyot A., Williams N., Grade J., Blease T., J. Polym. Sci., Polym. Chem. Ed. **1999**, 37, 4205.

19.   Vanderhoff J.W., Pure & Appl. Chem. **1980**, 51, 1263.

20.   Greene B.W., Sheetz D.P., J. Colloid Interface Sci. **1970**, 32, 96.

21.   Ottewill R.H., Satgurunathan R., Waite F.R., Westby M. J., Brit. Polym. J. **1987**, 19, 435.

22.   Rosen M.J., Wang H., Chen P., Zhu Y. Langmuir **2005**, 21, 3749.

23.   Rodehuser L., Chaumette H., Meyers A., Rogalska e., Gerardin C., Selve C. Amino acids **2000**, 18, 89.

24.   Tang R.H., Chacrabarti P.M. US Patent **1994**, 5296627.

25.   Dreja M., Tieke B. Macromol. Rapid Comm. **1996**,17, 825.

26.   Soula O., Petiaud R., Llauro M-F., Guyot A., Macromolecules 1999, 32, 6938.

27.   Urquiola M.B., Dimonie V.L., Sudol E.D., El Aasser M.S., J. Polym. Sci., Polym. Chem. Ed. **1992**, 30, 2619.

28.   Juang M.S., Krieger I.M., J. Polym. Sci., Polym. Chem. Ed. **1976**, 14, 2089.

29.   Tauer K., Goebel K.H., Kosmella S., Stahler K., Neelsen J., Makromol. Chem. Macr. Symp. **1990**, 31, 107.

30.   Urquiola M.B., Dimonie V.L., Sudol E.D., El Aasser M.S., J. Polym. Sci., Polym. Chem. Ed. **1992**, 30, 2631.

31.   Greene B. W., Sheetz D.P., Filer T.D., J. Colloid Interf. Sci. **1970**, 32, 90.

32.   Chen S.A., Chang H.S., J. Polym Sci., Polym. Chem. Ed. **1985**, 23, 2615.

33.   Montoya-Goni A., Sherrington D.C., Schoonbrood H.A.S., Asua J.M., Polymer **1999**, 40, 1359.

34.   Pattern T.E., Matyjaszewski K., Adv. Mater. **1998**, 10, 901.

35. Moad G., Chiefari J., Chong Y.K., Polym. Int. **2000**, 49, 993.

36. Ito K., Ono H., Yamashita Y., J. Coll. Sci. **1997**, 19, 28.

37. Isihara K., Tsuji T., Sakai Y., Nakabayashi N., J. Polym. Sci., Polym. Chem. Ed. **1994,** A32: 859.

38. Chen S.A., Hua M.Y., Macromolecules **1993**, 26. 7108.

39. Pratten M.K., Lloyd J.B., Horpel G., Ringsdorf H., Makromol. Chem. **1985**,186, 725.

40. Piirma I. "Polymeric surfactants and polymer colloid stabilization" in: The Polymeric Materials Encyclopedia, **1996**, CRC, New York.

41. Wanka G., Hoffmann H., Ulbricht W., J. Colloid Polym. Sci. **1990**, 268, 101.

42. Wesslen B., Wesslen K.B., J. Polym. Sci., Polym. Chem. Ed. **1992**, A30, 355.

43. Kim Y.H., Webster O.W., J. Am. Chem. Soc. **1990**, 112, 4592.

44. Soldi V., De Magalhaes E.N., Quina F.H., J. Am. Chem. Soc. **1988**, 110, 5137.

45. Arai K., Yamazaki K., Polymer **1993**, 25, 1169.

46. Creutz S., Jerome R. Langmuir **1999**,15, 7145.

47. Pirma I., Lenzotti J.R. J. British Polymer **1989**, 21, 45.

48. Forster S., Plantenberg T. Angew Chem. Int. Ed. **2002**, 41, 688.

49. Forster S., Antonietti M. Adv. Mater. **1998**,10, 195.

50. Okube T., Ise N. J.,Org. Chem. **1973**, 38, 3120.

51. Piirma I., Lenzotti J.R., British Polymer J. **1989**, 21, 45.

52. Ruckenstein E., Langmuir **1996**, 12, 6351.

53. Shih L.B., Shen E.Y., Chen S.H., Macromolecules **1988**, 21, 1387.

54. Binana –Limbele W., Zana R., Macromolecules **1988**, 23, 2731.

55. Kobayashi K., Sumitomo H., Macromolecules **1980**, 13, 234.

56. Gabizon A.A., J. Contr. Release **2001**, 73, 137.

57. Yalkowsky S.H., Techniques of Solubilization of Drugs. **1981**, Dekker. Inc. N.Y.

58. Levashov A.V., Pure & Appl. Chem. **1992**, 8, 1125.

59. Lian T., Ho R.J.Y. J. Pharm. Sci. **2001**, 90, 667.

60. Harada A., Kataoka K. Science, **1999**, 283, 5398.

61. Yasugi K. Nagasaki Y., Kato M., Kataoka K. J. Contr. Release **1999**, 62, 89.

62. Yeoh K.W., Chew C.H., Gan L.M., Koh L.L., J. Macromol. Sci. Chem. A27, **1990**, 6, 711.

63. Chew C.H., Gan L.M., J. Polym. Sci. Polym. Chem. Ed. **1985**, 23, 2225.

64. Oertel U., Buchhanmer H-M., Müller M., Nagel J., Braun H. G., Eichhorn K-J., Sahre K., Macromol. Symp. **1999**, 145, 39.

65. Liu S., Armes S.P., Langmuir **2003**, 19, 4432.

66. Bütün V., Billingham N.C., Armes S.P., J. Am. Soc. **1998**, 120, 11818.

67. Baska G., Landfester K., Antonietti M., Macromolecules **2000**, 33, 9228.

68. Burguire C., Pascual S., Coutin B., Macromol. Symp. **2000**, 150,39.

69. Drescher B., Scranton A.B., Klier J., Polymer **2001**, 42, 49.

70. Banez de P., Robinson K.L., Armes S.P., Macromolecules **2000**, 33, 451.

71. Li G., Yates M.Z., Johnson K.P., Lim K.T., Webber S.E., Macromolecules **2000**, 33, 1606.

72. Sommerdijk N.A.J.M., Holder S.J., Hiorns R.C., Jones R.G., Nolte R.J.M., Macromolecules **2000**, 33, 8189.

73. Zhang Q., Remsen E.E., Wooley K.L., J. Polym. Sci., Polym. Chem. **2000**, 38, 4805.

74. Zhang Q. , Remsen E.E., Wooley K.L., J. Am. Chem. Soc. **2000**, 122, 3642.

75. Fujimoto C. J., Chromatogr. A 871, **2000**, 415.

76. Gilbert R.G., Emulsion polymerisation: A Mechanistic Approach. Eds. Ottewill & Rowell, Academic Press, **1995.**

77. Luo Y., Tsavalas J.G., Schork F.J. Macromolecules **2001**, 34, 5501.

78. Landfester K., Bechhold N., Tiarks F., Antonietti M. Macromolecules **1999**, 32, 5222.

79. Landfester K., Bechthold N., Foster S., Antonietti M. Macromol. Rapid Commun. **1999**, 20, 81.

80. Choi Y. T., Sudol E.D., Vanderhoff J.W., El-Asser M.S. J. Polym. Sci. Polym. Chem. Ed. **1985**, 23, 2973.

81. Anderson C.D., Sudol E.D., El-Aasser M.S. Macromolecules **2002**, 35, 574.

82. Shielmi A., Storti G., Morbidelli M., Chem. Eng. Soc. **2001**, 56, 937.

83. Harkins W.D., J. Am. Chem. Soc. **1997**, 69, 11428.

84. Smith W.V., Ewart R.H., J. Chem. Phys. **1948**, 16, 592.

85. Piirma I., Polymeric surfactants: Surfactant Science Series **1992**, vol 42, Marcel Dekker, New York.

86. Goodall A.R., Wilkinson W.C., Hearn J., J. Polym. Sci. Polym. Chem. Ed. **1977**, 15, 2193.

87. Priest W.J., J. Phys. Chem. **1952**, 56, 1077.

88. Fitch R.M., Tsai C.H., in: Polymer Colloids **1971**, Ed. Fitch R.M., N.Y.

89. Ugelstad J., Hansen F.K., Rubber Chem. Technol. **1976**, 49, 536.

90. Hansen F.K., Ugelstad J., Emulsion Polymerisation, Piirma I., Ed. **1982**, Academic Press, NY.

91. Napper D.H., Gilbert R. G., J. Polym, Sci., Polym, Ed, **1979**, 16, 1953.

92. Hansen F.K., Ugelstad J., J. Polym, Sci., Polym, Chem. Ed. **1979**, 17, 3047.

93. Gaynor S., Qiu J., Matyajaszewski K., Macromolecules **1998**, 31, 5951.

94. Rizzardo E, et al. Patent no. PCT/AU98/00569, **1998.**

95. Hawthorne D.G., Moad G., Rizzardo E., Thang S.H., Macromolecules **1999**, 32, 5457.

96. Thang S.H., Chong Y.K., Roshan T., Mayadunne A., Moad G., Rizzardo E., Tetrahedron Letters **1999**, 40, 2435.

97. Tang C., Kowalewski T., Matyjaszewski K. Macromolecules **2003**, 36, 8587.

98. Wang A.R., Zhu S., Kwak Y., Goto A., Fukuda T., Monteiro M.J. J. Polym. Sci. Polym. Chem. Ed. **2003**, 41, 2833.

99. Monteiro M.J., de Brouwer H. Macromolecules **2000,** 34, 349.

100. De Brouwer H., Monteiro M.J. Macromolecules 2000, 33, 9239.

101. Tonge M.P., McLeary J.b., Vosloo J.J., Sanderson R.D. Macromol. Symp. **2003**, 193, 289.

102. Chiefari J., Chong Y.K., Ercole F., Krstina J., Le T.P., Mayadunne R.T.A., Meijs, G.F., Moad G., Moad C.L., Rizzardo E., Thang S.H., Macromolecules **1998**, 31, 559.

103. Le T.P., Moad G., Rizzardo E., Thang S.H., PCT Int. Appl. WO 9801478 A1 980115, Chem Abstr. **1998**, 128, 115390.

104 Chong Y.K., Le T.P., Moad G., Rizzardo E., Thang S.H., Macromolecules **1999**, 32, 2071.

105 Rizzardo E., Chiefari J., Chong B.Y.K., Ercole F., Krstina J., Macromolecular Symposia **1999**, 143, 291.

106. Tang J., Ding T., Daniels E.S., Dimonie V.L., Klein A., El-Aasser J. Appl. Polym. Sci. **2003**, 88, 30.

107. Tanko M.J., Pacut R., J. Am. Chem. Soc. **2001**, 123, 5703.

108. Yates D.G., Ottewill R.H., Goodwin J.W., J. Colloid & Interface Sci. **1977**, 62 (2) 356.

109. Zhao C-L., Holl Y., Pith T., Lambla M., Br. Polymer J. **1989**, 21, 155.

110. Ottewill R.H., "An Introduction to Polymer Colloids," Eds F.Candau & R.H. Ottewill, **1990**, 129.

111. Sakota K., Okaya T., J. Appl. Polym. Sci. **1976**, 20 (3) 1735.

112. Vijayendran B.R., J. Appl. Polym. Sci. **1979**, 23, 893.

113. Hoy K.L., J. Coat Technol. **1979**, 51, 27.

114. Gan L.M., Chew C.H., Yeoh K.W., J. Colloid & Interface Sci. **1990**, 137, 597.

115. Ryan K., Chem. Ind.**1988**, 359.

116. Pelton R., "Scientific Methods for the study of Polymer Colloids and their Applications," Eds. F. Candau & R.H. Ottewill, **1990**.

117. Stone-Masui J., Watillon A., J. Colloid & Interface Sci. **1975**, 52 (3) 479.

118. Fitch R.M., MacCarvill W.T., J. Colloid Sci. **1978**, 66 (1) 20.

119. Laaksonen J., Le Belle J.C., Stenius P., J. Electroanal. Chem. **1973**, 64, 207.

120. Kaye W.J., Colloid & Interface Sci. **1973**, 44, 384.

121. Matsuoka H., Ikada T., Yamaoka H., Hashimoto M., Takahashi T., Agamalian M.M., Wignall G. D., Langmuir **1999**, 15, 293.

CHAPTER 3

Synthesis and Characterisation of

Surfactant Monomers

3.1. Introduction

The synthesis of polymerisable surfactants (surfmers) involves the incorporation of a polymerisable functional group into the surfactant molecule. The selected surfmer 12-acryloyloxydodecanoic acid (12-ADA) was prepared by the esterification of a hydroxy acid, using a modified version of the method described by Finkelmann et al.[1] The surfmer 11-acrylamidoundecanoic acid (11-AAUA) and its corresponding sodium salt were prepared according to the method of Fujimoto.[2]

3.2. Experimental

3.2.1. Materials

The materials required for the synthesis of 12-ADA and 11-AAUA and their corresponding Na salts are tabulated in Table 3.1.

3.2.2. Equipment

Infrared spectra were recorded on a Perkin Elmer FT-IR Paragon model 1000 using NaCl windows.

Proton NMR spectra were obtained on a 300 MHz Varian VXR equipped with a Varian magnet or on a 600 MHz Varian Unity-Inova carrying an Oxford magnet.

Electron spray mass spectra (ESMS) were obtained on a Micromass Quattro (UK). Methanol was used to dilute the samples. A Rheodyne injector was used and the flow rate was 15 -20 μl/min.

Table 3-1. Materials used for the synthesis of 12-ADA, 11-AAUA and their Na salts

Surfactant to be prepared	Materials	Supplier and material state
12-ADA	11-hydroxydodecanoic acid	(Sigma) as supplied
	triethylamine	(Acros) as supplied
	dichloromethane	(Merk) as supplied
	acryloyl chloride	(Sigma) as supplied
	NaOH	(Sigma) as supplied
	Conc. HCl	
	Silica gel	
12-ADA Na salt	12-ADA	Prepared as described in Section 3.3.
	absolute ethanol	Dried as explained in Section 3.4
	NaOH	
	Mg	
	CCl_4	
11-AAUA	11-Aminoundecanoic acid	(Sigma) as supplied
	acryloyl chloride	(Sigma) as supplied
	dil. HCl	
11-AAUA Na salt	11-AAUA	Preparation as described in Section 3.5.
	dry absolute ethanol	Dried as explained in Section 3.4
	NaOH	

3.3. Synthesis of 12-acryloyloxydodecanoic acid

The 12-ADA and its sodium salt were prepared according to Scheme 3-1.
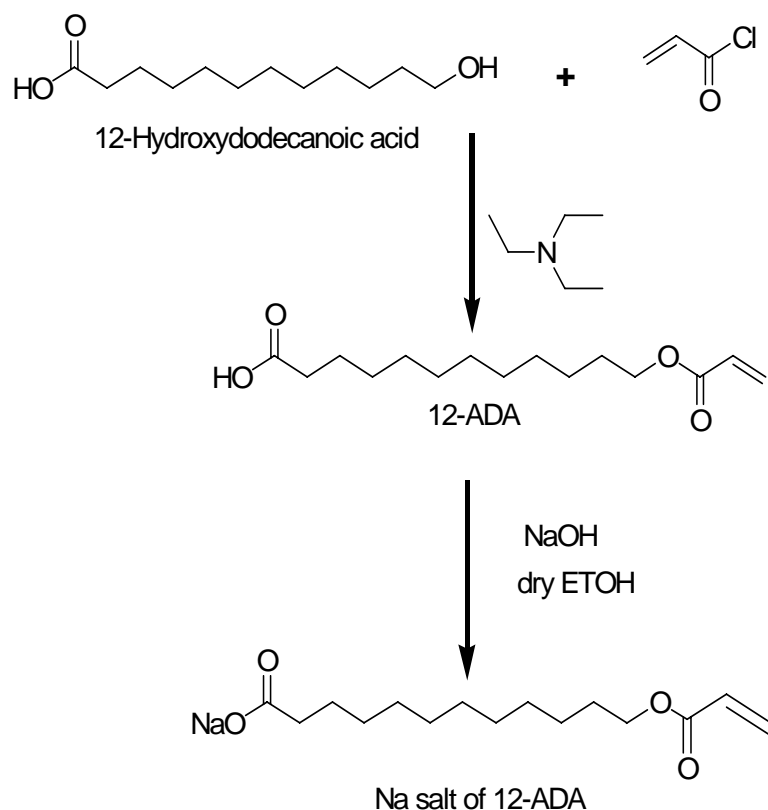
Scheme 3-1. Reaction scheme for the preparation of 12-ADA and its Na salt.

3.3.1. Experimental procedure

To 10 g (46,2 mmol) of 12-hydroxydodecanoic acid, 25,8 ml (184,9 mmol) of triethylamine was added and the mixture dissolved in 40 ml CH_2Cl_2. In a round-bottomed flask 16,7 ml (184,9 mmol) acryloyl chloride was dissolved in 22 ml CH_2Cl_2. The former mixture was then very slowly added to the acryloyl chloride solution, with stirring at -5 ºC. The resultant mixture was left to stir at 0 ºC for 24 hours. After this period, 11,3 g (282 mmol) of NaOH was dissolved in 25 ml distilled water and added to the mixture, with stirring, at -5 ºC. The reactants were then left to stir for a further 40 minutes. The resulting mixture was acidified, by slowly adding concentrated HCl, at -5 ºC, until the pH was about 1. The CH_2Cl_2 was removed in the dark to reduce the chances of premature polymerisation. The solid yellow product was then washed with cold water before being dried overnight in a vacuum oven at room temperature.

3.3.2. Purification of 12-ADA

The dry surfmer was dissolved in a mixture of 4:1 acetone/methanol, filtered and run through a 60-cm-long chromatographic column packed with silica gel, using an acetone/methanol solvent mixture. Different fractions were collected and verified using thin-layer chromatography. The total yield was 76%. Solvent was removed under vacuum in the dark, to avoid unwanted polymerisation. The product was analysed using proton NMR spectroscopy. The first fraction that emerged from the column proved to be 12-ADA.

3.4. Synthesis of the sodium salt of 12-ADA.

The surfmer 12-ADA was converted to its corresponding sodium salt using the procedure illustrated in Scheme 3-1.

Ethanol was dried as follows. First a mixture of the following was boiled under reflux for about 2 hours: 1 ml carbon tetrachloride, 5 g Mg and 50 ml absolute ethanol. Later, 950 ml absolute ethanol was added and the mixture refluxed for about 5 hours, after which it was distilled directly into a flask containing size 3 molecular sieves.

The sodium salt of 12-ADA was prepared by mixing 60,04 mol of surfmer dissolved in 300 ml of the dry absolute ethanol (prepared as described above), with NaOH dissolved in dry ethanol. The solution was stirred overnight at room temperature, after which solvent was removed under vacuum, in the dark. The product was dried in a vacuum oven at room temperature.

3.4.1. The critical micelle concentration of 12-ADA.

The sodium salt of 12-acryloyloxydodecanoic acid was dissolved and diluted in distilled water to prepare solutions of different concentrations. The surface interfacial tensions of the respective solutions were measured by using a torsion balance. The surface tension decreased with concentration until it remained constant. The results of the measurements are illustrated in Figure 3-1.
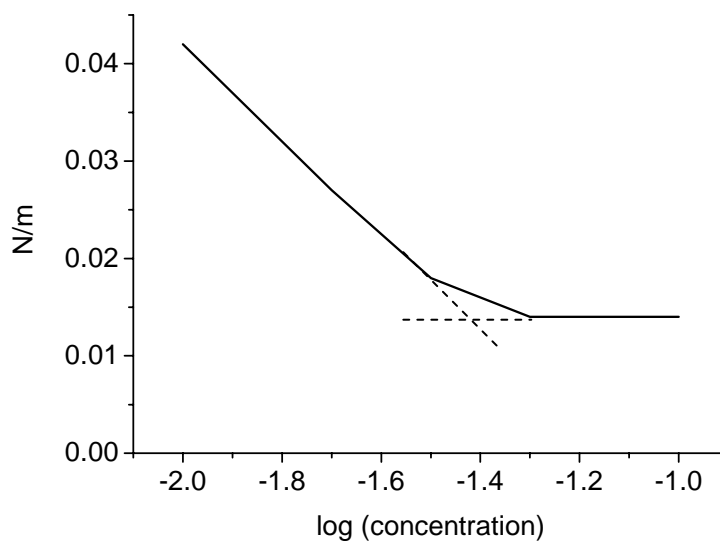
Figure 3-1. The critical micelle concentration of 12-ADA Na determined using a torsion balance.

3.5. Synthesis of 11-aminoundecanoic acid

3.5.1. Experimental procedure

The surfmer 11-AAUA and its sodium salt were prepared according to the procedure illustrated in Scheme 3-2. An aqueous solution of ethanol (250 ml absolute ethanol / 35 ml distilled water) was used to dissolve 10 g (50 mmol) 11-aminoundecanoic acid. To this solution, 6 g (150 mmol) of NaOH was added carefully, and dissolved. Then 6 ml acryloyl chloride (72 mmol) was added dropwise and the reaction mixture stirred for approximately three hours at just below 10°C, after which it was filtered. The filtrate was then acidified with dilute hydrochloric acid and added to 4 litres of distilled water. The white precipitate that formed was collected after filtration. The crude product was recrystallised from aqueous ethanol, filtered and dried before being analysed by Fourier-transform infrared (FTIR), proton nuclear magnetic resonance (^{1}H-NMR) and electrospray mass spectrometry (ESMS). The yield obtained was 85 wt %.
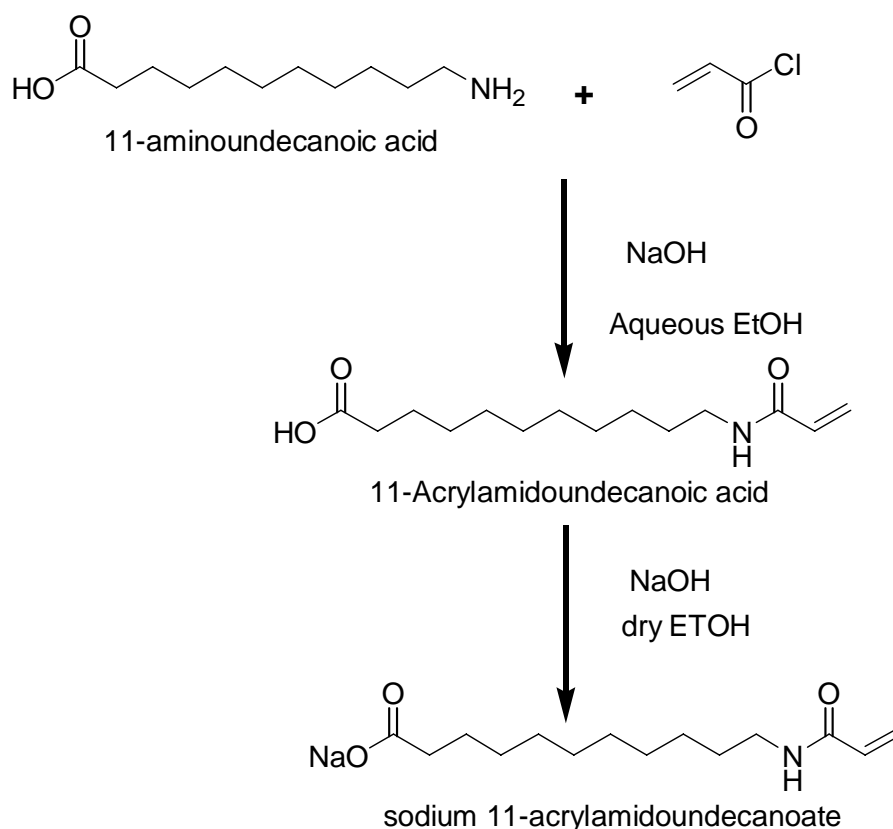
Scheme 3-2. Reaction scheme for the preparation of 11-AAUA and its Na salt.

