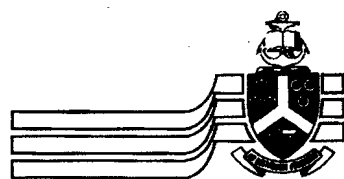




**SYNTHESIS AND CHARACTERIZATION OF
LOW MOLECULAR MASS AMPHIPHILIC
BLOCK COPOLYMERS AND POTENTIAL
USE IN SURFACTANT ASSISTED
PARTICLE MICRO-MIXING**

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Thesis

SYNTHESIS AND CHARACTERIZATION OF LOW MOLECULAR MASS AMPHIPHILIC BLOCK COPOLYMERS AND POTENTIAL USE IN SURFACTANT ASSISTED PARTICLE MICRO-MIXING

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SYNOPSIS

In industry the effective mixing and de-agglomeration of two solid particles is vital in applications that require the intimate contact of homogeneously mixed reagents. One such application is in the preparation of pyrotechnic delay elements with reproducible burn speeds.

The concept of surfactant assisted particle micro-mixing is proposed. This theory is based in the use of two amphiphilic polymeric surfactants to form two separate stable dispersions of the two solid particles to be mixed, but with the subsequent requirement that the dispersants are able to interact with each other. The formation of the individual dispersions allows for the deagglomeration of the particles and thus their preparation for homogeneous mixing, which is facilitated by the interacting surfactants.

Low molecular mass block copolymers of styrene and acrylic acid and poly(ethylene oxide)-poly(propylene oxide) (PEO-PPO) surfactants are the proposed dispersants which will allow for the surfactant interaction by means of hydrogen bonding between the poly(acrylic acid) block and the PEO. The poly(styrene-co-acrylic acid) block copolymer will be synthesised via Atom Transfer Radical Polymerisation (ATRP) and subsequently used in the dispersion experiments.

The synthesis of the polystyrene macroinitiators to initiate the block copolymerisation of the t-butyl acrylate was carried out satisfactorily, with good molecular masses and molecular mass distributions. In addition, ¹H-NMR analysis carried out on the polystyrene macroinitiators confirmed their synthesis.

The use of the polystyrene macroinitiators was successful in synthesising poly(styrene-co-t-butyl acrylate) block copolymers with slightly higher polydispersities in comparison to the macroinitiators themselves, but acceptable.

Hydrolysis of the poly(styrene-co-t-butyl acrylate) block copolymer to poly(styrene-co-acrylic acid) was successful in the presence of trifluoroacetic acid as catalyst. Attempts to hydrolyse in basic conditions (NaOH) and alternatively in acidic conditions (HCl) were not successful.

Use of the poly(styrene-co-acrylic acid) amphiphilic block copolymer to emulsion polymerise styrene requires the ionised form of the polymer and was therefore not favourable to observe surfactant-surfactant hydrogen bonding. In addition, attempts to synthesise a wax emulsion stabilised by a PEO containing surfactant proved to be unsuccessful.

Subsequently, the micro-mixing experiments were carried out by using a poly(acrylic acid) stabilised melamine dispersion and a commercially available PEO containing surfactant stabilised wax emulsion. The interaction between the melamine and the poly(acrylic acid) allows for the formation of a stable melamine dispersion at above 7% poly(acrylic acid) : melamine ratio (mass basis).

Analysis by SEM shows that without the poly(acrylic acid) dispersant no wax particles are found to occur on the melamine particle surface. However, in an attempt to determine whether the amount of wax interaction increases with poly(acrylic acid) content, it was found that in the absence of poly(acrylic acid) dispersant, the most amount of wax precipitated out with the melamine. This is possibly attributable to the preferential occlusion of the wax particles between the melamine particles rather than surface attachment.

Introduction of the poly(acrylic acid), however, shows via SEM analysis that the hydrogen bond interaction between the acrylic acid group and the ethylene oxide group does occur, since the attachment of the wax particles on the melamine particle surface is observed.