3.5.2. Synthesis of the sodium salt of 11-AAUA

The sodium salt of 11-AAUA was prepared in a similar manner to the salt of 12-ADA (see Section 3.4). The yield of the Na salt of 11-AAUA was 74%.

3.6. Results and discussion

The proton NMR spectra of the surfmers 12-ADA and 11-AAUA, dissolved in deuterated chloroform were obtained on a Varian Gemini unit. Figure 3-1 shows the spectrum of 12-ADA, in which characteristic signals due to the protons of an acrylate are observed. The chemical shifts due to protons of $CH_2=CH-$ relative to the tetramethylsilane (TMS) signal are observed at 5,8 to 6,4ppm as expected, while those due to the $-CH_2-$ of $HOOC-CH_2-$ are at about 2,22ppm and the $-CH_2-$ of the group $-CH_2-O-C(O)-$ are around 4,15ppm. Figure 3-2 shows the proton NMR

spectrum of 11-AAUA in which peaks at 5,6 and 6,3ppm are observed. The signals observed at about 5,6-6,3ppm are due to the $CH_2=CH-$ protons while the $-CH_2-$ protons in $-HN-CH_2-$ and $-CH_2-COOH$ give rise to signals at about 3,3 and 2,3ppm respectively. The signals observed were characteristic of an acrylamide.

The IR spectra of both 12-ADA and 11-AAUA showed characteristic infrared absorption frequencies due to C=O at about 1690-1760cm^{-1} and C=C stretching at around 1600-1650 cm^{-1}. The IR spectra of the sodium salts of 12-ADA and 11-AAUA also showed characteristic absorption bands when compared with the corresponding acids.
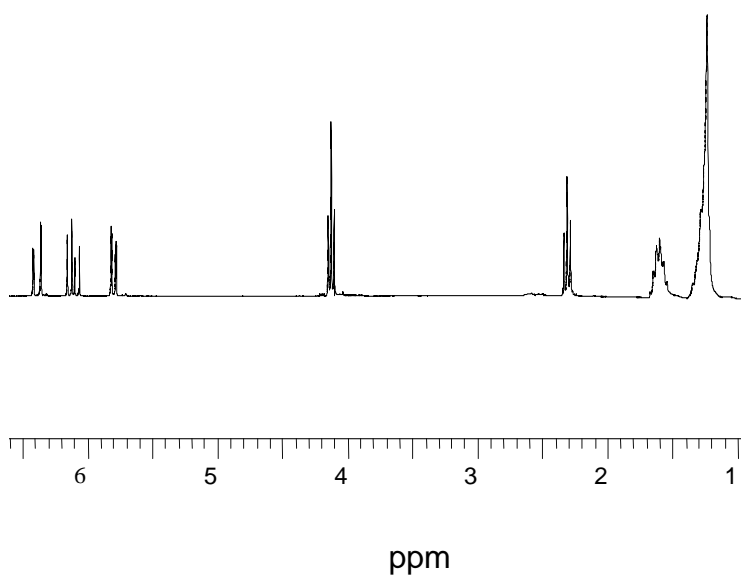
Figure 3-2. ^{1}H-NMR spectrum of 12-ADA in CDCl$_3$.
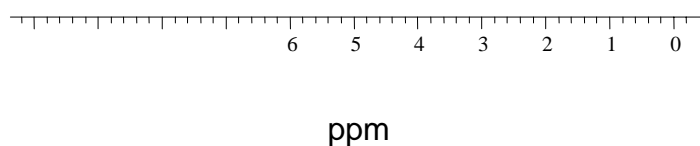
Figure 3-3. ^{1}H-NMR spectrum of 11-AAUA in CDCl$_3$.

The spectra of the surfmers and their corresponding salts showed absorptions that are typical of acrylate and acrylamide groups. The IR spectra of both 12-ADA and 11-AAUA showed absorptions due to the C=O absorptions at about 1760 cm^{-1} and the C=C absorptions at about 1650 cm^{-1}. The spectra of the salts also showed typical shifts in their absorptions when compared with their corresponding acids.[3]

The ESMS spectrum of 12-ADA shown in Figure 3-4 clearly shows that the main fragment is the monomer which has a molar mass of 270,06 g/mol, probably due to the molecular ion. It is proposed that the signal with m/z = 324,55 is therefore due to the molar mass of the surfmer plus a small fragment from the cleavage of 12-ADA at the weak bond C–O. The fragment accounts for a mass of about 55 g/mol, which, when added to the 270 g/mol, brings the total mass to about m/z = 325.
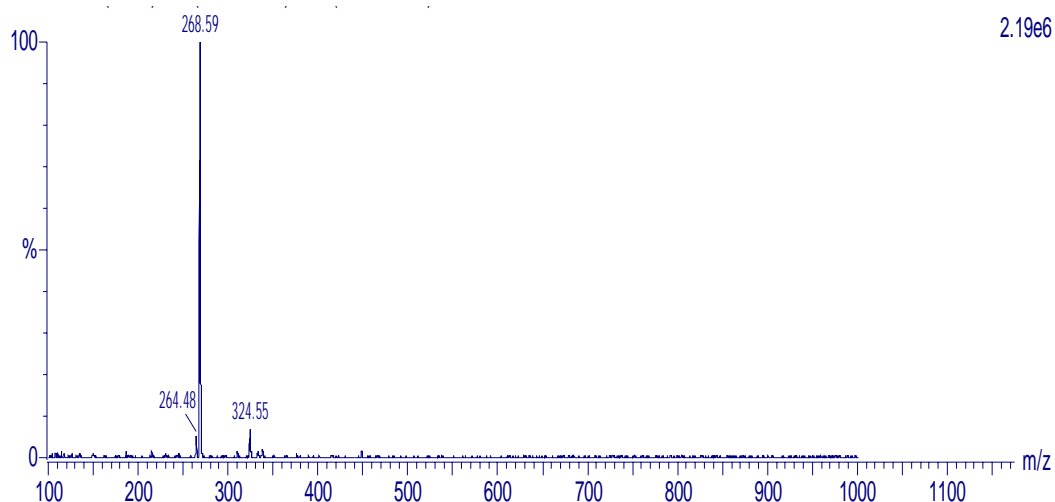
Figure 3-4. ESMS spectrum of a fresh sample of 12-ADA.

The surfmers were thus considered to be pure enough to continue with the next stage of the synthesis i.e.,

1) to use the surfmers to prepare RAFT oligomers that would be used as polymeric surfactants in the emulsion polymerisation of styrene, and

2) to use the surfmers as polymerisable surfactants in the emulsion polymerisation of styrene.

After ^{1}H-NMR and IR analyses confirmed the double bonds of the surfmer to be still present and the structure of 12-ADA confirmed, a closer investigation of the properties of the surfmer was undertaken. On further investigation it was found that 12-ADA could dissolve in dichloromethane but could not do so after standing for a while just a day exposed to the air and natural daylight. It was further shown that the surfmer was not of uniform morphology, as seen in the SEM micrograph in Figure 3-5. Analysis of the SEM micrograph also showed 12-ADA to be composed of areas of chain-like arrangements and some non-distinct areas.
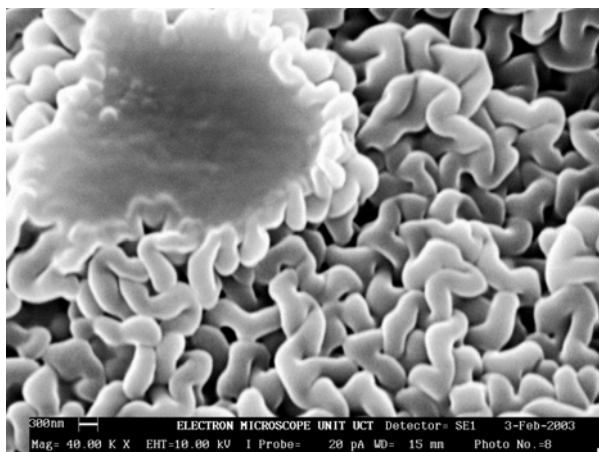
Figure 3-5. SEM micrograph of 12-ADA which had been standing for 2 days.

This behaviour of 12-ADA may have been due to the molecule undergoing self-association through intermolecular bonding[4] or to the formation of dimers[5] or even supramolecular structures.[6] Such structures may be the result of electrostatic interactions such as hydrogen bonds,[7] which have been associated with such structures, together with liquid crystalline areas created around the hydrophobic spaces. The hydrogen bonding in carboxylic acids such as 12-ADA may lead to linkages such as those shown in the hypothetical structure in Figure 3-6.
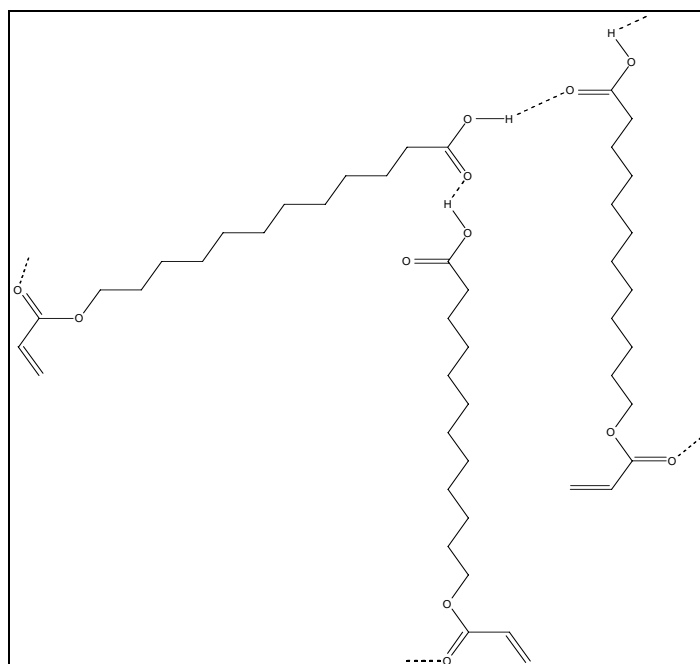
Figure 3-6. A hypothetical structure of an associated molecule of 12-ADA.

In a molecule of polar and non-polar regions there is a tendency for the non-polar regions to associate at the exclusion of the polar ends, as is reported to happen with some biomolecules.[8] In such a case, this association of non-polar regions is termed "hydrophobic bonding".[9]

Also, the difficulty in dissolving 12-ADA may be due to the way the molecule distributes the polar and hydrophilic carboxylic ends into a solvent, while the non-polar and hydrophobic olefinic end regions are distributed away from the solvent, as illustrated in a "loop" conformation illustrated in Figure 3-7.[10] The behaviour of 12-ADA in this case is not the same as that of a molecule that has a hydrophilic head and a hydrophobic tail. The carboxylic end is expected to preferentially distribute in the solvent phase while the olefinic end would be distributed in the air phase.

The surfmer 11-AAUA was expected to behave in the same way as 12-ADA, in Figures 3-6 and 3-7, but no such case has been reported for the acrylamide. The differences in the electro-negativities of oxygen and nitrogen might be the cause of the different behaviours.
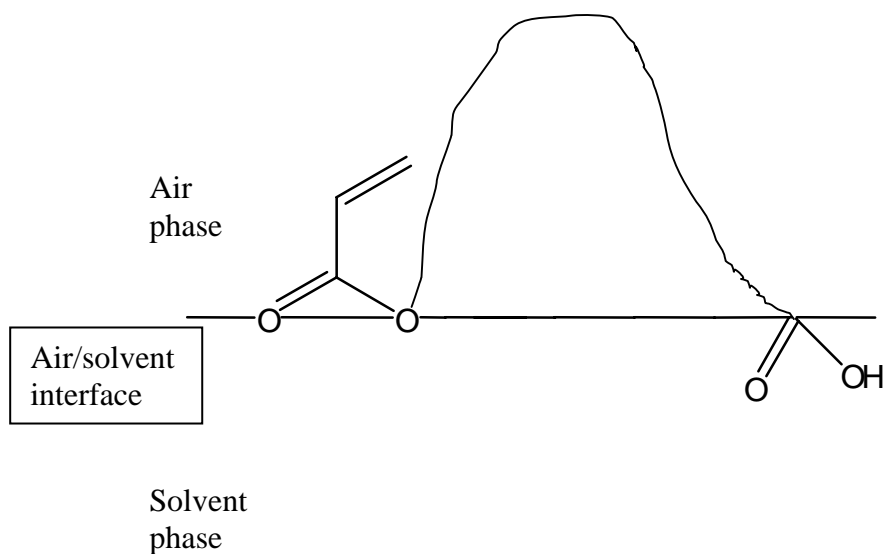
Figure 3-7. Interaction of 12-ADA with solvent at an air/solvent interface.

When WAXS analysis of 12-ADA was undertaken the samples were held together by aluminium foil to allow irradiation to come from all angles. Figure 3-8 shows the WAXS spectrum obtained for 12-ADA.
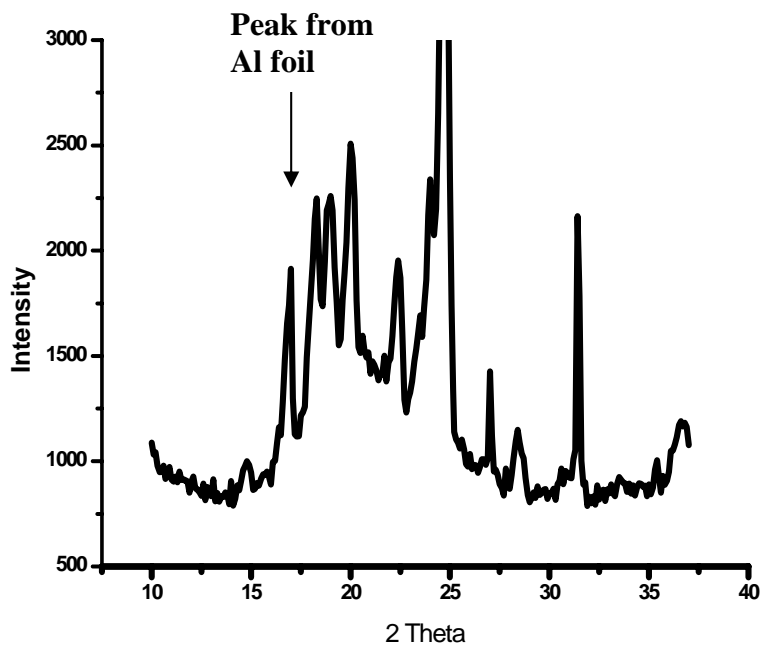
Figure 3-8. WAXS spectrum of 12-ADA.

The scattering intensity around $2\theta = 17$ was due to the Al foil used to hold the sample in place (established from a WAXS spectrum of the Al foil only). The scatter due to the foil was not considered when examining the crystallinity of samples. It can be seen from the spectrum in Figure 3-8 that the scattering intensity of 12-ADA suggests that it is highly crystalline. The RAFT copolymers 12-ADA/AA (1:1) and 12-ADA/AA (1:5) show that the 2θ values of 25,1; 28,2 and 32 show scattering intensities due to crystallinity.

3.7 References

1.   Finkelmann H., Scafheutle M.A., Colloid Polym. Sci. **1986**, 264, 786.
2.   Fujimoto C., J Chromatography A, **2000**, 871, 415.
3.   Kemp W., "Organic Spectroscopy" 3rd Ed, **1991**.
4.   Alcock N.W., Bonding and Structure, Ellis-Horwood, Chichester, **1990**.
5.   Lindoy L.F., Atkinson I.M., in Self-Assembly in Supramolecular Systems, 1st Ed.. RSC/Springer, **2000**, 224.
6.   Yang J., Marendaz J-L., Geib S.J., Hamilton A.D.,Tetrahedron Lett. **1994**, 35, 3665.
7.   Aakeroy C.B., Seddon K.R., Chem Soc. Rev. **1993**, 22, 397.
8.   Jorgensen W.L., Severance D.L., J. Am. Chem. Soc. **1990**, 112, 4768.
9.   Schneider H-J., Kramer R., Simova S., Schneider U., J. Am. Chem. Soc. **1988,** 110, 6442.
10.   Hamid S.M., Sherrington D.C., Polymer **1987**, 28, 325.

CHAPTER 4

Synthesis & Characterisation of RAFT Reagents, Polymers and Copolymers

4.1. Introduction

Two types of RAFT reagents were prepared, one from the initiator 2,2-azobisisobutyronitrile (AIBN) and the other from 4,4-azobis(4-cyanovaleric acid) (ACP) which were both dithiobenzoates, were prepared as described in the literature,[1,2] and incorporated as chain transfer agents in RAFT polymerisation processes. The RAFT reagents were used to try to control the radical polymerisation of surfmers to prepare oligomers of controlled molecular masses. In both cases the RAFT compounds were prepared by first preparing Grignard reagents, which were then converted to dithioacids, and reacted with DMSO to give bis-thiobenzoyl disulphide compounds. The intermediate products were analysed by proton NMR before use in the synthesis. The disulphide compounds were then reacted with azo-initiator to give the RAFT reagents. A general outline of the syntheses is given in Scheme 4-1.

Grignard Reagent

↓

Dithioacid

↓

Bis-thiocarbonyl disulfide

AIBN initiator ↙   ↘ ACP initiator

AIBN-based RAFT reagent   ACP-based RAFT reagent
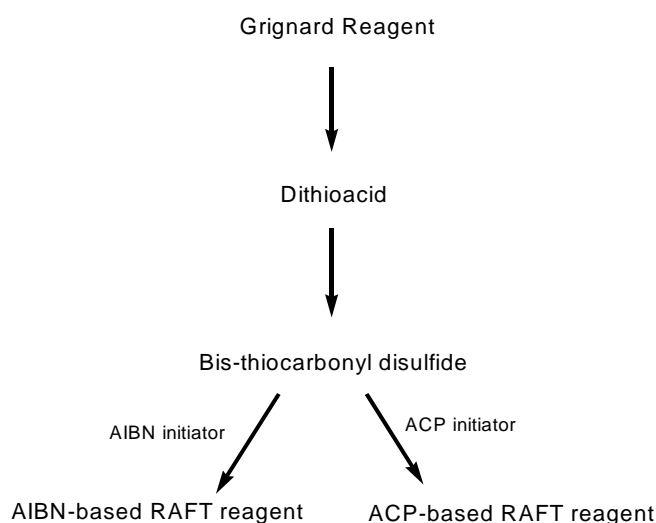
Scheme 4-1. An outline of the syntheses of AIBN- and ACP-based RAFT reagents.

4.2. Synthesis of RAFT reagents

4.2.1. Materials

The materials used for the synthesis of the RAFT reagents are tabulated in Table 4.1.

Table 4-1. Materials used for the synthesis of RAFT reagents

RAFT reagent to be prepared	Materials
AIBN-RAFT	AIBN initiator (Sigma)
	Bromobenzene (Acros)
	Carbon disulphide
	Mg turnings
	Diethyl ether
	THF, refluxed and distilled from a
	Na/benzophenone/THF mixture
ACP-RAFT	Same as above except for AIBN initiator which was replaced by ACP initiator.

4.2.2. Synthesis of Grignard intermediates and dithioacid

Magnesium turnings, 2 g (82 mmol), and a crystal of iodine were added to a dry flask. Bromobenzene, 8,65 ml (82 mmol) and 100 ml dry THF were added to the flask and the contents stirred. The stirring mixture was warmed to about 30 ^{o}C and then the temperature was controlled at below 40 ^{o}C, using an ice bath. A greyish-green mixture resulted. When all the Mg turnings had been consumed, the reaction was terminated by rapid cooling. Carbon disulphide, 4,95 ml (82 mmol), was added slowly to the cooled product while continuing to maintain the temperature below 40 ^{o}C. The resulting solution was brown then red. Water was then added slowly and carefully. About 300 ml of water was added, resulting in a precipitate, which was filtered off. The THF was removed under vacuum to give a red Grignard reagent which was acidified to a pH of 1 with fuming HCl (15 ml) by slowly adding the acid. The colour of the mixture changed from red to a pink/purple colour, which later turned cloudy

before giving a persistent pink colour at a pH of 1. The product, dithiobenzoic acid, was extracted with diethyl ether. The water layer was extracted using 100 ml diethyl ether in order to recover remaining dithioacid. The dark red etherial phase was dried with anhydrous magnesium sulphate, filtered, and the ether removed under vacuum (using a vacuum pump). This resulted in a thick, red, oily product, which was analysed by ^{1}H-NMR. Scheme 4-2 summarises the reactions:
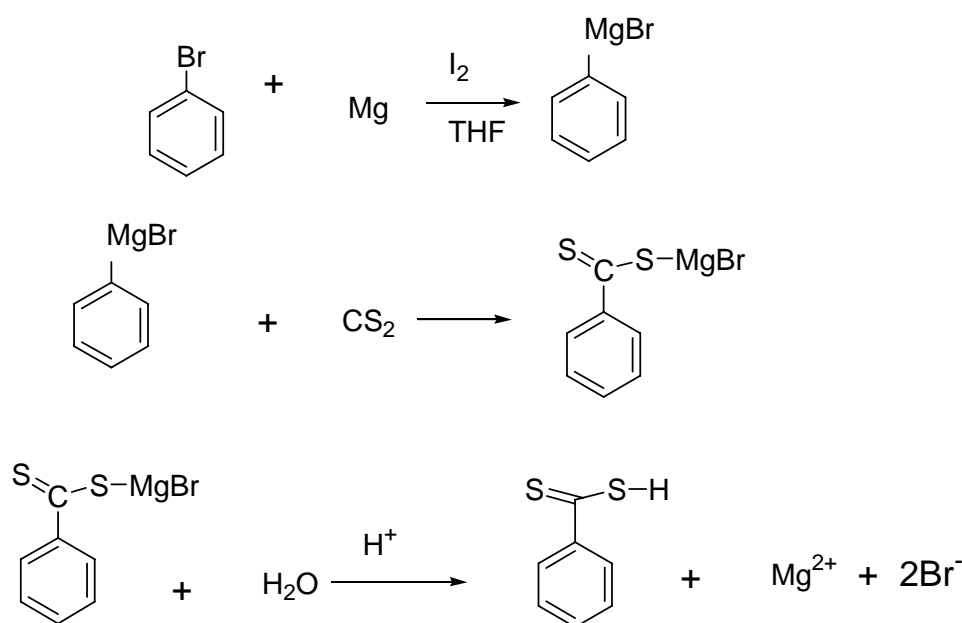
Scheme 4-2. Synthesis of the dithioacid.