Although results show that the surfactant-surfactant interaction allows for the micro-mixing of particles, some refinement is required with respect to the systems that this phenomenon can be applied to. In addition, factors such as particle type, particle size and surfactant type will influence the micro-mixing interaction. It is therefore



recommended that these factors be investigated in order to completely identify the micro-mixing phenomenon.

KEYWORDS: styrene, butyl acrylate, acrylic acid, block copolymer, polymeric surfactant, particle mixing.

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1. Introduction

Surfactants, i.e. surface-active agents, are amphipathic structures that have the ability to modify the properties of a surface or an interface. They provide an invaluable tool for improving the processes and interactions that take place at such boundary regions and subsequently have wide application in various fields of industry. Their functional properties include detergency, foaming, wetting, emulsification, solubilisation and dispersion (Lynn & Bory, 1995:478). Conventional surfactants are traditionally small molecules, but the advent of polymeric surfactants has opened many novel applications that require more stability.

Polymeric surfactants (commonly block or graft) have been used as dispersion stabilizers (emulsion polymerisation) (Burguière, Pascual, Coutin, Polton, Tardi, Charleux, Matyjaszewski & Vairon, 2000), compatibilizers in immiscible polymer blends (Piirma, 1992: 1), flocculants in water purification and sewage treatment (Piirma, 1992: 1) and as particle dispersants (Shvets, Karpov & Popov, 1987; Poncet-Legrand, Lafuma & Audebert, 1999; Duivenvoorde, van Nostrum, Laven & van der Linde, 2000).

A difficulty that is observed in industry is the effective mixing and de-agglomeration of two solid particles, especially when the intimate contact of reagents that are homogeneously mixed is vital in obtaining reliable results. One such application is in the preparation of delay elements with reproducible burn-speeds in the pyrotechnic field.

It is therefore proposed to investigate the concept of surfactant assisted particle micro-mixing, with the assistance of an amphiphilic polymeric surfactant. The diagram below describes the use of the synthesised amphiphilic poly(styrene-co-acrylic acid) block copolymer to disperse styrene particles and subsequently mix this dispersion with a poly(ethylene oxide) – poly(propylene oxide) (PEO-PPO) stabilised wax dispersion (Figure 1). The dispersants are chosen such that when the dispersions are mixed, they are able to interact by means of hydrogen bonding (acid group of acrylic acid block hydrogen bonds with ethylene oxide group of PEO block) and thus facilitate the subsequent flocculation of a homogeneous mixture of two solid particles (Figure 2).

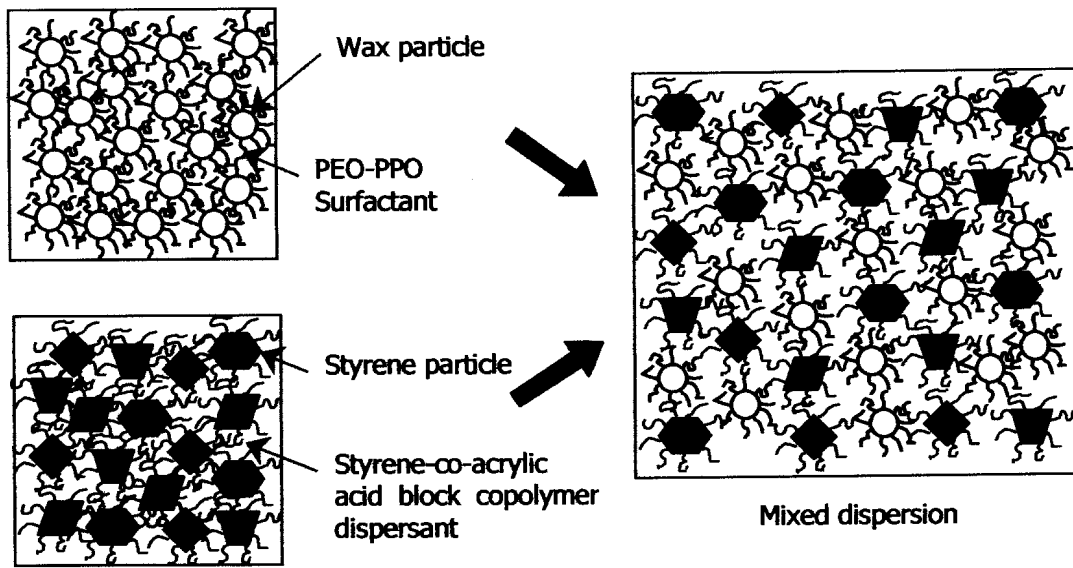


Figure 1: Schematic diagram of surfactant assisted micro-mixing.

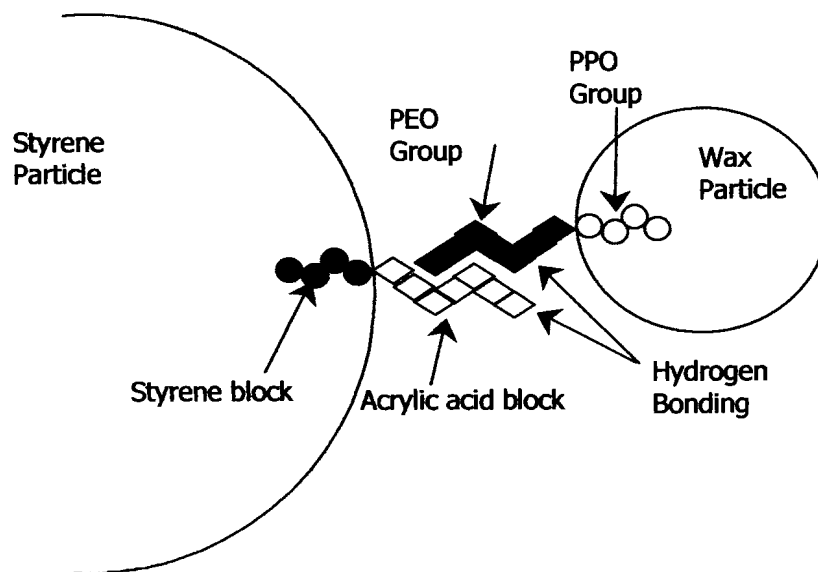


Figure 2: Schematic representation of hydrogen bonding between the poly(acrylic acid) block of the poly(styrene-co-acrylic acid) block copolymer and the PEO group of the PEO-PPO surfactant.

Low molecular mass (~ 4000) di- and triblock copolymers of styrene and acrylic acid were synthesised via atom transfer radical polymerisation (ATRP). The molecular mass and molecular mass distributions of the polymers synthesised were determined by size exclusion chromatography (SEC) and matrix assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS). $^1\text{H-NMR}$ was used to characterise the polymers synthesised. Scanning Electron Microscopy (SEM) was used to observe the particle micro-mixing.

2. Literature Review

2.1 POLY(STYRENE-CO-ACRYLIC ACID) BLOCK COPOLYMERS

Conventional free radical polymerisation has been used for the synthesis of a variety of polymers, with different applications (Odian, 1981: 179). However, it is well known that free radical polymerisation provides little control over the synthesis of polymers within a narrow range of molecular masses, resulting in polymers with wide polydispersity indices (Li, Howell, Dineen & Priddy, 1997). The inherent drawback of radical polymerisation is bimolecular termination, either by combination or disproportionation, resulting in a range of polymer lengths and a broad molecular mass distribution. If bimolecular termination can be eliminated, polymerisation will only consist of initiation and propagation. The elimination of chain terminating reactions allows for the radicals to retain their chain growth capability. Thus, when initiation occurs simultaneously or faster than propagation, the polymer chains will grow almost uniformly. This allows for the control of the number average molecular mass and a narrower polydispersity index (Sawamoto & Kamigaito, 1999).

Anionic polymerisation is a living polymerisation mechanism and many block copolymers have been synthesized using this mechanism. However, a great drawback of anionic polymerisation is the rigid conditions required for the synthesis process i.e. inert atmosphere, low temperatures and specifically purified monomers and solvents (Piirma, 1992:18).