4.2.3. Synthesis of bis(thiocarbonyl) disulphide

To the dithiobenzoic acid 25 g (172 mmol) prepared as described in Section 4.2.2, 25 ml (353 mmol) DMSO, a few crystals of iodine and 100 ml ethanol solvent were added at room temperature and the mixture was stirred for about an hour before refrigerating it overnight. The pinkish precipitate that formed was filtered and washed with ethanol before being dried in a vacuum oven. The resulting product, bis(thiocarbonyl) disulphide (BTBS), was a pink crystalline product, obtained in a yield of 32,5%. It was analysed by proton NMR. The synthesis is illustrated in Scheme 4-3.
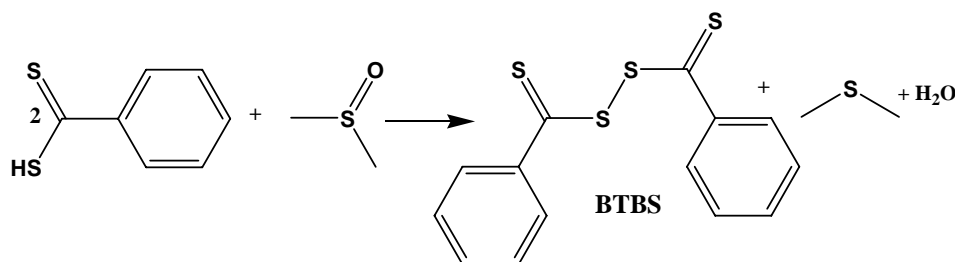
Scheme 4-3. Synthesis of bis (thiocarbonyl) disulphide.

4.2.4. Synthesis of 4-cyano-4-(thiobenzoylthio)pentanoic acid

The final stage in the preparation of the RAFT reagent 4-cyano-4-(thiobenzoylthio)pentanoic acid (ACP-RAFT) is illustrated in Scheme 4-4. It involved reacting the bis-thiocarbonyl disuphide with the azo-initiator azobis (4-cyanopentanoic acid) (ACP). The disulphide, 4,16 g (13,6 mmol), dissolved in 100 ml ethyl acetate, was added to the initiator, 5,33 g (14,3 mmol), also dissolved in 100 ml ethyl acetate. The reaction mixture was stirred and flushed with nitrogen, after which the mixture was allowed to reflux for about 40 hours. The resulting dark red solution was purified by running it through a 60-cm silica gel chromatographic column. A 3:2 mixture of heptane/ethyl acetate was used as the elution solvent. Solvent was then removed and the product dried under vacuum. The pink crystals that resulted were analysed using ^{1}H-NMR and ESMS. The yield obtained was 36%.

4.2.5. Synthesis of 4-azobisiso-(thiobenzoylthio)butyronitrile

The same procedure as described for the RAFT reaction with the azo-initiator, azobis (4-cyanovaleric acid) was carried out with the AIBN initiator, as illustrated in Scheme 4.4. In this case 4,05 g (13 mmol) bis(thiobenzoyl) disulphide and 3,26 g (19,8 mmol) AIBN initiator were dissolved in 100 ml ethyl acetate before being refluxed for 40 hours. The crude product was again purified by passing it through a silica gel column, using a 3:2 heptane/ethyl acetate solvent mixture. Analysis by TLC showed that further purification was required. This was done by using a silica gel chromatographic column and was performed by eluting the material with a 5:1 mixture of heptane/ethyl acetate, in this case.
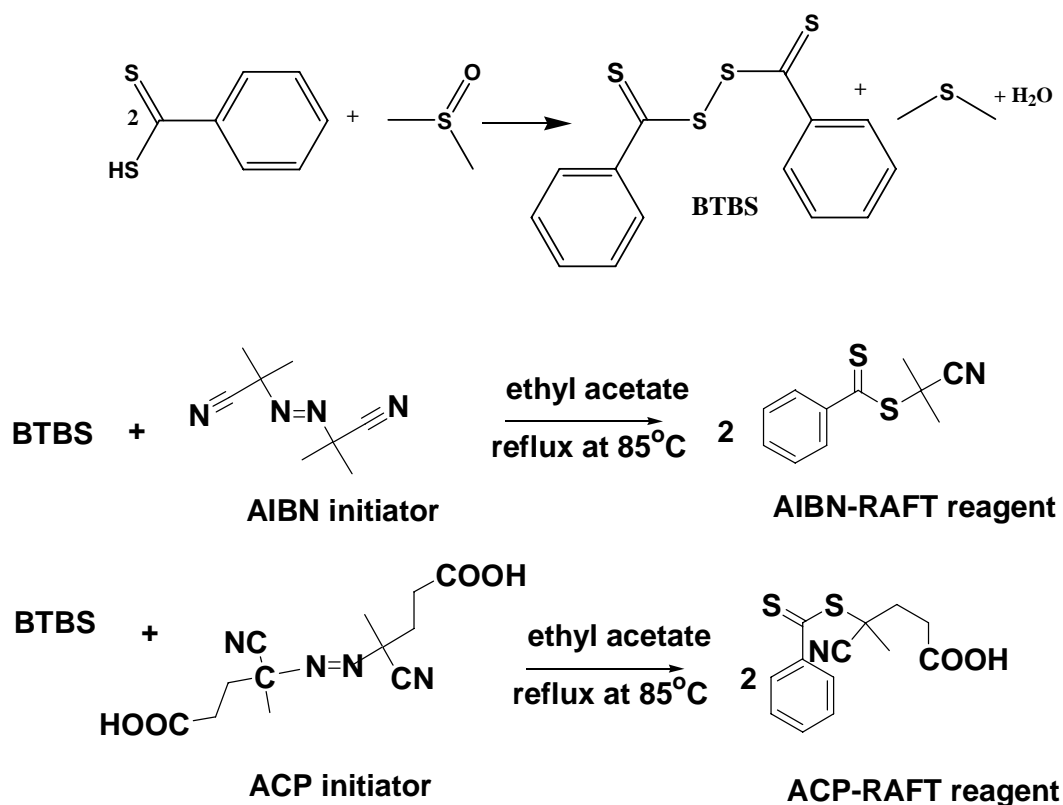
Scheme 4-4. Synthesis of RAFT reagents from dithioacids.

The resulting RAFT compound was a dark red, oily substance. It was obtained in a yield of 28%. Analysis was carried out by means of ^{1}H-NMR and ESMS.

4.2.6. Results and Discussion

The ^{1}H-NMR and ESMS spectra of the RAFT reagents were obtained on a Varian 300 MHz Jeol NMR spectrophotometer and a Varian ESMS respectively. Deuterated chloroform was used as solvent for both analyses. The spectra are shown in Figures 4-1 and 4-2.
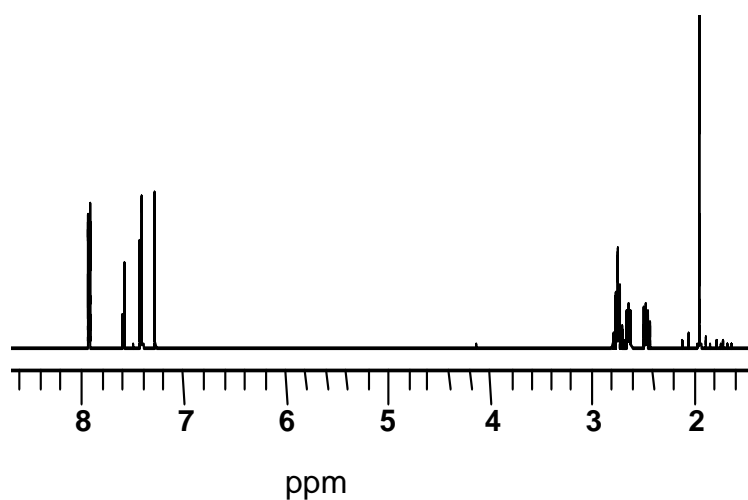
Figure 4-1. ^{1}H-NMR spectrum of the ACP-RAFT reagent in CDCl$_3$.
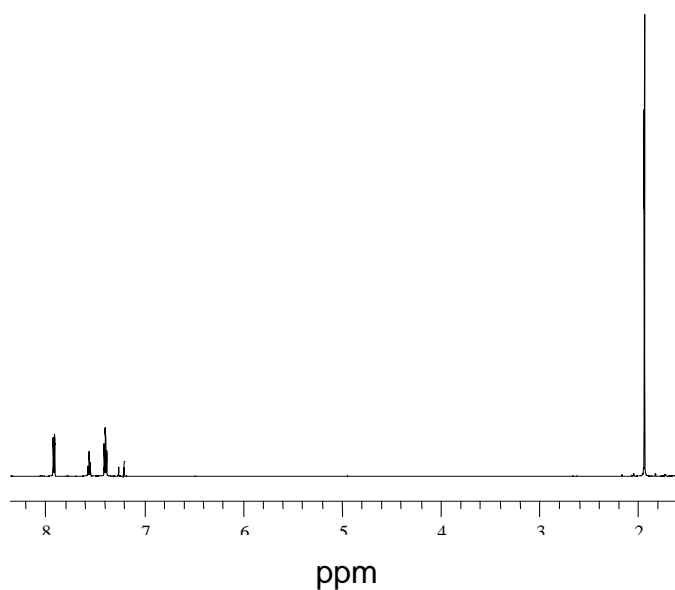
Figure 4-2. ^{1}H-NMR spectrum of the AIBN-RAFT reagent in CDCl$_3$.

The ^{1}H-NMR of the ACP-based RAFT compound, in Figure 4-1, shows signals due to meta- and para- protons of the aromatic ring. The signals at 1,95ppm are due to the methyl protons, while those around 2,4 to 2,7ppm are due to the CH$_2$ protons, and those around 2,75 to 2,8ppm result from coupling of the nearby protons. The spectrum of the AIBN-based RAFT reagent shown in Figure 4-2 shows three main

signals, between 7,4 and 8ppm. These are due to aromatic protons in the ortho-, meta- and para of the aromatic ring i.e., two ortho- protons give signals at 7,9ppm, the 2 meta- protons at 7,4 and the single para- proton at 7,6ppm. The large peak at about 1,95ppm is due to the CH_3 protons.
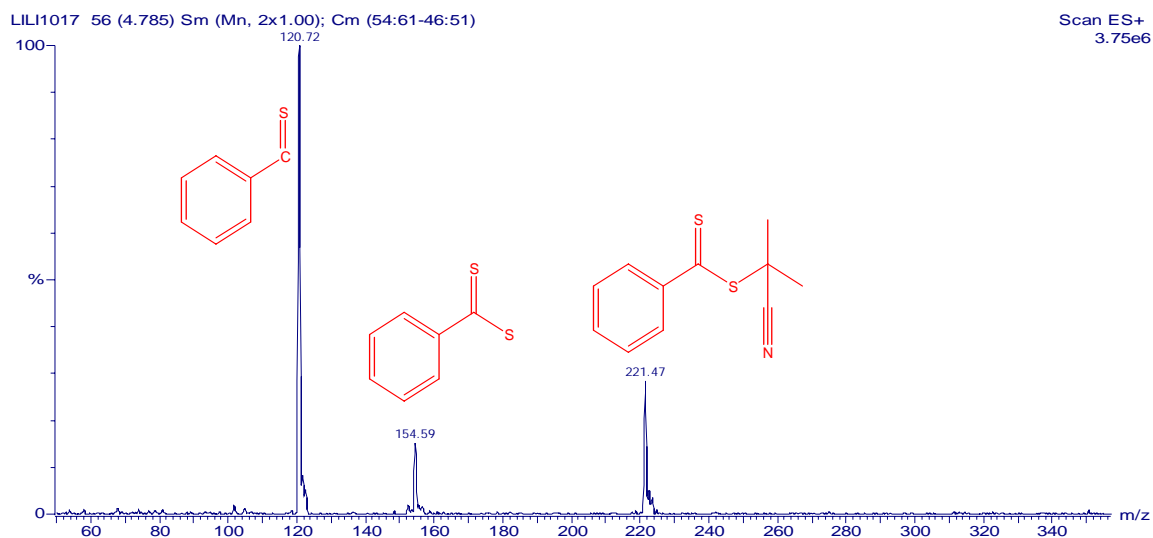
Figures 4-3. The ESMS spectrum of the AIBN-RAFT reagent.

The ESMS spectrum of the AIBN-RAFT reagent, presented in Figure 4.3, shows the peaks at m/z = 121 and m/z = 154 related to RAFT fragments, while the peak at 221 is due to the AIBN-RAFT reagent.

The above spectra of the RAFT compounds prepared from dithioesters and azo-initiators showed the compounds to be reasonably pure, about 85% for the AIBN-RAFT and about 90% for the ACP-RAFT, and suitable for use in subsequent polymerisation reactions.

4.3. Synthesis of RAFT polymers of styrene

4.3.1. Introduction

Chain transfer agents such as RAFT reagents have been used to control radical polymerisation, leading to products with controlled molecular masses and molecular mass distributions.[3] RAFT agents with the general structure Z-C(S)S-R were chosen for use in the study so as to ensure high transfer constants.[4] The Z group activating the C=S bond towards radical addition and the R group which needs to be a good free-radical leaving group should be capable of re-initiating free radical polymerisation.[5] The AIBN- and ACP-based RAFT agents have Z and R moieties that provide high transfer constants that should lead to oligomers with narrow polydispersities. In addition, the ACP-RAFT agent should lead to the synthesis of narrow-polydispersity polymers containing end functionality in a simple single-step process, without the need for lengthy protection and de-protection steps. In order to test the effectiveness of the transfer reagents, RAFT polymerisations of a conventional monomer such as styrene were carried out.

4.3.2. Calculation of quantities of RAFT reagent

The quantities of RAFT agent and initiator used were calculated from Equation 2.4, described in Section 2.4.1, and reported in the literature.[6]

$$M_n = M_{RAFT} + \frac{[M]_0 \cdot x \cdot M_m}{[RAFT]_0 + 2f[I]_0 \cdot \left(1 - e^{-k_d \cdot t}\right)}$$

see Equation 2.4 (Section 2.4.1)

where:

M_n is the target molecular mass of the polymer/oligomer [g/mol]

M_{RAFT} is the molecular mass of RAFT agent [g/mol]

$[M]_0$ is the initial concentration of monomer [mol/l]

M_m is the molecular mass of monomer [g/mol]

x is the fractional conversion of monomer

$[RAFT]_0$ is the initial concentration of RAFT agent [mol/l]

f is the efficiency factor (fraction of initiator radicals that will form polymers)

$[I]_0$ is the initial concentration of the initiator [mol/l] and

k_d is the dissociation rate constant of the initiator

t is the time of reaction [s].

The ratio of $[RAFT]_0$ to $[I]_0$ was chosen as 10:1 and therefore $[I]_0$ in the above equation is substituted with $1/10 \cdot [RAFT]_0$. The initiator AIBN was estimated to have an efficiency factor (f) of 0,7 in the reaction, resulting in Equation 4.1.

$$M_n = M_{RAFT} + \{ [M]_0 \cdot x \cdot M_m \} / \{[RAFT]_0 + 2 \times 0,7\{ [RAFT]_0 /10\} \cdot (1 - e^{-k_d t})\} \quad 4.1$$

When $[RAFT]_0$ is made the subject of Equation 4.1 we obtain Equation 4.2, from which the initial concentration of the RAFT agent can be calculated.

$$[RAFT]_o = \{[M]_o \times M_m\} / \{(M_n - M_{RAFT}) \ 1 + 0,14\} \ (1 - e^{-k_d t}) \quad\quad 4.2$$

RAFT polymerisations of styrene and methyl methacrylate were carried out to determine the effectiveness of the prepared RAFT reagents in controlling polymerisation reactions.   Only once the RAFT reagents had been shown to successfully act as effective chain transfer agents in the polymerisations were they to be used to prepare oligomeric surfactants of controlled molecular mass and polydispersity.

4.3.3. RAFT polymerisation of styrene

4.3.3.1. Materials

The following materials were used for the RAFT polymerisation of styrene:
destabilised styrene monomer (vacuum distilled), recrystallised AIBN initiator (Sigma) and the prepared reagent 4-azobisiso(thiobenzoyl) butyronitrile (AIBN-RAFT).

4.3.3.2. Experimental procedure

The RAFT polymerisation of conventional styrene was carried out in bulk in a 3-neck flask with 149,37 g (1,43 mol) styrene, 0,23 g (2,8 mmol) AIBN initiator and 1.84 g (0,83 mmol) AIBN-RAFT agent. The flask and reactants were stirred, purged with N_2 and heated to 80 °C. The reaction was allowed to run for 80 minutes. At intervals of 40, 60, 80 and 100 minutes, samples of the flask contents were withdrawn using a syringe, and weighed. The samples were rapidly frozen to stop further polymerisation, precipitated and dried. The polymers weighed before being analysed by ^{1}H-NMR and GPC. The results are given and discussed.

4.3.4. Results and Discussion

Figure 4-4 illustrates a typical spectrum of the RAFT oligomers obtained during the polymerisation of styrene.
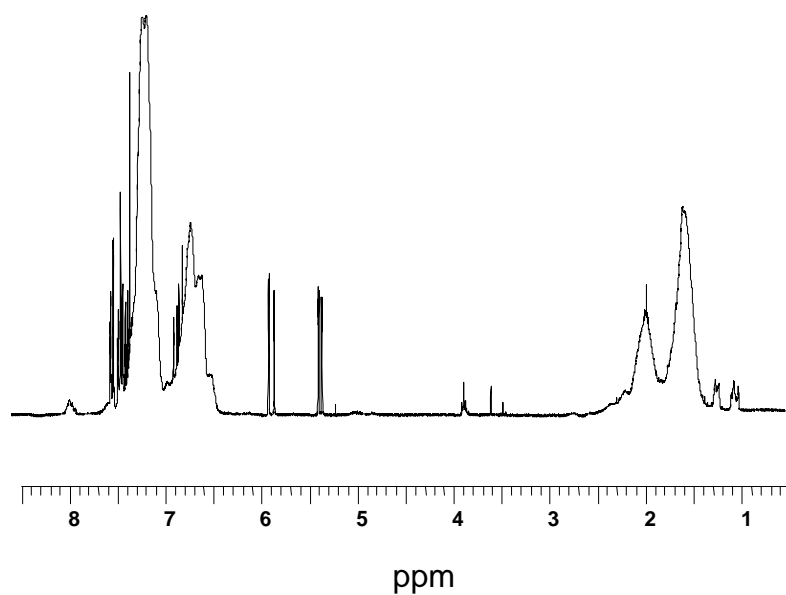
Figure 4-4. ^{1}H-NMR spectrum of oligomeric AIBN-RAFT PS (obtained after 80 min of polymerisation).

The proton shifts due to the RAFT moiety appear in the same region as the protons from the aromatic ring of the polystyrene, hence the rather large signal at about $\delta7,2$. The CH_2 proton signals from the PS appear as expected, at about $\delta2$, while those due to the CH_3 from the RAFT reagent appear at about $\delta1,95$.

The molar masses of the prepared polymers were determined by GPC. A plot of the molar mass against time, as illustrated in Figure 4.5, shows a linear relationship. This is an indication that there was effective control of the molar masses.
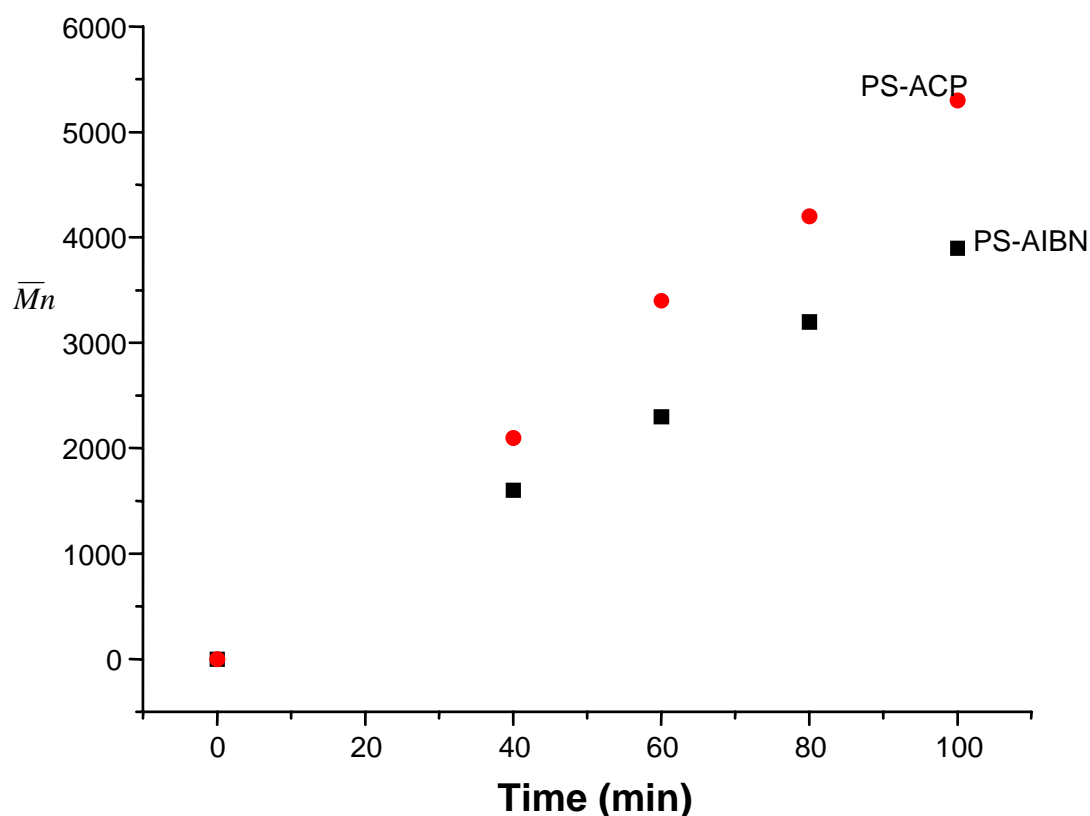
Figure 4-5. Variation in molar mass of PS-RAFT oligomers with time.

As can be seen in Figure 4-5 there was a steady increase in the molar masses of polymers as polymerisation progressed.

4.4. Polymerisation of 12-ADA

4.4.1. Introduction

The monomer 12-ADA has poor solubility in the common polymerisation reaction solvents. This may be attributed to some of the reasons discussed in Section 3.6. Although not ideal, DMSO and acetic acid, in which 12-ADA is only slightly soluble at room temperature, were chosen as the polymerisation solvents. A polymerisation temperature of 75 °C was chosen to enable as efficient a generation of radicals as possible, based on the initiator's dissociation constant in the polymerisation solvent.[7] The aim of the polymerisation was to obtain controlled molecular mass oligomers of 12-ADA using ACP-RAFT and AIBN-RAFT reagents instead of polymers such as the

trimers shown in Figure 4-6. The use of trimers instead of higher oligomers (which are usually expected with higher oligomers of high molecular mass) can prevent potential solubility problems.

In the calculation of $[RAFT]_0$, the value of M_n can only be seen as an approximation since the following assumptions had to be made:

- *X* was taken as 1, assuming a complete conversion,

- f was taken as 0,7 – assuming that 70% of initiator radicals would form polymer chains, [8] and

- the dissociation constant k_d of $1,52 \cdot 10^{-4}$ s^{-1} (which is the k_d value for AIBN in DMSO at 75 °C) [9] was used for AIBN in acetic acid at 75 °C.

Using these values, together with reaction times, the necessary concentration values of RAFT agent and initiator for the oligomerisations were calculated.
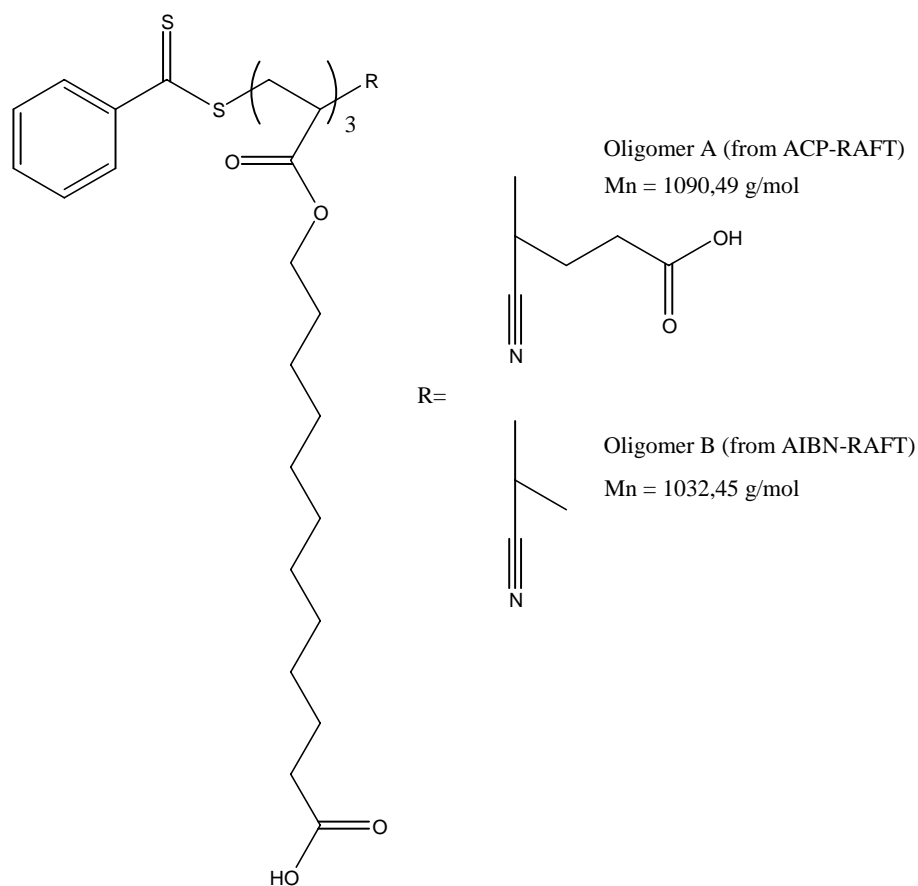
Figure 4-6. Structure and molar masses of trimeric oligomers of 12-ADA.

4.4.2. Reaction conditions for RAFT oligomerisation of 12-ADA

A summary of the reaction conditions for the RAFT polymerisations is given in Table 4.2.

Table 4-2. Reaction conditions used for the RAFT polymerisation of 12-ADA

RUN	solvent / temperature	RAFT	reaction time [h]	[RAFT] [mmol]
A	CH₃COOH / 75°C	ACP-RAFT	60	0,99
B	CH₃COOH / 75°C	AIBN-RAFT	60	0,99
C	CH₃COOH / 75°C	No RAFT	60	0
D	DMSO / 75°C	AIBN-RAFT	60	0,99
E	DMSO / 75°C	ACP-RAFT	90	0,99
F	DMSO / 75°C	AIBN-RAFT	90	0,66

4.4.3. Experimental procedure

The procedure described here was applicable to the experimental runs from A to E, with the correct concentrations, solvents and RAFT agents substituted (see Table 4.2.). In a 3-neck flask, 3,7 mmol 12-ADA and 0,99 mmol RAFT reagent were dissolved in 10 ml solvent and degassed for 1 h. The mixture was heated to 75 °C until a homogeneous, oily solution was obtained. AIBN initiator, 0,33 mmol, dissolved in 1 ml of solvent, was degassed and added through a septum. The mixture was stirred for 60 hours at 75 °C under nitrogen, after which the reaction was terminated with 5 ml methanol.

After removing most of the acetic acid under vacuum, the product was diluted by adding 10 ml dichloromethane. The reaction mixture was purified by column chromatography using silica gel (0,063-0,2 mm/70-230 mesh-*Macherey-Nagel*). A

1:2 mixture of ethyl acetate/dichloromethane was used as elution solvent. The latter solvent mixture was determined by TLC experiments.

An example of the purification procedure used for run D is described here: Seven chromatographic fractions were isolated from the polymerisation in DMSO. These fractions were later divided into three groups based on results of TLC analysis. The first group comprised fractions which were yellowish in colour. The second group comprised some that were light brown, while others were pinkish in colour. The solvent had to be changed to methanol for the third group, which comprised darker brown fractions of product. All the three fractions (groups) were then analysed. For each of the products of the RAFT polymerisations in DMSO and acetic acid, a similar work-up to the one done for run D was carried out. The work-up of the oligomerisation products using a silica gel column was not very efficient as there was no clear distinction between the different fractions along the column. A small fraction of the oligomeric product could not be eluted from the column, which meant that the yields were only estimates. Due to the constraint in the use of the solvents DMSO and acetic acid, further problems with drying and analysing the samples were encountered.

The products were analysed by ^{1}H-NMR, ESMS and elemental analysis (EA). The results are given in Section 4.4.4.

4.4.4. Results and discussion

Analysis of the products from the polymerisation run D in DMSO by ^{1}H-NMR spectroscopy gave representative spectra as shown in Figure 4.7. The first fraction clearly shows proton signals similar to those of the monomer. The second fraction still contained monomer but has an aromatic ring signal. This could have emanated from an attached RAFT moiety which is what must have given the pinkish tint to the second group of the eluted products. The absence of double bonds in the last fraction suggests that oligomerisation had occurred and that this was the desired polymer, the yield of which was only 26 wt %. The collective yield of the monomeric fractions was 62 wt %, suggesting that the polymer that remained on the column could account for around 10%.
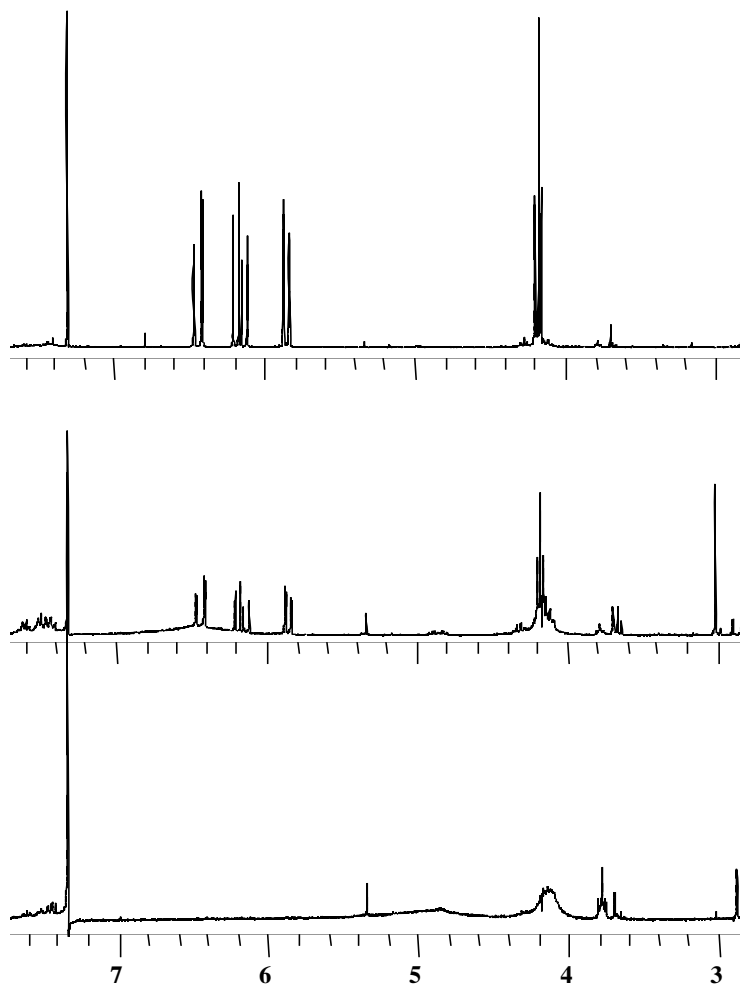
Figure 4-7. ^{1}H-NMR spectra of fractions of products (dissolved in CDCl$_3$) from polymerisation run D.

The oligomers could not be purified further because they could not be dissolved in most solvents. The ESMS spectra of some of the typical oligomers obtained are shown in Figure 4.8.
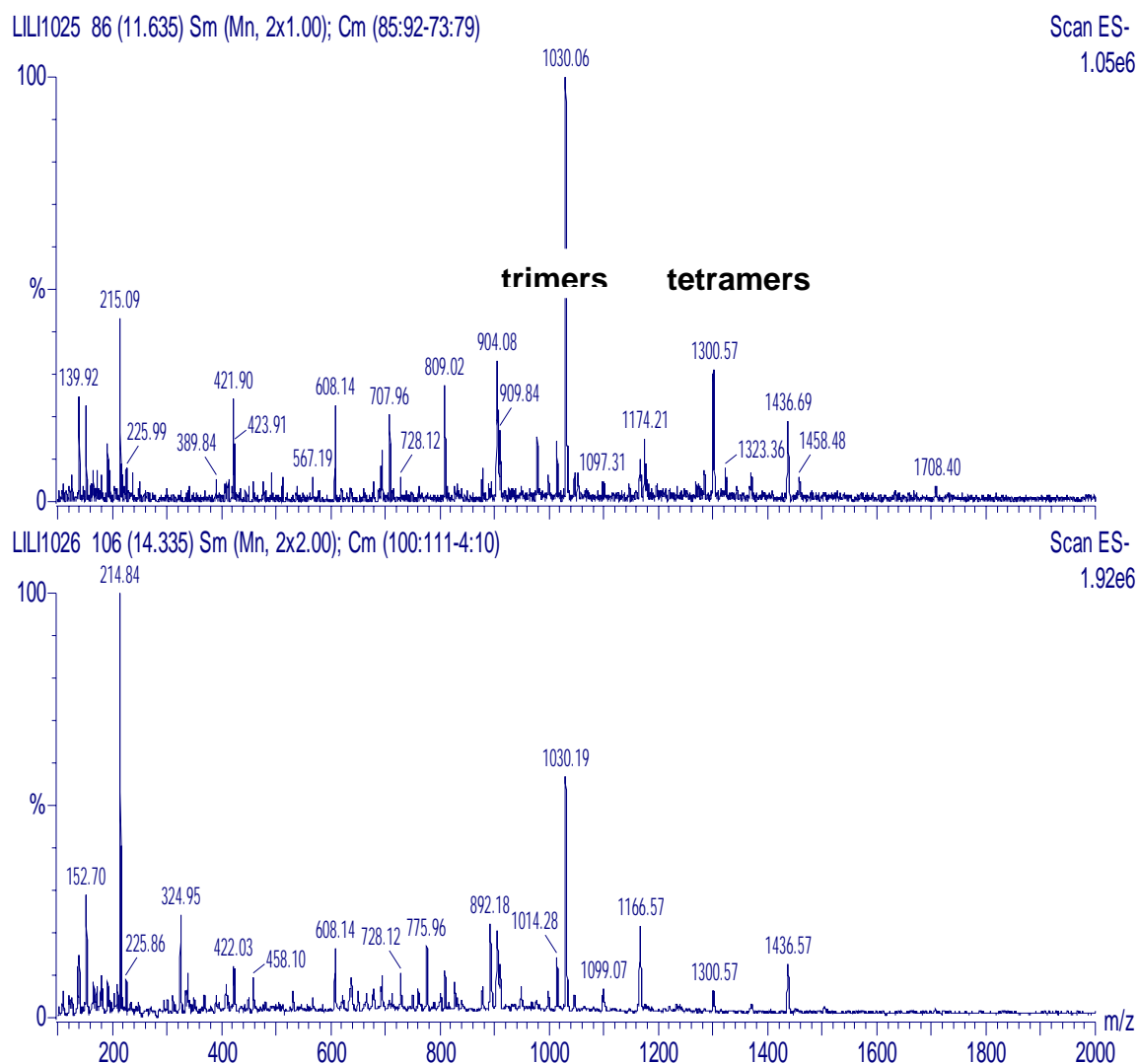
Figure 4-8. ESMS spectra of oligomers from Runs D (top) and B (bottom).

The spectra in Figure 4.8 represent products from run D in DMSO and run B in acetic acid. For the ESMS analysis of product D, which is similar to that of product B, a mixture of acetonitrile and methanol was used as solvent, to try to dissolve as much of the sample as possible. The largest peak in both the spectra, at about m/z = 1 030, relates to the molar mass of the trimer of 12-ADA with the RAFT moiety. The peak at about m/z = 215 relates to the loss of the fragment $CH_2=CH–C=O$, which signifies possible cleavage of the weak ester linkage of C–O. The mass of the fragment is 55 g/mol, which when subtracted from the molar mass of 12-ADA of 270 g/mol gives 215 g/mol.

The ESMS spectra also showed a number of low molar mass peaks that could not be assigned. They nonetheless confirmed the presence of trimers and tetramers which were possibly some of the lower oligomers produced in the synthesis. The yields (weight fractions) of the polymerisation products were very low. They ranged between 23-27 wt% for the RAFT polymerisations, independent of solvents or temperature used, and were about 34 wt% for the polymerisation without RAFT agent, which consisted of a product that could not be dissolved in most solvents – Illustrating absence of control of the molar mass. The experimental run without RAFT reagent gave a product which could not be dissolved in available solvents, precluding analysis by GPC and NMR.

There was no remarkable difference in yield or solubility of the oligomers when prepared by using the two different RAFT agents. Decreasing the $[RAFT]_0/[I]_0$ ratio from 10 to 6 to get faster initiation did not result in higher yields. The polymerisation of surfmers using DMSO or acetic acid as solvents resulted in some oligomers with a RAFT moiety. One way to overcome the problem of poor solubility was to prepare a sodium salt of the oligomeric products. The salts were expected to be water-soluble.

The sodium salt of the oligomer of Run D was prepared the same way as described for the sodium salts of surfmers. The oligomeric salt dissolved sparingly in deuterated water, allowing the ^{1}H-NMR spectrum shown in Figure 4.9 to be obtained.
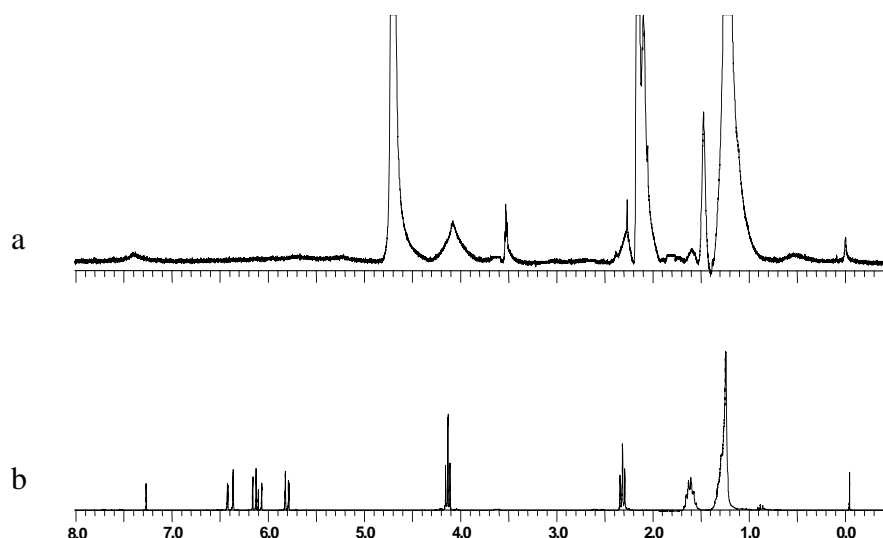
Figure 4-9. ^{1}H-NMR spectrum of oligomeric salts of 12-ADA (top) & 12-ADA surfmer (below).

The spectrum was highly magnified to show the presence of the RAFT moiety in the oligomer. The very large peaks are due to D_2O in which the salt was dissolved and to a trace of acetone which was added to aid solubility. GPC spectra of the surfmer, oligomers and copolymers are shown in Figure 4-10.

Although the products of the polymerisation without RAFT could not dissolve in most solvents, some fractions were dissolved in DMAc at a temperature of about 50 °C and GPC measurements of these fractions were made. Both oligomerisation and polymerisation products showed double or triple distributions. The first distribution with a lower molecular mass average was probably due to the presence of unreacted 12-ADA. The molecular mass and the polydispersity for the non-RAFT polymerisation products were found to have the largest average molecular mass and polydispersity, as illustrated by the curve designated Lilian 5 in Figure 4-10. The average molecular mass of these polymers and polydispersity were about $\overline{Mn}$ = 4900 and $\overline{Mw}$ = 47000; MWD = 9,6; while the molecular mass and polydispersity of the RAFT oligomers were comparably lower, about $\overline{Mn}$ = 1300 and $\overline{Mw}$ = 3000; MWD = 2,3. The copolymers had similar molecular masses to those of the oligomers although the distributions were relatively higher.
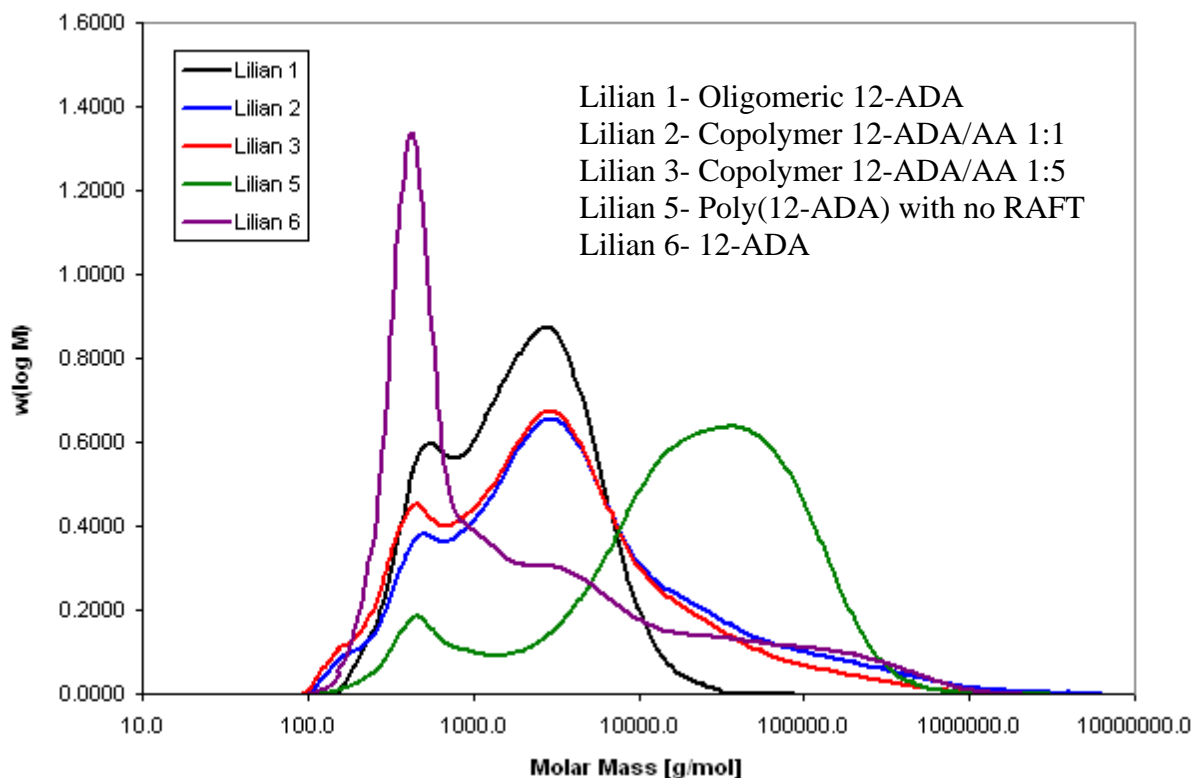
Figure 4-10. Molar mass of surfactant and oligomers of 12-ADA, measured by GPC.

The homopolymerisation of 12-ADA and its Na salt were not easy; the polymerisations were attempted several times, using a variety of conditions. Attempts to polymerise in water were unsuccessful. One of the reasons for the low polymerisation rates may be the self-assembly nature of 12-ADA. The existence of associated dimers in 12-ADA may be explained by findings of Lindoy and Atkinson[10] and Aakeroy and Seddon.[11] The low polymerisation rates could also have resulted from the supramolecular structure formation described by Yang et al.[12]

Elemental analysis of the oligomeric surfactants was carried out to determine their molecular masses. They were found to correspond to the mass of the trimers, which was also confirmed using analysis by ESMS. A Fisons mode 1108 elemental analyser was used to record combustion for elemental analysis. The results of elemental analysis of an oligomer of 12-ADA obtained from Run D, described in Section 4.4.2, are shown in Table 4.3. The measured amount of sulphur was much lower than the value calculated for the case in which RAFT was attached to each oligomer chain. The measured amount of nitrogen was slightly higher. These discrepancies could be due to impurities (unreacted monomer and recombined

82

initiator). It could also be evidence that some oligomers had formed without RAFT agent attached. Elemental analysis was therefore considered to be an unreliable method for estimating molar masses here.

Table 4.3. Results of elemental analysis of an oligomer of 12-ADA from Run D

		C [%]	H [%]	S [%]	N [%]
theoretical (calculated)	Trimer	65,2	8,6	6,2	1,4
	Tetramer	51,7	6,8	4,9	1,1
Measured		59,2	8,6	3,6	1,8

4.5. Synthesis of copolymers of ADA

4.5.1. Copolymerisation of RAFT oligomers with 12-ADA

The first aim here was to attempt to reinitiate polymerisation of the RAFT oligomers of PS[13] in order to prepare oligomeric block copolymers of 12-ADA and PS or PMMA, as well as copolymers of 11-AAUA with PS.

4.5.1.1. Experimental procedure

Polystyrene of molecular mass 4000 g/mol (1,49 g), prepared with AIBN-RAFT transfer agent, was used as the starting material. To a reaction flask containing the PS, 1mol/L of 12-ADA was added, under nitrogen, and the mixture heated. When the temperature had reached 75 °C, AIBN initiator (0,062 mmol) was added and polymerisation was allowed to progress. Some samples were withdrawn from the reaction flask at different time intervals to monitor the reaction using GPC. No reaction seemed to have occurred after 24 hours (which was more than adequate time for the initiator to be still active) and so the reaction was terminated. The reaction was also repeated with ADA in ethyl acetate, and again copolymerisation did not occur. Evidently the secondary carbon thio attachment of the styryl end-group would not fragment preferentially to the secondary carbon thio attachment of the acrylic-group end of the 12 ADA attachment to lead to the intermediate radical.

It was therefore decided to prepare copolymers of 12-ADA with acrylic acid (AA) for possible use as polymeric stabilisers in the emulsion polymerisation of styrene. This

was to be done using a batch copolymerisation. The copolymers were expected to adsorb onto the PS particles.

4.5.2. Copolymerisation of 12-ADA with acrylic acid

4.5.2.1. Introduction

Copolymers of 12-ADA and AA were prepared in order to first investigate their properties and then their use as polymeric surfactants in the emulsion polymerisation of styrene. The RAFT reagent AIBN-RAFT was used in two of the copolymerisations to try to control the molecular masses of the copolymers. One copolymerisation was carried out without a transfer agent, as a control experiment. As there are no reported examples of the controlled synthesis of copolymers of 12-ADA, it was difficult to predict the reactivity ratios of the monomers with respect to each other in the presence of RAFT reagents. However, reaction conditions were subsequently based on copolymerisation reactions of 12-ADA with AA carried out to produce gels using a crosslinker, as reported by Karino et al.[14]

The crosslinked gels were prepared by copolymerising AA and 12-ADA using methylenebisacrylamide as the crosslinker.

In order to estimate reactivity ratios for 12-ADA and AA, use was made of a study by Uchida et al.[15] which involved copolymerisation reactions between AA and stearyl acrylate with a crosslinker to form gels. Here the reactivity ratios of stearyl acrylate and AA were quoted as 3:0,5, the total monomer concentration as 3 mol/L, the crosslinker was 1 mol % of methylenebisacrylamide and the initiator was 1 mol % AIBN. The reactions were carried out under nitrogen for 24 hours at 60°C.

In this study, copolymers of 12-ADA with AA were prepared using a RAFT transfer reagent to try to control the molecular mass during the copolymerisation. Some of the properties of the resulting polymers were studied. The total monomer content was also kept at 3 mol/L and the initiator at 1 mol %.

4.5.2.2. Materials

AA from Acros (vacuum distilled)

12-ADA (prepared)

Absolute ethanol

AIBN initiator from Sigma (recrystallised).

4.5.2.3. Experimental procedure

Three copolymerisation reactions were carried out in 25-ml flasks. The surfmer 12-ADA and acrylic acid, in quantities tabulated in Table 4.4, were dissolved in 10 ml ethanol to promote transfer to solvent. To the monomer solutions in reactions 2 and 3, 0,198 g (0,9 mmol) AIBN-RAFT agent was added, with stirring. The mixture was degassed under vacuum by three freeze-thaw cycles and the reaction then brought up to 60 °C. Initiator, dissolved in a little ethanol and degassed, was added through the septum as soon as the contents of the flask reached 60 °C. The polymerisation reaction was allowed to continue for 20 hours before being stopped by rapid cooling. The specific conditions for each of the three reactions are summarised in Table 4-4.

Table 4-4. Reaction conditions for the copolymerisation of 12-ADA and AA

Reaction	12-ADA (mol)	AA (mol)	Initiator (mol)	RAFT agent (mol)	Temp °C
1	1,5	1,5	1	0	60
2	1,5	1,5	1	3	60
3	0,5	2,5	1	3	60

The product from the copolymerisation without RAFT reagent (reaction 1) formed a gel. It was washed in water and dried in a vacuum oven. The yield of this copolymerisation was 71%. The products of reactions 2 and 3 were precipitated in petroleum ether and dried in a vacuum oven. The yields of these copolymerisations were 42% and 45% respectively. The copolymers were analysed by GPC and WAXS.

4.5.3. Analysis of the copolymers

The copolymers from reactions 2 and 3 were dissolved in dimethyl acetamide (DMAc) by leaving them to stir in the solvent overnight at 40 °C. The solutions were filtered and then run through a GPC column at 50 °C. A refractive index detector was used.

Wide angle X-ray scattering is generally used to investigate polymer morphology and to deduce structural information. The wavelengths covered are of about a few angstrom units, which are equivalent to those of the inter-atomic distances in crystalline phases. The intensity of X-ray scattering, which is obtained from different diffraction patterns, is measured. The diffraction patterns vary with the angle of scatter.

Braggs Law is used and scatter is described by the equation:

$$n\lambda = 2d\sin\theta \qquad\qquad 4.3$$

where:

n   is the integral number of wavelengths

λ   is the wavelength

d   is the spacing between points of scatter

2θ   is the scattering angle.

The samples examined by WAXS were mounted using Al foil to hold samples in place while X-rays hit the sample at an angle. The scatter from the Al foil only was obtained. This was excluded when scatter from each compound was considered. The copolymers prepared both with and without using the RAFT polymerisation process were also measured.

4.5.4. Results and discussion

The GPC traces for the copolymers 12-ADA/AA 1:1 and 1:5 are illustrated in Figure 4-10 by the curves Lilian 2 and Lilian 3 respectively. The copolymer obtained from the copolymerisation of 12-ADA and AA without RAFT could not be dissolved to any extent in the GPC solvent, namely DMAc, and no suitable solvent could be found. The copolymerisations of 12-ADA with AA in the presence of AIBN-RAFT transfer agents gave molecular masses, which, although they were higher than those of the oligomer of 12-ADA, were obviously less than the copolymer without RAFT – which did not even dissolve in the DMAc. The 1:1 RAFT copolymers had molar mass values of around $\overline{M}n$ = 1600 and $\overline{M}w$ = 15000; MWD = 9,4 while the 1:5 RAFT copolymer had values of about $\overline{M}n$ = 1300 and $\overline{M}w$ = 5700; MWD = 4,4.
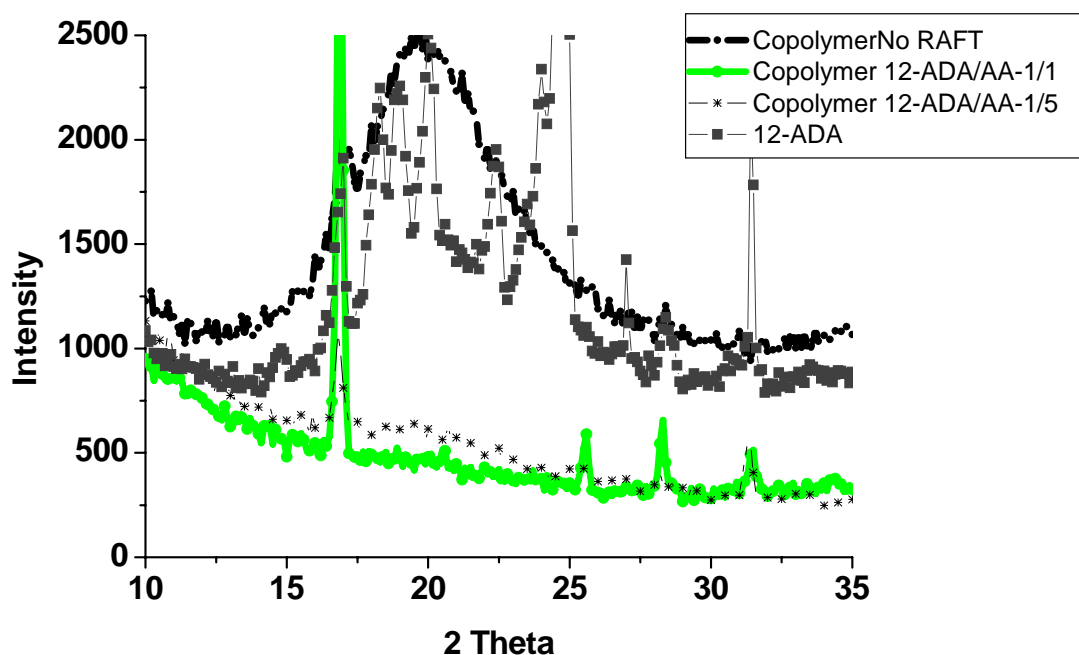
Figure 4.11. WAXS spectra of 12-ADA and its copolymers.

The copolymer with a ratio of 1:1 12-ADA/AA gave copolymers that were more crystalline (as indicated in Figure 4-11 by the scatter at 25,8 and 28) than the copolymer with the 1:5 ratio of 12-ADA/AA. The copolymer with no RAFT reagent gave a product that seemed to be highly amorphous. When compared with the highly-crystalline 12-ADA, it can be seen that copolymerisation led to a loss of crystallinity.

4.6. References

1. Rizzardo G., Le, T.P., Moad G., Thang, S.H., Patent No. PCT/US97/12540.
2. Thang S.H., Chong Y.K., Mayadunne T.A., Moad G., Rizzardo E., Tetrahedron Letters **1999**, 40, 2435.
3. Chiefari J., Chong Y.K., Ercole F., Krstina J., Jeffery J., Le T.P.T., Mayadunne R.T.A., Meijs G.F., Moad C.L., Moad G., Rizzardo E., Thang S.H., Macromolecules **1998**, 31, 5559.
4. Mayadunne R.T.A., Rizzardo E., Chiefari J., Chong Y.K., Moad G., Thang S.H., Macromolecules **1999**, 32, 6977.

5. Moad G., Ercole F., Johnson C.H., Krstina J., Moad C.L., Rizzardo E., Spurling T.H., Thang S.H., Anderson A.G., ACS Symp. Ser. **1997**, 685, 332.

6. Le T.P.T., Moad G., Rizzardo E., Thang S.H., PCT Int. Appl. WO 9801478 A1 980115.

7. Neuman R.C., Pankratz R.P., J. Org. Chem. **1971**, 36, 4046.

8. De Brouwer J., Tsavalas J.G., Schork F.J., Monteiro J.M., Macromolecules **2000.**

9. Brandrup J.; Immergut E.H.; McDowell W., Eds. Polymer Handbook. 2nd Ed. **1975**, II-3.

10 Lindoy L.F., Atkinson I.M., in: Self-Assembly in Supramolecular Systems, 1st Ed., RSC/Springer, **2000**, 224.

11. Aakeroy C.B., Seddon K.R., Chem Soc. Rev. **1993**, 22, 397.

12. Yang J., Marendaz J-L., Geib S.J., Hamilton A.D., Tetrahedron Letters **1994**, 35, 3665.

13. Moad G., Chiefari J., Chong Y.K., Krstina J., Mayadunne R.T.A., Postma A., Rizzardo E., Thang S.H., Polymer International **2000**, 49, 993.

14. Karino T., Masui N., Hiramatsu M., Yamaguchi J., Kurita K., Naito S., Polymer **2002**, 43, 7467.

[1]5. Uchida M., Kurosawa M., Osada Y., Macromolecules **1995**, 28, 4583.

CHAPTER 5

Synthesis and Characterisation of Polystyrene Latices Prepared by Emulsion Polymerisation

5.1. Introduction

The development of latices containing functional groups has been under investigation for a long time. The reason for the interest in these polymers arises from their wide variety of properties, which can be achieved through the modification of the surface properties of such latices.[1] One way of preparing such functionalised latices involves the use of functional comonomers that contribute towards the colloidal stability of the particles. Functionalised latices can also be used to modify the properties of polymers.[2] Carboxylic monomers containing terminal carboxylic acid groups have been used as functional monomers in emulsion polymerisation recipes and the resulting products are referred to as carboxylated latices.[3]

There are several advantages associated with incorporating carboxylic acid groups into polymers:

- they provide the polymers with sites for post-polymerisation reactions, such as for bio-molecule binding,
- they enhance the chemical and mechanical stability of the latex,
- they enhance the adhesion of polar substrates, and
- they control the rheology of the latices.[4]

In this study, surfmers and oligomeric surfactants containing carboxylic acid groups, prepared as described in Chapter 3, are used as particle stabilisers in the polymerisation of styrene. Initially, the extent to which each surfactant emulsifies a starting emulsion was estimated by examining the stability of the mixed emulsion just prior to polymerisation. It was considered to be of interest to encapsulate nanoparticles in carboxylated latices to create "smart materials".

5.2. Materials

In both the pre-emulsion tests and the emulsion polymerisation of styrene the following reagents were used: styrene monomer, sodium borate buffer solution (pH 8 and pH 3 for the surfmers, and pH 8 for oligomers), the appropriate surfactant, and $K_2S_2O_8$ initiator. Although most carboxylated latices are normally prepared at pH values of 3 to 4, a pH 8 buffer was mainly used in these experiments. This was done for two reasons: to ensure an approximately constant pH during the emulsion polymerisation process, and because it was found that the acid surfmers and oligomeric surfactants (which were not soluble at pH 3) were all soluble to some extent in the buffer solution at pH 8. The buffer solution was prepared from double-deionised (DDI) water and sodium borate. In addition to 12-ADA, 11-AAUA, their respective Na salts, and the oligomeric surfactants, the conventional surfmer SDS was also used as surfactant for both the pre-emulsion and polymerisation experiments at a pH of 8. The reagents used for the emulsion polymerisation of styrene using different surfactants are tabulated in Table 5-1.

The surfactants used in the pre-emulsion tests and emulsion polymerisations were: 12-ADA; 12-ADA Na; 11-AAUA; 11-AAUA Na; SDS; poly (12-ADA); and a copolymer, poly (co-ADA/AA). Sodium borate, ($Na_2B_4O_7.10H_2O$) buffer solutions at pH 8 or pH 3 were used for the surfmers, while only pH 8 buffer was used for the oligomers and copolymers.

Table 5-1. Reagents used in the emulsion polymerisation of styrene

Processes	Materials	How obtained
Pre-emulsion test and emulsion polymerisation	Surfactant	Prepared as described in Section 3.3.
	Distilled styrene (Sigma)	Washed with KOH and vacuum distilled
	Potassium persulphate (Sigma)	Recrystallised from distilled water
	Na borate (Acros) buffer solution in DDI water (pH 8)	Prepared from a primary standard

5.3. Pre-emulsion tests

5.3.1. Experimental

Pre-emulsion tests to determine the extent to which emulsification of the reactant mixture occurred at room temperature prior to emulsion polymerisation were carried out.   To examine the extent to which a surfactant emulsified reactants, each surfactant was in turn thoroughly mixed together with the other components of a polymerisation recipe and the stability of the mixed emulsion estimated by noting the time it took for the mixture to separate into aqueous and oily phases. Pre-emulsion tests were used to "measure" the extent of emulsification in each mixture containing the different surfactants, before polymerisation in a procedure such as the one reported by Cochin et al.[5] The emulsifying efficiency of each surfactant was taken as the time it took for the oily and water layers to separate at room temperature. This could be taken as an estimate of the extent of stabilisation of the monomer droplets in the system.   For emulsification with the oligomeric surfactants, 0,5 wt % of surfactant (w.r.t. weight of monomer) was used.   The tests were performed in duplicate, and repeated.

For each pre-emulsion test the surfactant was first dissolved in the buffer solution in a flask. Styrene monomer and initiator were then added. The mixture was stirred and purged with N_2 gas. The mixture was left to stir for 1 h, after which the mixture was quickly poured into a test tube and left to stand at room temperature. The time it took for the mixture to separate into aqueous and organic layers was noted.

5.3.2. Results and discussion

A summary of the results of these tests is given in Table 5-2. The results were fairly reproducible to within about ± 3 minutes.

Table 5-2. Estimation of pre-emulsion stability observed for different surfactants

Surfactant	Conc. of surfactant (wt % w.r.t. styrene)	Time taken for separation to occur (min)
SDS	2	160
12-ADA	2	190
12-ADA Na	2	24
11-AAUA	2	16
11-AAUA Na	2	9
Poly(ADA-AIBN)	0,5	150
Poly(ADA-ACP)	0,5	860
Poly (AAUA)	0,5	130
Copol(ADA/AA)	0,5	22

From the results it is clear that the emulsion formed with the RAFT oligomer poly (ADA-ACP) gave the most stable emulsion. This may have been partly due to the extra hydrogen bonding from the -COOH groups of the longer chain molecules plus the -COOH from the ACP-RAFT moiety. The 12-ADA/AA copolymer-stabilised latex was not well emulsified in 1 hour. This could have been due to competing effects from the different hydrophobes of AA and 12-ADA.

5.4. Emulsion polymerisation of styrene

5.4.1. Materials and polymerisation conditions

The materials used for emulsion polymerisation are tabulated in Table 5-1. The initiator was only added after the reaction temperature had been increased to 80°C, to allow uniform polymerisation.

Typical reaction conditions for the emulsion polymerisation were: 20 min premixing at high shear rate (500 rpm) and reaction at 80 ºC for 3 h at low shear rate (300 rpm). Similar reactants and conditions were used for the styrene polymerisation with the oligomeric surfactants except that the amount of oligomeric surfactant used was 0,5 wt% of oligomer w.r.t. styrene instead of 1-4 wt% for surfmers.

5.4.2. Experimental procedure

The surfactant (1-4 wt% for surfmer or 0,5 wt% for oligomer) was first dissolved in buffer solution in a flask. Styrene monomer was then added to the solution of surfactant and the contents of the flask stirred and purged with nitrogen. The content of the flask was brought up to 80 °C before the $K_2S_2O_8$ initiator, which had been dissolved in 1 ml of buffer solution and purged with nitrogen, was added through a septum. The reaction mixture was stirred at a high shear rate for the first 20 minutes and at a low shear rate for the rest of the reaction. Each polymerisation was allowed to run for a total time of 3 hours before the reaction was stopped by rapid cooling.

5.4.3. Cleaning of latices

Before any analysis and characterisation of the polystyrene latices could be carried out there was need to purify the latices as far as possible. This was done because, by nature of its being a heterogeneous process, a variety of by-products are always produced in an emulsion polymerisation process. These could include: unreacted monomer, initiator fragments, added salts, oligomeric species and even polyelectrolytes which may be formed by the polymerisation of water-soluble monomers, if present in the aqueous phase.

Also, polymer latices, like most colloids, have high specific interfacial areas which can be easily contaminated through adsorption. A few latex cleaning methods were tried in order to purify the prepared PS latices.

5.4.3.1. Filtration of latices

The latices were filtered through a funnel packed with a weighed amount of glass wool. Coagulant left on the glass wool was dried and weighed. The extent of coagulation was estimated for each emulsion polymerisation reaction by weighing the amount of dry coagulant resulting from the polymerisation.

5.4.3.2. Use of ion-exchange resins

Equal quantities of Dow cationic and anionic exchange resins[6] (Sigma) were each thoroughly washed with deionised water. The respective resins were mixed and packed into a cylindrical glass column plugged with glass wool at one end. Using large volumes of deionised water, the resins were washed by stirring in a large quantity of DDI water, decanting the water and repeating the process until the water remained clean and had a low conductance. The conductivity of eluted water was measured and the washing stopped when the water eluted had nearly the same conductance as that of the deionised water. In this experiment, the conductivity of the eluted water was 1,70 X 1µS before latex was poured down the column and collected as eluent.

5.4.3.3. Dialysis

A semi-permeable membrane was used to clean the latex by dialysis.[7] The latex was placed in a tube of dialysis membrane closed at one end and tightly clipped at the other to avoid leakages. The membrane was then placed in a large beaker of deionised water and dialysis allowed to proceed. The water was changed every two days over a 2-week period. The conductance of the water was measured at each change. The latex was deemed clean when the conductivity was low and approached that of deionised water.

5.4.3.4. Centrifugation

The use of centrifugation to purify latices has been reported.[8] The latices prepared in the present study were cleaned with deionised water using an ultracentrifuge operating at 1200 rpm. Freshly deionised water was added to the centrifuged latex and the mixture stirred vigorously before being poured into vials, and centrifuged. The contaminated water was then decanted. Each time after centrifuging, freshly deionised water was added to the latex and the latex redispersed by stirring. The process was repeated four times for each latex.

5.4.3.5. Coagulation during polymerisation

The coagulant accumulating from each polymerisation was collected as the residue of the filtration of the product latices with glass wool. This was then dried and weighed. The results of coagulation are summarised in Table 5-3.

Table 5-3. Coagulation resulting from the use of different surfactants

●

Surfactant	Mass of coagulant (mg)	Mass of reactants (mg)
SDS	8	$1,2 \times 10^4$
12-ADA	28	$1,2 \times 10^4$
12-ADA Na	10	$1,2 \times 10^4$
11-AAUA	12	$1,2 \times 10^4$
11-AAUA Na	9	$1,2 \times 10^4$
Poly(ADA-AIBN)	78	$0,3 \times 10^4$
Poly(ADA-ACP)	42	$0,3 \times 10^4$
Poly(AAUA-AIBN)	45	$0,3 \times 10^4$
Copolymer (ADA/AA)	30	$0,3 \times 10^4$

5.4.4. Results of latex cleaning

Of the described methods for latex cleaning, the use of filtration by glass wool followed by use of ion-exchange resins proved to be the most effective for the purification of the latices prepared in this study. Although there are drawbacks

associated with the use of most of the cleaning methods that were used,[9] it was found that the combination of the above two methods offered the best and most reasonable compromise, and most of the latices were adequately purified using these methods. Some of the purification methods were too harsh for use with some of the latices, especially those stabilised with SDS, the 11-AAUA Na salt and the 12-ADA Na salt. These three types of latices could not withstand centrifugation in which sonication was used to redisperse the latex after the latex solid had collected at the bottom of the vial. It was difficult to redisperse the latex adequately to give particle sizes similar to those prior to the centrifugation. Also, the SDS latex and the ADA-ACP-stabilised latex were destabilised by the dialysis treatment. This was noticed when particle sizes of the purified latices were compared before and after dialysis.

5.5. Stability of emulsions

The stability of an emulsion was tested by introducing external conditions that are capable of destabilising the emulsion, followed by an estimation of the extent of the coagulation that results. Such coagulation, which results from the coalescence of latex particles, was then used as a measure of instability. Some of the external conditions that can bring about coagulation of particles in latices are mechanical agitation, addition of electrolyte and long-term storage.

5.5.1. Mechanical stability of a PS latex

In order to estimate the mechanical stability of polystyrene latex the following procedures were undertaken to agitate the latex: a small amount of latex was added to a round-bottom flask, the contents of the flask were frozen and degassed by drawing a vacuum before warming and thawing. The contents were then stirred vigorously. This freeze-degas-thaw process was repeated five times.

The extent of coagulation was measured and estimated as follows: The latex was filtered using a piece of weighed glass wool, which was then dried under vacuum overnight and reweighed. The masses of latex before and after freeze-thawing the samples were compared and interpreted as follows:

- the latex was deemed **stable** if there was no noticeable difference in the mass of dry glass wool before and after filtration,
- it was **coagulated** if there was 20 wt % precipitation,
- there was **little coagulation** for 10 wt % and less precipitation, and
- there was **some coagulation** for 3 wt % or less precipitation.

The above notation was used to summarise the results in Tables 5-4 to 5-6. The percentages given are w.r.t. the amount of total solids. The results of the freeze-thaw tests performed on the different latices are tabulated in Table 5-4.

Table 5-4. Stability of PS latices after five freeze-thawing cycles

Surfactant used in latex	Stability of new latex on fifth thawing	Stability of 12-month-old latex on fifth thawing
SDS	coagulation	coagulation
12-ADA	stable	some coagulation
12-ADA-Na	some coagulation	little coagulation
11-AAUA	stable	little coagulation
11-AAUA-Na	coagulation	coagulation
Poly (ADA)-RAFT	stable	stable
Copolymer (ADA/AA 1:1)	stable	little coagulation

5.5.2. Stability of latices against electrolytes

Small quantities of electrolyte were added to small amounts of prepared latex. The mixture was stirred and the extent of coagulation examined after each addition. The electrolytes that were used were NaCl, $CaCl_2$, Na_2SO_4. The latex was filtered using a piece of weighed glass wool, which was dried under vacuum overnight and reweighed. The respective masses of coagulant produced after electrolyte addition were measured and interpreted as described in Section 5.6.1. A summary of the results is tabulated in Table 5-5.

Table 5-5. Results of latex stability tests on adding electrolyte

Type of electrolyte added	electrolyte (conc.)	Stability of 12-ADA-stabilised latex	Stability of ADA-AIBN & ACP-RAFT oligomer-stabilised latex	Stability of SDS- stabilised latex	Stability of AAUA-stabilised latex
Sodium chloride	0,01M	stable	stable	stable	stable
	0,05M	stable	stable	stable	stable
	0,1M	stable	stable	stable	stable
	0,2M	stable	stable	stable	stable
Calcium chloride	0,01M	stable	stable	l. coagulation	stable
	0,05M	stable	stable	coagulation	stable
	0,1M	stable	stable	coagulation	stable
	0,2M	stable	stable	coagulation	l. coagulation
Sodium sulphate	0,01M	stable	stable	stable	stable
	0,05M	stable	stable	stable	stable
	0,1M	stable	stable	stable	stable
	0,2M	stable	stable	stable	stable

l. coagulation: little coagulation

5.5.3. Stability of latices on storage

The different latices were examined after different storage times to check for any coagulation which may have occurred. Each of the latices was examined after storage in the dark for 6, 18 and 34 months. The results are tabulated in Table 5-6.

Table 5-6. Resultant coagulation of various latices after periods of storage

Surfactant in latex	6 months	18 months	34 months
12-ADA	stable	stable	stable
12-ADA-Na	stable	stable	some coagulation
11-AAUA	stable	some coagulation	some coagulation
11-AAUA-Na	stable	some coagulation	little coagulation
Poly(ADA), ACP-RAFT	stable	stable	stable
Poly(ADA), AIBN-RAFT	stable	stable	some coagulation
Poly(co-ADA/AA)	stable	stable	little coagulation
SDS	stable	coagulation	coagulation

5.6. Results and Discussion

Results of the pre-emulsion tests gave an indication of the extent of emulsification of a mixture that occurs when surfactants are stirred together with other starting materials prior to polymerisation. It was found that the emulsion formed from the RAFT oligomer poly (ADA-ACP) gave the most stable emulsion (stable over 860 minutes) followed by the emulsion formed with 12-ADA (stable over 190 minutes). This may have been due to the intermolecular associations of which 12-ADA is capable of (already described in Section 3.6). Such associations would no doubt lead to some extra emulsification. The loop conformation of 12-ADA in which the hydrophilic parts preferred to distribute themselves in a polar solvent would have contributed to maintaining the -COOH groups in the water phase. In the pre-emulsion tests, surfactant was first dissolved in buffer before the addition of the other components and before the start of the 1 hour of stirring.

The extra hydrogen bonding from the -COOH groups of the longer chains plus the -COOH from the ACP-RAFT moiety may explain the extraordinary extent of emulsification of the emulsion mixture by the poly (ADA-ACP) compared to that of the AIBN-RAFT. This observation is further noticed in the stability of latex on prolonged periods of storage.

The 12-ADA/AA copolymer-stabilised latex was not well emulsified in the pre-emulsion tests even though stable latices were obtained on polymerisation. This indicated that some strong stabilising forces may have been achieved through copolymerisation, suggesting some inherent stability brought about by the addition of 12-ADA units, and not from the shorter AA units. It seems as if loops might have been formed as the AA copolymerised in the tail section while the rest of the -COOH groups were in the head section.

The freeze-dried latices of 12-ADA, 11-AAUA and the polymeric surfactant-stabilised latices remained stable for 34 months, while the SDS, 11-AAUA-Na, 12-ADA Na salt and copolymer ADA/AA (1:1)-stabilised latices were not as stable over the same period. Although the Na salts of 12-ADA and 11-AAUA produced relatively more stable latices than SDS did, the acid forms and the RAFT polymers (with a higher opportunity for H-bonding) seemed to give even more stable particles. The stability of surfmer-stabilised latices against most agitation forces suggests that chemical bonding did seem to occur between surfmer and latice particles. The SDS particles showed a significant amount of coagulation 18 months after preparation as shown in the SEM micrographs shown later in this chapter. This may indicate a reduction in or loss of stabilisation through some desorption taking place slowly on storage. Addition of $CaCl_2$ also coagulated the latex and the destabilisation was even more significant in the freeze-thawed SDS-stabilised latex.

Even the oligomers poly (ADA-AIBN) and poly (ADA-ACP) were successfully used as surfactants in the emulsion polymerisation of styrene. The polystyrene latices produced were slightly tinted beige, which must have been from the RAFT reagent. The reddish colour of the reagent was not apparent during emulsion polymerisation which may suggest chemical bonding of the RAFT moiety. One noticeable aspect of the emulsion polymerisations using polymeric surfactants as well as with 12-ADA

was that more coagulant was obtained with 12-ADA and its oligomers during emulsion polymerisation than with the other surfactants, including SDS. This may have been due to the insolubility of 12-ADA in water and of the large polymeric surfactants which carried a relatively large hydrophobic moiety.

5.7. Characterisation

Purified latices were characterised in various ways. A major limiting factor in using some of the standard characterisation methods was found to be the limited solubility of some of the prepared compounds in common solvents.

For an approximation of molar mass, matrix-assisted laser desorption/ionisation with time of flight (MALDI-TOF) techniques were used. Light scattering and microscopic methods were used to determine the size of the prepared latex particles, their polydispersities and their morphology, and to estimate the extent of particle stabilisation in latices prepared by emulsion polymerisation. Wide angle X-ray scattering (WAXS) was used to examine the crystallinity of the latices prepared. Thermal analysis was used to estimate the thermal properties of the prepared compounds. Purified latices were also titrated, by conductometry, to estimate the extent of coverage of particles with surface groups. Latices were also freeze-dried before being coated with gold and analysed by scanning electron microscopy.

SEM results gave indications of particle size, uniformity, coagulation of particles, and estimation of stability.

The stability of an emulsion was examined using different methods, to facilitate a comparison of the extent of latex stabilities of emulsions prepared with different surfactants.

5.7.1. Matrix-assisted laser desorption/ionisation with time of flight (MALDI-TOF)

Mass spectrometry offers absolute molar mass analysis regardless of chemical nature, and was therefore considered as a useful analytical method to use. MALDI-TOF is one of the mass spectrometric methods suitable for polymers because it can be used to measure high molecular masses without fragmentation. The use of MALDI-TOF mass spectrometry for characterisation of polymers is well reviewed in a book by Pasch and Schrepp.[10] The method allows single polymer chains with molecular masses below 50 000 g/mol to be resolved, leading to the determination of repeat units and end-groups.

For MALDI-TOF analysis the samples were first dissolved in THF or THF/DMAc and then mixed with a solid matrix. They were then irradiated with laser light from a MALDI-TOF spectrometer Kratos PC Kompact Maldi 4 model, using a delayed-extraction negative mode at 20000 volts. Figures 5-1 to 5-4 show MALDI-TOF spectra obtained for some of the surfactants.
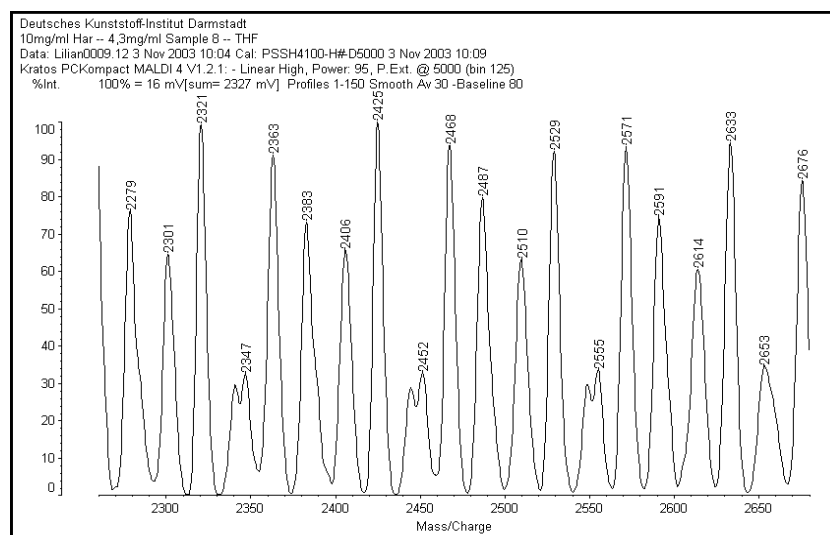
Figure 5-1. MALDI-TOF spectrum of 12-ADA-stabilised latex at high resolution.

The mass/charge difference between similar peaks such as at 2321 and 2425 was found to be 104. This is consistent with that of styrene units, thus confirming the product to constitute mainly polystyrene.
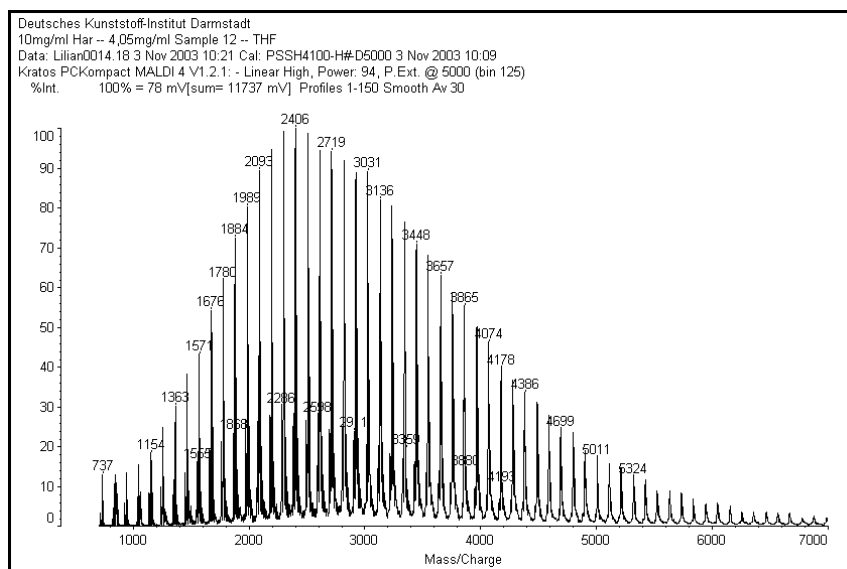

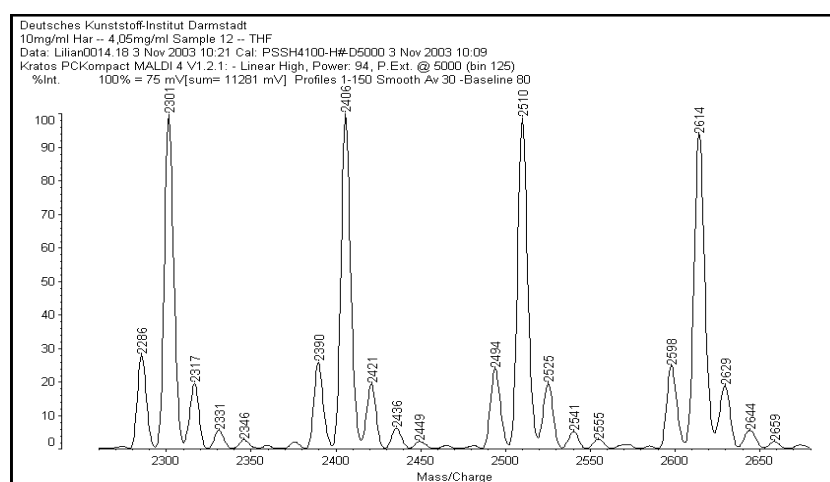**Figure 5-2.** MALDI-TOF spectrum of styrene latex from copolymer (12-ADA/AA-1:1).

Figure 5-3. A further-resolved MALDI-TOF spectrum of styrene latex from the surfactant (12-ADA/AA-1:1).

The MALDI-TOF results showed the copolymer-stabilised latex from a 1:1 ratio of 12-ADA to AA (12-ADA/AA-1:1) to correspond to a mass/charge of about 2500 g/mol, as shown in Figure 5-2. The copolymer-stabilised latex was further resolved as shown in Figure 5-3. There were similarities with the 12-ADA-stabilised latex shown in Figure 5-1. The latices were of comparable molar mass. The presence of AA in the

104

copolymer-stabilised latex probably led to the differences in the peak structures, size and number. Results contribute to confirming that reaction occurred between 12-ADA and AA, resulting in the copolymer that stabilised the latex, the MALDI-TOF spectrum of which is illustrated in Figure 5-3.

5.7.2. Wide angle X-ray scattering (WAXS) analysis

The samples examined by WAXS were mounted using Al foil to hold samples in place while X-rays hit the sample at an angle (as already described in Section 4.5.4). The copolymers prepared with and without using the RAFT polymerisation process were measured by WAXS.

The WAXS spectra of 12-ADA and its oligomers and polymers of ADA are show n in Figure 5-4. The WAXS spectra of PS latices and 12-ADA are given in Figure 5-5. The spectrum of 12-ADA was included in these two figures to allow direct comparisons to be made.

The scatter from the Al foil was observed at about 17,0, as expected. Both the oligomeric and polymeric 12-ADA-based compounds exhibited crystallinities that differed from the highly-crystalline surfmer 12-ADA. The RAFT-oligomer appeared to have a low crystallinity, as indicated by the absorptions at about 20, 25,5 and 31,8.
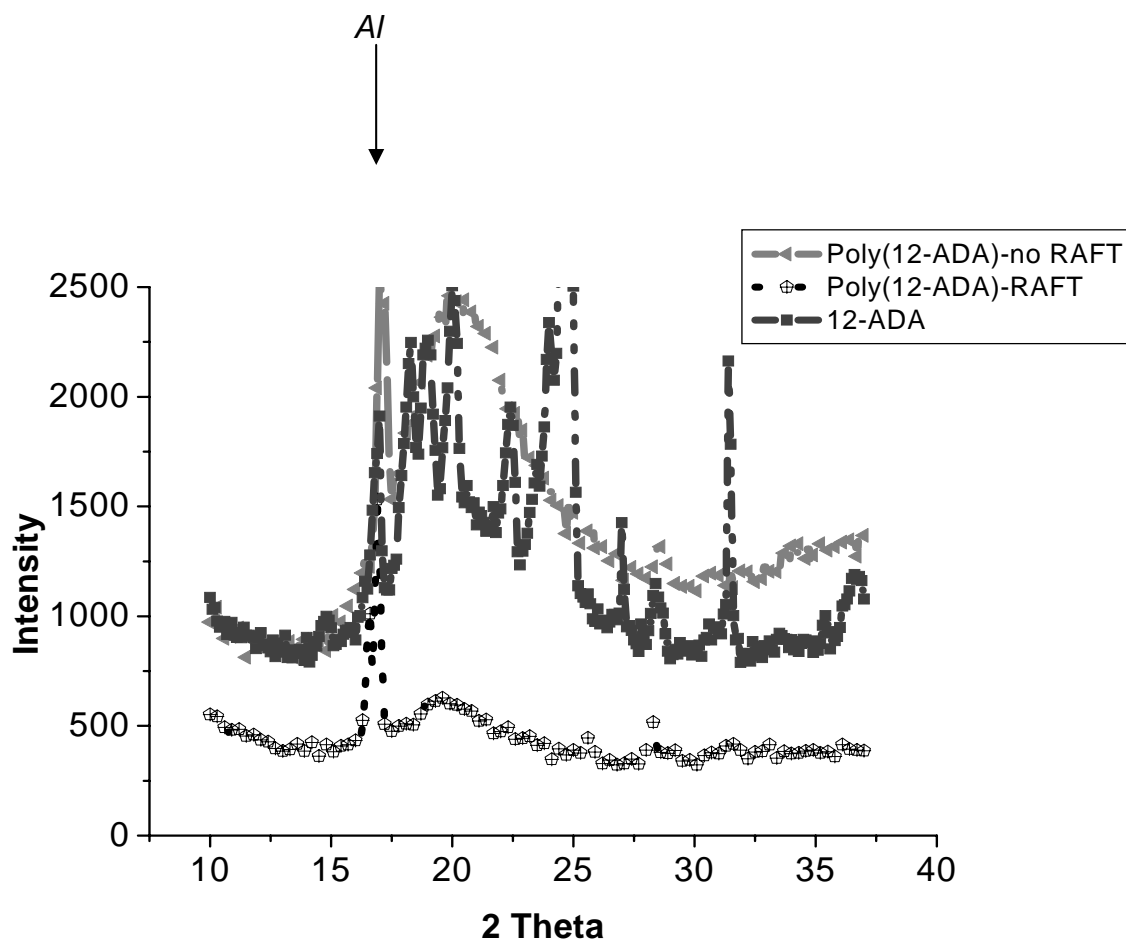
Figure 5-4. WAXS spectra of 12-ADA and oligomers and polymers of 12-ADA.

The polymerisation of 12-ADA led to a product of higher amorphicity and lower crystallinity compared to the morphology of the surfmer, but there was a large dilution effect. The non-RAFT compound had an even lower crystallinity, similar to the crystallinity of the non-RAFT copolymer of 12-ADA/AA.
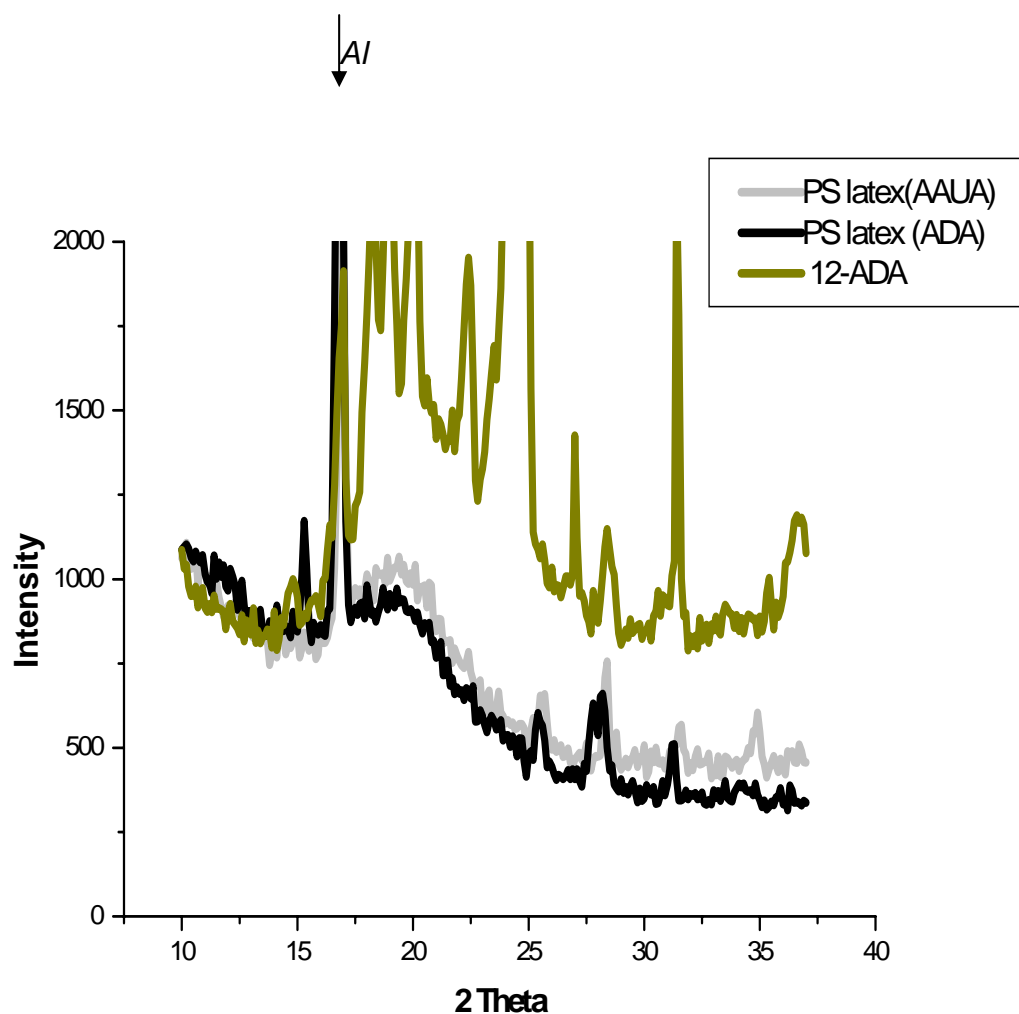
Figure 5-5. WAXS spectra of PS latices and 12-ADA.

Both the PS latices prepared using 11-AAUA and 12-ADA retained a measure of crystallinity, as indicated by the absorptions at about 25, 27,5 and 31,8 shown above.

5.7.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was carried out using a Mettler Toledo DSC 822e thermal analyser. In the TGA mode the thermal analyser measures weight changes in a material as it is heated, cooled, or held at a constant temperature in an inert atmosphere. This analysis can give a fast estimation of composition and thermal stability. The results of the TGA analysis of latices prepared with different surfactants are illustrated in Figure 5-6.
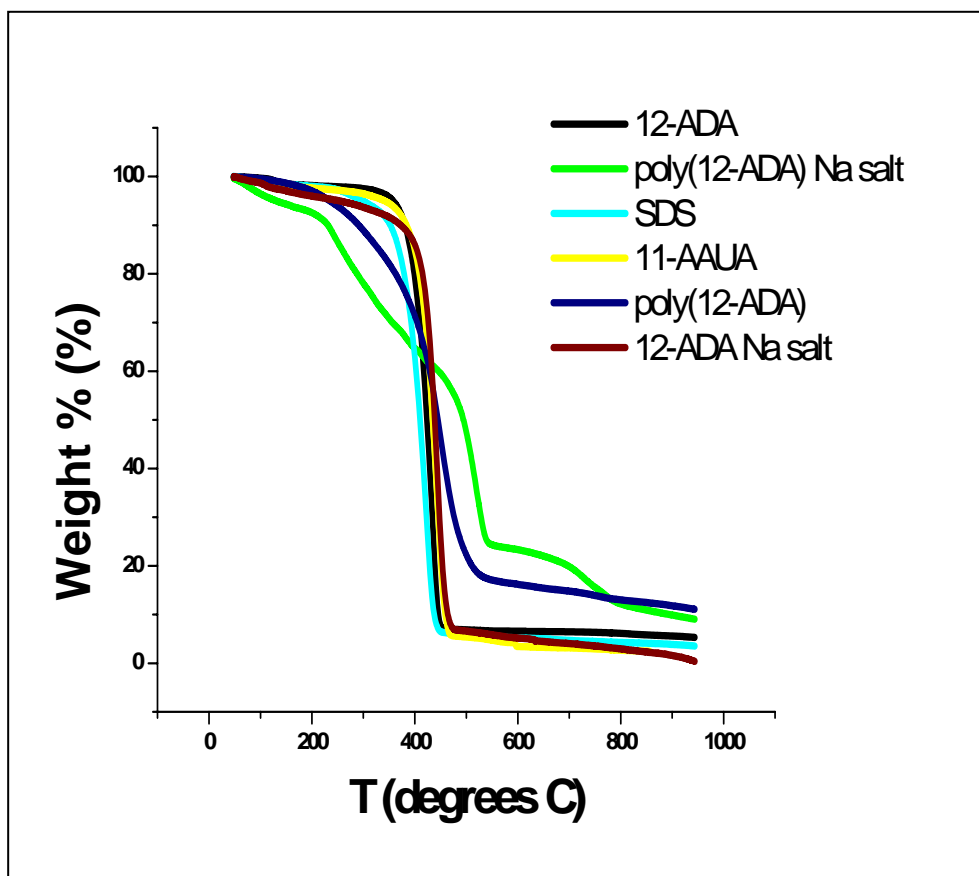
Figure 5-6. TGA analysis of latices prepared with different surfactants.

The curves observed in Figure 5-6 show that the weight loss of the latices prepared from the RAFT oligomeric surfactants was faster than those prepared with surfmers and SDS at temperatures 200 ^{0}C to 400 ^{0}C. At temperatures greater than 400 ^{0}C, all the surfmer and SDS-stabilised latices were degraded to 0-5 weight % while the oligomer-stabilised latices had a slower weight loss and remained with 10-20 weight %. Although there were no significant differences in the thermal stabilities of all the latices, the different degradation rates might suggest different mechanisms of weight loss occurring between the oligomer-stabilised latices and the other surfactant-stabilised latices. It seems as if the oligomer-stabilised latices were reduced to much smaller but perhaps more thermally stable compounds which could withstand temperatures of 500 ^{0}C.

5.7.4. Determination of particle size and polydispersity

Particle size was determined by dynamic light scattering (DLS) using a Malvern Zetasizer. DLS differs from traditional light scattering techniques in that while the latter methods measure the average scattered intensity of particles, DLS makes use of the time behaviour of scattered intensities obtained from the suspension of particles.

After the latices were prepared and purified they were dispersed in a millimolar NaCl diluent and poured into glass cell cuvettes before being the scattered intensities were measured at 25 ºC and at 90-degrees angle. The results are tabulated in Table 5-7. Figures 5-7 and 5-8 illustrate respective unimodal and bimodal distributions of particle size diameters.
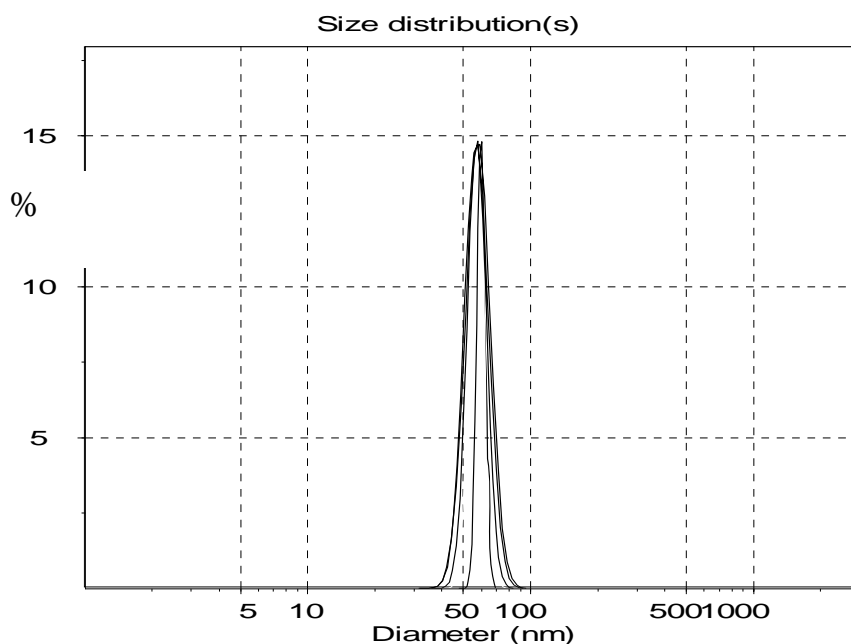

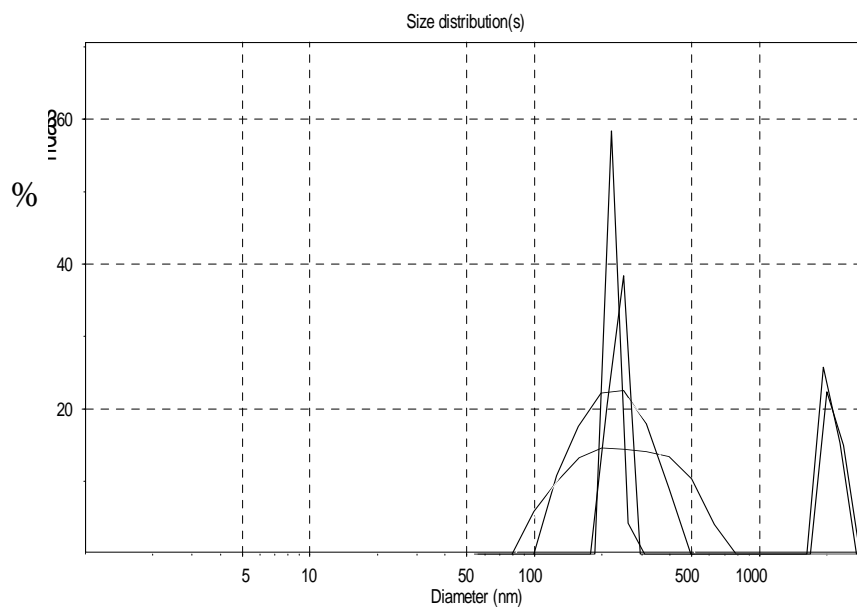**Figure 5-7.** A unimodal particle size distribution for the 2 wt % SDS-stabilised latex.

Size distribution(s)

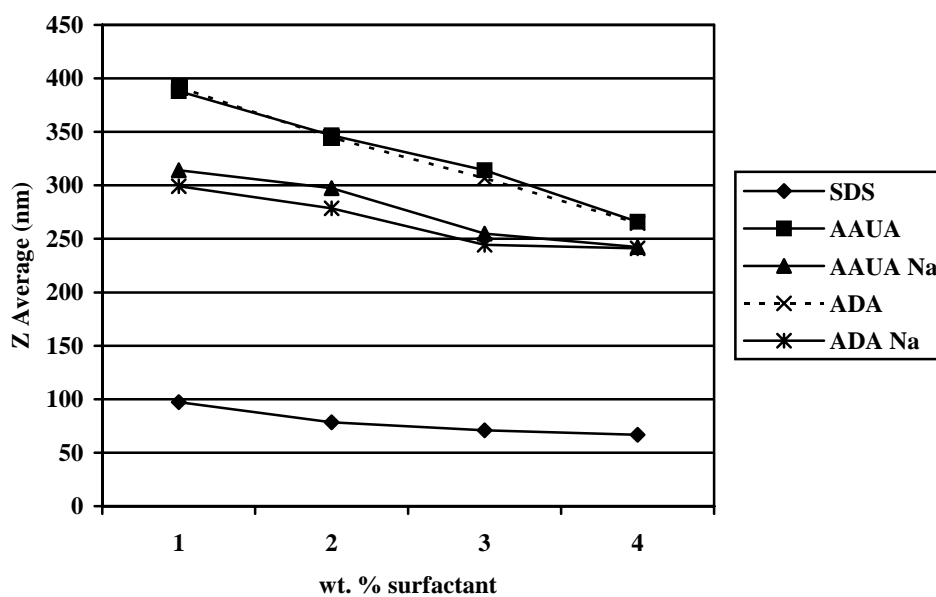**Figure 5-8.** A bimodal particle size distribution for the 2 wt % 12-ADA-stabilised latex.

Figure 5-9. The relationship between particle diameter and surfactant concentration.

The average diameters of the latex particles prepared with different surfactants were plotted against the weight of surfactant used. The results are shown in Figure 5-9.

Table 5-7. Latex particle sizes and polydispersities

Surfactant	pH	Surfactant Wt %	Z_{Ave}(nm)	Polydispersity	Distribution
SDS	8	1	97	0,04	unimodal
SDS	8	2	78	0,03	unimodal
SDS	8	3	71	0,04	unimodal
SDS	8	4	67	0,01	unimodal
SDS	3	3	57	0,01	unimodal
SDS	3	4	54	0,01	unimodal
ADA	8	1	392	0,17	bimodal
ADA	8	2	345	0,34	bimodal
ADA	8	3	307	0,44	bimodal
ADA	8	4	265	0,50	bimodal
ADA Na	8	1	299	0.17	unimodal
ADA Na	8	2	279	0,13	unimodal
ADA Na	8	3	244	0,12	unimodal
ADA	3	3	136	0,36	bimodal
ADA	3	4	188	0,29	bimodal
AAUA	8	1	388	0,13	unimodal
AAUA	8	2	347	0,12	unimodal
AAUA	8	3	314	0,03	unimodal
AAUA	8	4	266	0,07	unimodal
AAUA Na	8	1	314	0,05	unimodal
AAUA Na	8	2	297	0,03	unimodal
AAUA Na	8	3	255	0,01	unimodal
AAUA Na	8	4	242	0,03	unimodal
polyADA-RAFT	8	0,5	661	0,20	bimodal
polyAAUA-RAFT	8	0,5	344	0,64	bi/trimodal
polyADANa-RAFT	8	0,5	609	0,43	bi/trimodal

The surfactant SDS was successfully used as a stabiliser for the emulsion polymerisation of styrene as indicated by the dynamic light scattering results, which showed SDS-stabilised polystyrene particles with diameters of low polydispersity. The latices produced when 11-AAUA was used as surfactant in emulsion polymerisation also indicated stability through the production of fairly uniform latex particles of low dispersity. However, when 12-ADA was used as surfactant a bimodal distribution in the size of particle diameter was shown, as illustrated. The Na salt of 12-ADA showed a mainly unimodal distribution unlike the acid which gave a predominantly bimodal distribution. This suggests that the stabilisation mechanism for 12-ADA was different from that occurring in the case of SDS and the Na salt of 12-ADA. The Na salt with -COONa as opposed to a free -COOH acid does seem to sterically-stabilise PS latex particles using a different mechanism (more ionic). The bimodal distribution may suggest that 12-ADA-stabilised latex could be formed by a droplet-entry type mechanism in addition to a homogeneous mechanism while the 12-ADA salt-stabilised latex must have followed a regular droplet entry-type of emulsion polymerisation kinetics. Both the AAUA acid and the corresponding salt-stabilised latices seemed to follow regular emulsion polymerisation kinetics of the droplet-entry type mechanism. In fact, when used in emulsion polymerisation of styrene, the surfmers led to the preparation of latices composed of 12-ADA or 11-AAUA fragments with styrene units. After a period of 6 months and more, dynamic light scattering measurements showed large particles sizes and polydispersities for the SDS-stabilised latices whereas, both the 11-AAUA and 12-ADA-stabilised latex particles did not change much over the same period of time. This indicates a strong stabilising effect at play when surfmers are used as emulsifiers in emulsion polymerization compared with the conventional SDS.

Generally, larger particle size diameters than those obtained with corresponding surfmer-stabilised latex were a common feature with polymeric surfactants. This can be attributed to the lower surfactant concentrations used as well as the relatively longer chains of the molecules. The particle sizes of the RAFT oligomer-stabilised and the 12-ADA-stabilised latices showed a large molecular mass distribution, which was found to be bimodal in most cases, resulting in even larger polydispersities, as shown in Table 5-7. On analysis by SEM and TEM the latices produced were large distinct spherical particles of different sizes, which corroborate the results of the light

scattering results. Two distinct size-populations were evident in the oligomer-stabilised latices, suggesting that more than a single droplet entry mechanism occurred in addition to the normal mechanisms of particle formation.

5.7.5. Surface analysis of PS latices

In order to try to understand more about the surface properties of latex, the surface charge density is usually determined in order to estimate the surface coverage of a latex particle with stabilising groups.[11] The surface charge of latex particles was determined by direct titration using conductometry. The method involves titrations in which conductivity changes in the suspending medium are measured and plotted to determine the equivalence point. Only two latices were analysed using conductometry because the method was rather expensive. The analysis was therefore done to test the effectiveness of the analytical method in examining surfaces of latice particles.

The surface charge of latex particles due to carboxyl groups as well as due to sulphate groups (from the potassium persulphate initiator) was determined by direct conductometric titration for 12-ADA and 11-AAUA-stabilised latices. The measurements were done by Interfacial Dynamics Corporation, Tualatin, USA. The experimental data so obtained is illustrated in Figures 5-10 to 5-13 and a summary of which is tabulated in Table 5-8.

Conductometric titration results are used to estimate the charge densities of the functional groups on the surface of the latex particle. This allowed a comparison of the extent of surfactant cover of the particles to be made. The Figures 5-10 to 5-13 are given as recorded at Interfacial Dynamics Corporation.
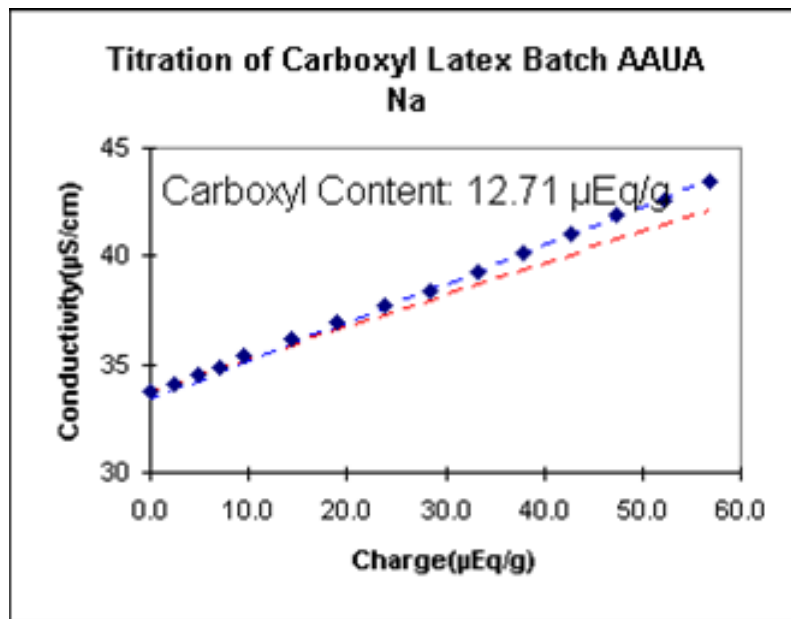
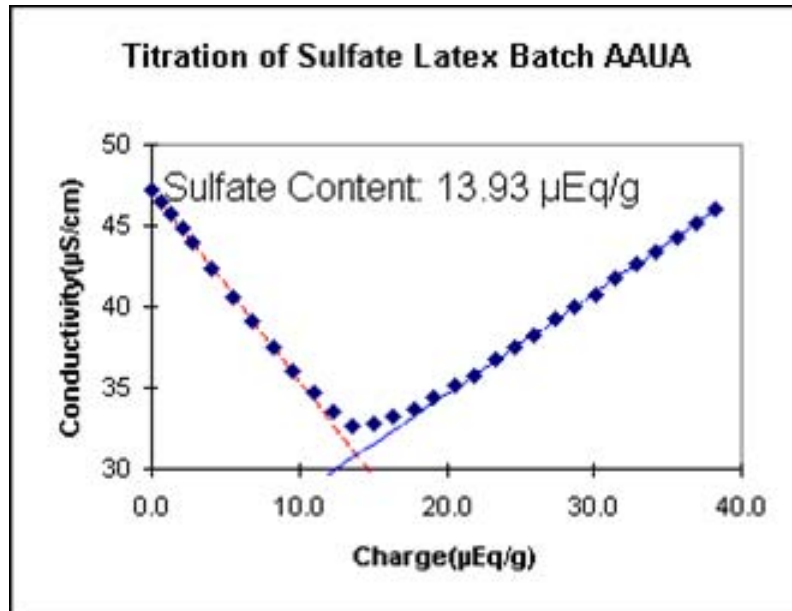**Figure 5-10.** Conductometric titration for carboxyl in 11-AAUA-stabilised latex.

Figure 5-11. Conductometric titration for sulphate in 11-AAUA-stabilised latex.
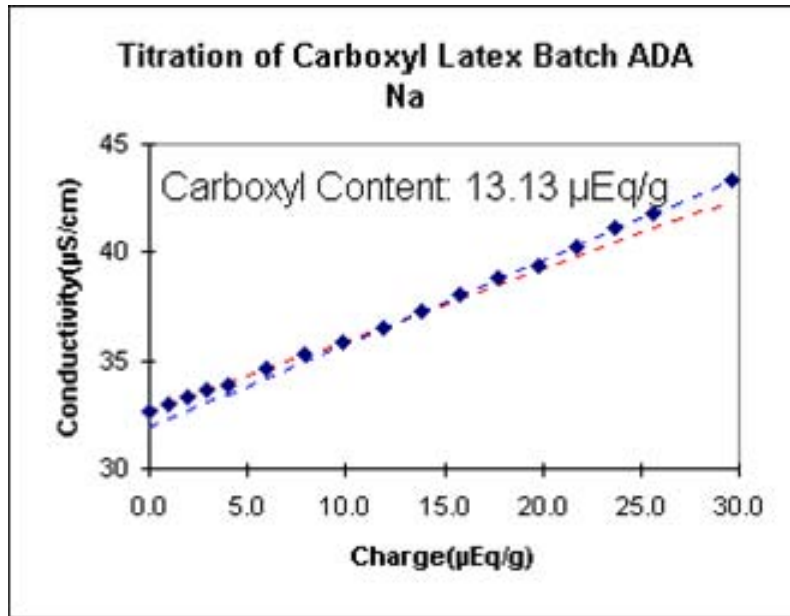
Figure 5-12. Conductometric titration for carboxyl in 12-ADA-stabilised latex.
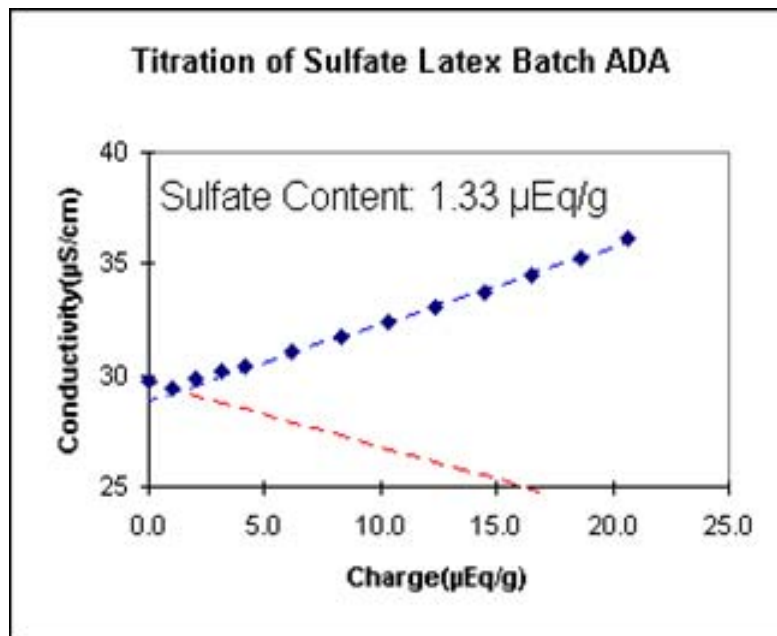

Figure 5-13. Conductometric titration for sulphate in 12-ADA-stabilised latex.

Table 5-8. A summary of conductometric measurements for surfmer-stabilised latices

Sample	Strong acid (μEq/g)	Weak acid (μEq/g)
AAUA	13,9	None
AAUA Na	None	12,7
12-ADA	1,3	None
12-ADA Na	None	13,1

The results showed that there are two sources of surface functional groups, namely the strong acid groups from sulphate in the potassium persulphate initiator fragments and weak acid groups from the carboxylic acid groups chemically bonded surfmer. The figures recorded in μEq/g correspond to the abundance of strong acid (sulphate ions and carboxylic acid) groups found on the surface of the latex.

It was however shown, through the titrations, that the 11-AAUA acid-stabilised latex had the largest coverage by strong acid groups i.e., 13,9 μEq/g, followed by 12-ADA with 1,3 μEq/g. This suggests that 12-ADA-stabilised latex which seemed more stable than the other latices during stability tests may have "buried" its carboxylic acid groups because it did not show any presence of surface groups due to COOH but instead showed the strong sulphate groups. The 12-ADA-stabilised latices examined after purification must have had the COOH surface groups at that stage. This observation points to the possibility that the carboxylic acid groups may have been buried in the latex which even adds credence to the theory of the formation of associated molecules which would not leave free carboxyls for measurement by titration. The strong acid groups, which are sulphates, arise from the initiator potassium persulphate which was used to initiate emulsion polymerisation. There are more carboxyl acid groups in the Na salt surfmers, which may suggest that the Na ions may have had a "shielding" effect from burial of the COOH groups. It seems

as if the carboxyl groups as well as the sulphate groups in 12-ADA helped stabilise the latex regardless of the location of the groups.

5.7.6. Scanning electron microscopy (SEM)

Scanning electron microscopy is widely used in the analysis of polymers. The information obtained from such analysis is generally in the form of magnified images of the topography of materials. A limitation of using SEM for polymer analysis is that there might be specimen charging, which is bound to occur when non-conductive materials are scanned. Further, the electron beam can cause structural damage when it hits the material and this may result in the appearance of artefacts. Microscopic analysis on latices that had been previously freeze-dried and gold-sputtered onto metal sample holders was carried out using a Leica-Leo Stereoscan 440 Scanning Electron Microscope. Gold was used as a conductive coating to reduce specimen charging. The micrographs were used to examine particle morphology and estimate particle stability. Examples of some of the SEM micrographs obtained are given in Figure 5-14 to Figure 5-20.
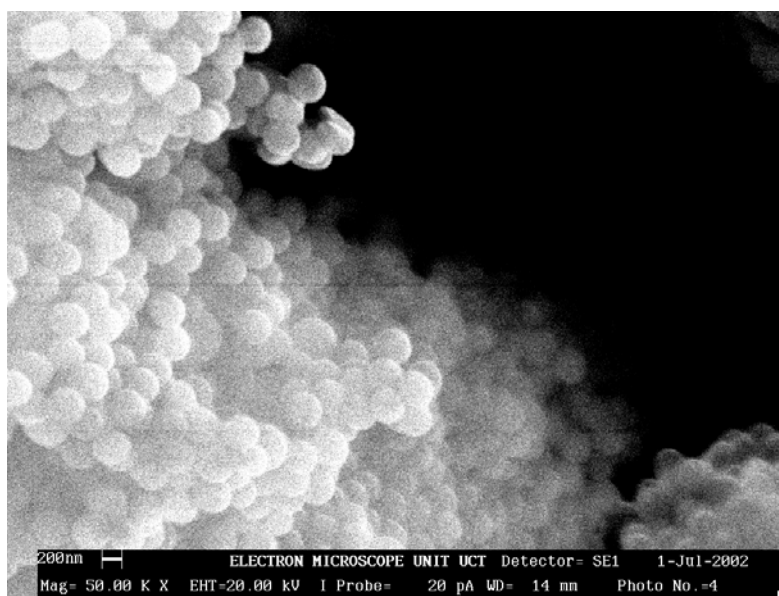

Figure 5-14. SEM micrograph showing 12-ADA stabilised latex particles, 6 months after preparation (1 mm = 80 nm).
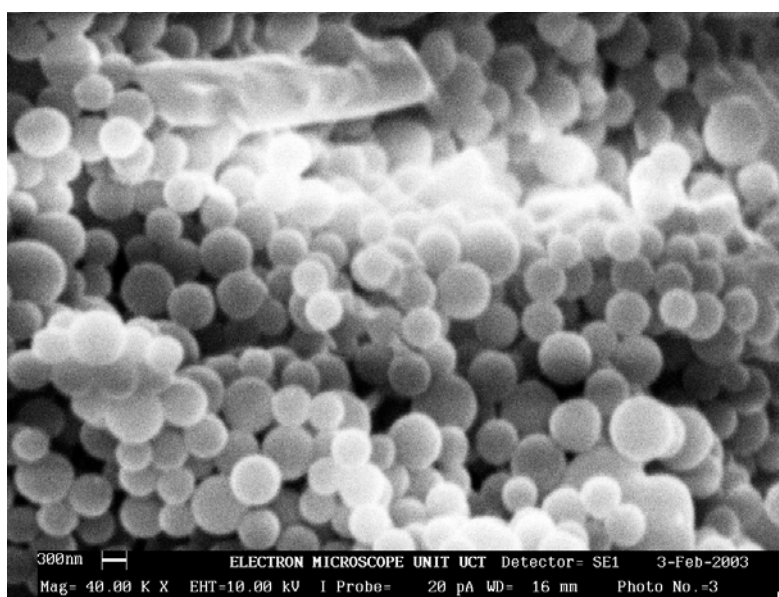
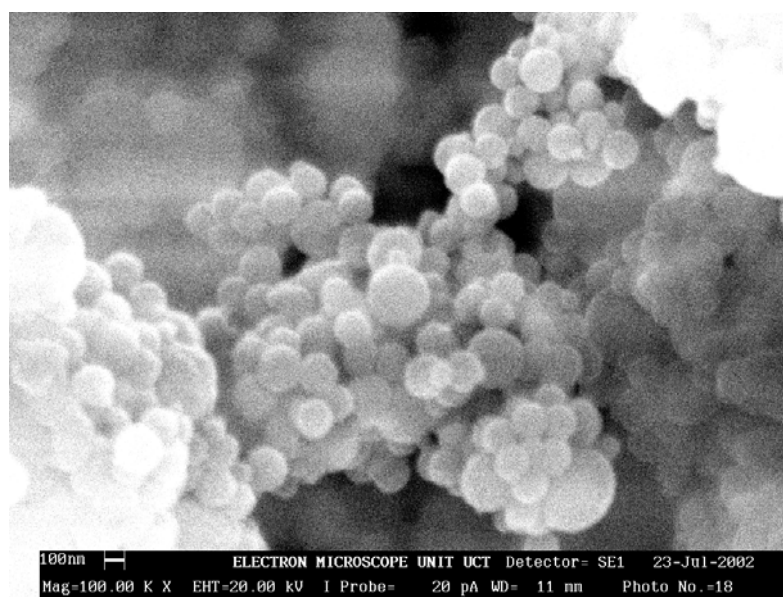**Figure 5-15.** SEM micrograph of 12-ADA stabilised latex particles, 11 months after preparation (1 mm = 100 nm).

Figure 5-16. SEM image of AAUA-stabilised latex particles, 6 months after preparation (1 mm = 40 nm).
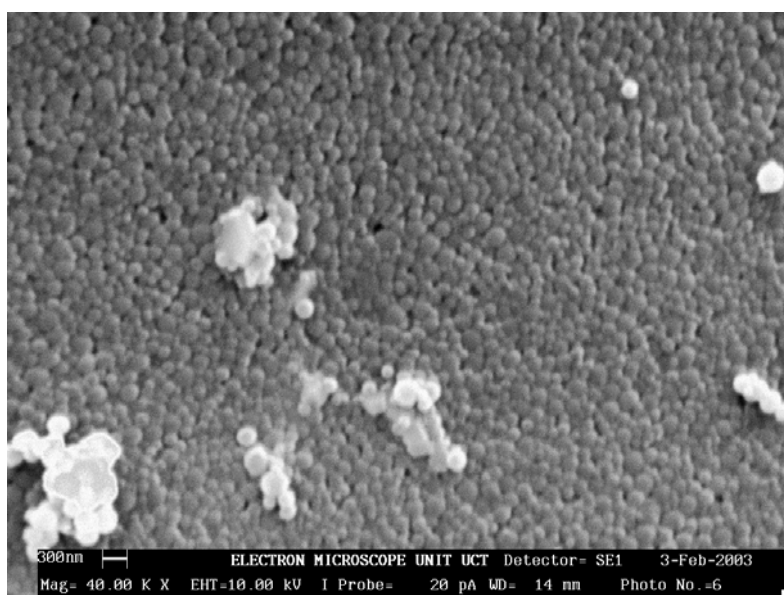
Figure 5-17. SEM image of AAUA-stabilised latex particles, 10 months after preparation (1 mm = 100 nm).
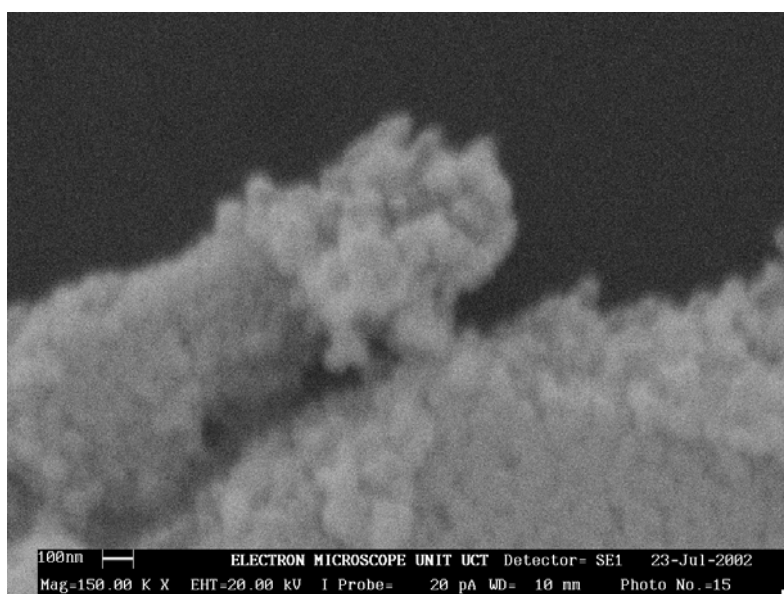

Figure 5-18. SEM image of SDS-stabilised latex particles, 6 months after preparation (1 mm = 25 nm).
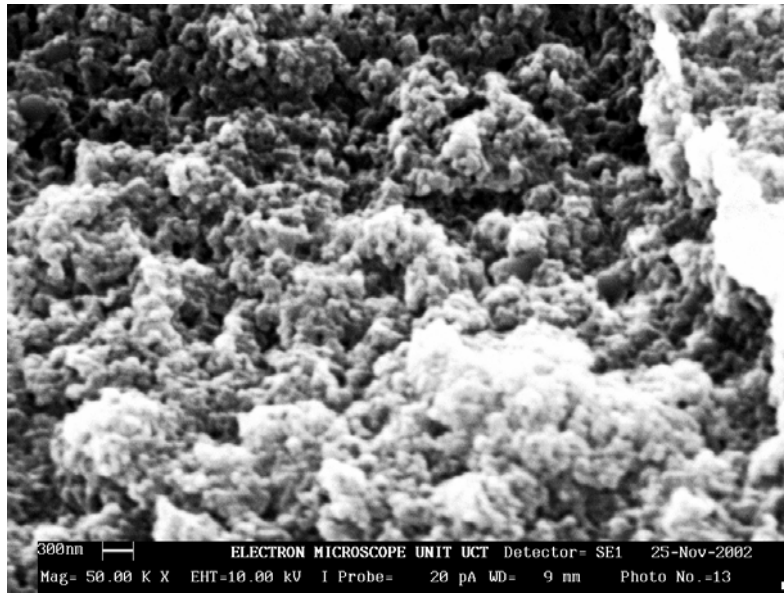
Figure 5-19. SEM image of SDS-stabilised latex particles, 10 months after preparation (1 mm = 75 nm).

Figure 5-20. SEM image of SDS-stabilised latex particles, 13 months after preparation (1 mm = 100 nm).
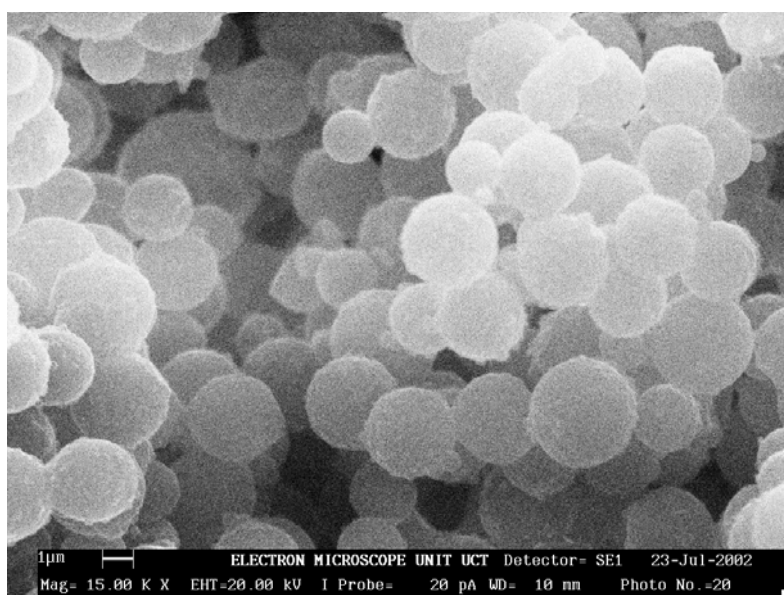
Figure 5-21. SEM image of poly(12-ADA/ACP-RAFT)-stabilised latex particles, 6 months after preparation (1 mm = 250 nm).
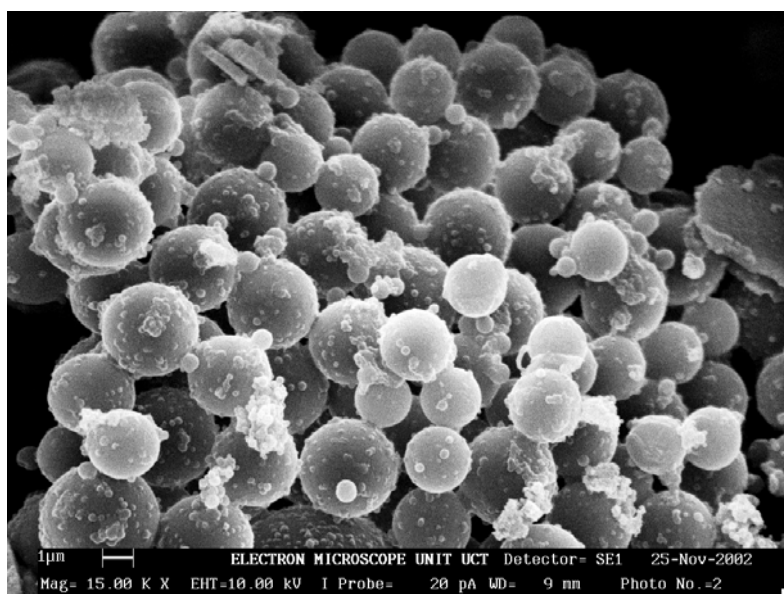

Figure 5-22. SEM image of poly (12-ADA/ACP-RAFT)-stabilised latex particles, 10 months after preparation (1 mm = 250 nm).

In general, the 12-ADA-stabilised particles maintained their spherical shape even after almost a year's storage as illustrated by the micrographs in Figures 5-14 and 5-15. This could also be seen with the 11-AAUA-stabilised particles, in Figures 5-16

and 5-17, although these were smaller in size. The SDS-stabilised particles did not maintain the spherical shape for long and coagulation occurred fairly early, as shown in Figures 5-18 and 5-19. There was little change in the particle size of latices prepared with polymeric surfactants even upon prolonged storage.   Also, the spherical shapes of the particles of the latices were also maintained even after harsh treatment, such as the addition of electrolytes and five freeze-thaw cycles, as indicated by SEM analysis.   This suggests that 12-ADA, 11-AAUA and oligomeric surfactants stabilised the latex particles well.   The latex particles were still stable even when stored for long periods.

5.7.7. Transmission electron microscopy

Transmission electron microscopy can be used to provide detailed structural information such as atomic dimensions and is capable of obtaining information within the range 1-100 nm. The main disadvantage of using TEM is that it can only be used on thin samples, less than $1\mu m$ thick.   A TEM sample therefore requires special preparation. In this investigation, specimen samples were prepared by extrusion in a mini extruder. The TEM micrographs of latices prepared using oligomeric surfactants are shown in Figure 5-23. The micrograph illustrates a multimodal distribution.
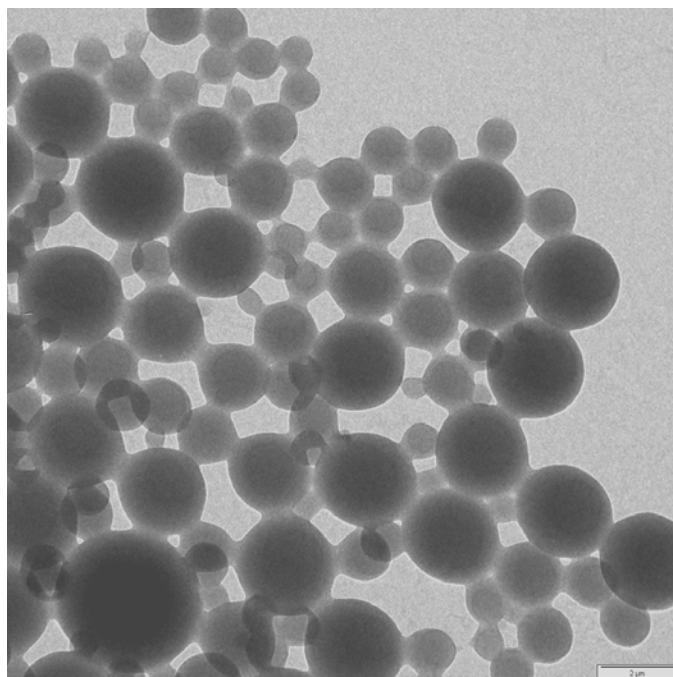
Figure 5.23. TEM micrograph of poly (12-ADA/ACP-RAFT)-stabilised latex.

It can be seen that the particle diameters ranged from about 300 nm to > 1 μm, which suggests a complex mechanism of stabilisation. Some melting during the TEM analysis could have occurred to give the appearance of linkages within the molecules. The TEM results for the oligomer-stabilised latex showing a multimodal size distribution helps confirm the SEM results to a large extent.

5.8. References

1. Nzudie D.T., Dimonie V.L., Sudol E.D., El-Aasser S. J. Appl. Polym. Sci. **1998,** 70, 2729.

2. Liu L.J., Krieger I.M., J.Polym. Sci., Polym. Chem. Ed. **1981**,19, 3013.

3. Greene B.W., and Sheetz D.P.J. Colloid Interf. Sci. **1970**, 32, 96.

4. Schulz D.N., Glass J.E., Polymers as Rheology Modifiers, ACS. Symp. Ser., **1991**, 462, 18.

5. Cochin D., Lawschewski A., Nallet F., Macromolecules **1997**, 30, 2278.

6. Van den Hul H.J., Vanderhoff J.W., Br. Polym. J., **1970**, 2, 121.

7. McCarvill W.T., Fitch R.M., J. Colloid Interface Sci. **1978**, 64 (3) 403.

8. Guillaume J.L., Pichot C., J. Polym. Sci., Polym. Chem, A 26, **1988**, 1937.

9. Chonde Y., Krieger I.M., J. Colloid Interf. Sci. **1980**, 77, 138.

10. Pasch H., Screpp W., MALDI-TOF Mass Spectrometry of Synthetic Polymers, **2003,** XVIII, 298, 158.

CHAPTER 6

Conclusions and Recommendations

6.1. Conclusions

The research work presented in this dissertation has led to new knowledge concerning the uses of 12-acryloyloxydodecanoic acid and also its sodium salt as surfactant monomers and as starting materials in the synthesis of acrylate-based polymeric surfactants of low molecular mass, using the RAFT process. It has been shown that the surfactants produced could be used as emulsifiers and latex stabilisers for the emulsion polymerisation of styrene. In addition to learning more about the properties of the surfmer 11-acrylamidoundecanoic acid it was also confirmed and its sodium salt could also be used as an emulsifier and stabiliser in the emulsion process.

It was shown in Chapters 3 and 4 that the syntheses of the surfmers could be achieved relatively easily whereas the novel RAFT polymerisations of the surfmers to produce polymeric surfactants and copolymers with acrylic acid were not as easy. The work done in this research should provide new information to facilitate the study of 12-ADA and its use as a surfmer. Possible polymerisation conditions for the novel RAFT synthesis of acrylate-based 12-ADA have been established determined and oligomeric surfactants prepared, although more research can be done in this area in future. Oligomers were successfully prepared by using AIBN or ACP-RAFT chain transfer agents confirming the successful use of the prepared RAFT reagents as chain transfer agents. The preparation of oligomers with low molecular masses using the RAFT process was useful in the synthesis because it was possible to prepare f PS oligomers which were moderately soluble in some solvents while the polymers without RAFT could not be solubilised. Thus it can be concluded that in the absence of RAFT reagent very high molecular mass compounds are obtained when 12-ADA is polymerized.

The surfmers and the oligomeric surfactants based on 12-ADA were successfully used in the emulsion polymerisation of styrene as evidenced by the distinct spherical particles of relatively low particle-size polydispersity of the PS latices produced. As expected of true surfactants, particle size and polydispersity decreased with increasing surfactant concentration. With the oligomers acting as surfactants, the particle sizes were large, and the resulting latices were extremely stable for months, similarly to the surfmer-stabilised ones. The SDS-stabilised latices were however not as stable, especially under conditions of five freeze-thaw cycles. The high thermal stability of PS latices stabilised by RAFT oligomeric surfactants suggests potential for their use in thermal applications. Conditions for the emulsion polymerisations could be varied in future work to establish the best conditions for such syntheses.

Characterisation of the PS latex showed the different properties of the RAFT oligomer-stabilised latex compounds. The RAFT moiety in the RAFT oligomers seemed to control molecular mass to some degree through living polymerisation mechanisms. Emulsion polymerisation is well known for producing high molecular weight products but the RAFT oligomers led to PS latices of low molecular masses.

It is interesting to note that all of the surfmers and polymeric surfactants studied acted as efficient stabilisers, regardless of whether they were used in their acid or salt forms. Larger latex particles were produced with surfmers and polymeric surfactants compared with those of SDS-stabilised latices. The polydispersities of 12-ADA and 11-AAUA-stabilised latices were also relatively low. The normal polymerisation of 12-ADA gave amorphous polymers which were impossible to dissolve in most solvents.

6.2. Recommendations

It is recommended that the physical and chemical nature of 12-ADA be studied in the future, to allow its self-assembling properties to be fully exploited. There is no doubt that the unusual stability it imparted to a PS latex, even under extreme conditions, may have something to do with the extra stability of the structure obtained from a number of 12-ADA units.

Although the focus of the present study was on the use of surfmers and polymeric surfactants in the conventional emulsion polymerisation of styrene, it would be interesting to extend this work to miniemulsions, in order to produce smaller latex particle sizes, which would extend the area of application.

The polymerisation of 12-ADA using the RAFT process can be further studied as there is good potential for its use in the production of latices of controlled molecular mass and of high thermal stability. A variation in the amount and type of RAFT transfer agent could be undertaken and the products evaluated for their latex-stabilising properties.

The influence of factors such as polymerisation solvent, pH and variation of RAFT concentration can be studied further to help fully understand the polymerisation of 12-ADA which has a good potential to lead to future "smart materials".