Atom transfer radical polymerisation (ATRP) (Figure 3) is also a living polymerisation mechanism. This method involves the reversible abstraction of a halogen atom from an alkylhalide ($R - X$) to a lower oxidation state metal (M^n) complexed to a ligand (L), to generate a radical (R^*) and a higher oxidation state metal complex ($M^{n+1}L$). The radical then adds monomer ($\text{---}Y$) to generate the polymer chain. The molecular weight is controlled, as both initiation and deactivation are rapid, allowing for the chains to grow uniformly (Davis & Matyjaszewski, 2000).

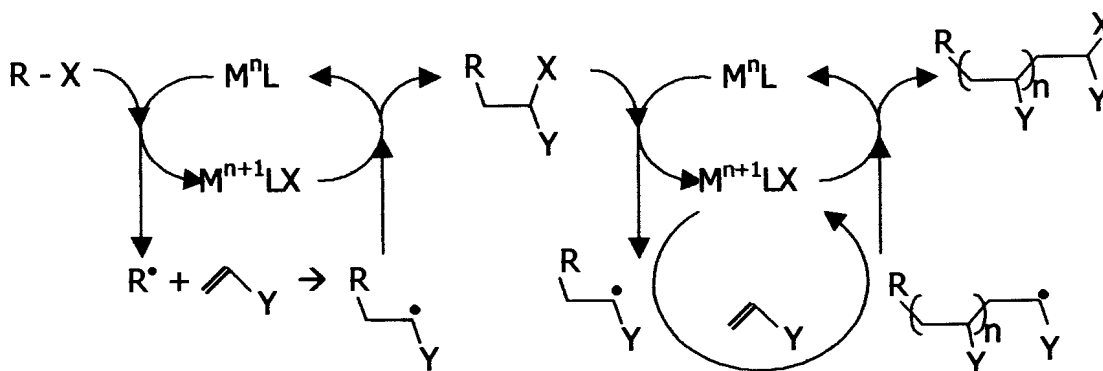


Figure 3: Diagrammatic representation of ATRP showing the reversible abstraction of the halogen atom to the metal ligand complex and the "living" nature of the radical.

Block copolymers of acrylic acid and styrene can be synthesized using the ATRP mechanism. The block copolymer is prepared by the block copolymerisation of t-butyl acrylate and styrene followed by the subsequent hydrolysis of the t-butyl group to generate the acrylic acid block.

The styrene-t-butyl acrylate block copolymer can be synthesised by means of ATRP of t-butyl acrylate by using a $CuBr/CuBr_2/PMDETA$ (N,N,N',N'',N''-pentamethyldiethylenetriamine) catalyst system. The monofunctional poly(t-butyl acrylate) can be synthesised by using a monofunctional alkyl halide initiator, namely methyl 2-bromopropionate. A difunctional poly(t-butyl acrylate) macroinitiator can be synthesised by using a difunctional alkyl halide initiator such as dimethyl 2,6-dibromoheptanedioate (DMDBHD). The mono- and difunctional poly(t-butyl acrylate) macroinitiators are subsequently used to initiate the polymerisation of styrene (Davis & Matyjaszewski, 2000).

Instead of using a functionalised poly(t-butyl acrylate) polymer to initiate the polymerisation of styrene, a functionalised polystyrene macroinitiator can be synthesised to initiate the polymerisation of t-butyl acrylate. In this method the conventional initiator for the synthesis of the monofunctionalised polystyrene, 1-phenylethylbromide, is used. The structure of the 1-phenylethylbromide initiator is uniform with the polystyrene chain and therefore does not introduce any foreign entities into the polymer chain. A difunctional polystyrene macroinitiator is synthesised using DMDBHD as initiator (Davis, Charleux & Matyjaszewski, 2000).

Since the metal-halide (CuBr) catalyst used in ATRP is sensitive to the action of an acid, it is necessary to carry out the polymerisation using protected monomers, such as t-butyl acrylate, which will then undergo deprotection (hydrolysis) to form the polyacid. Thus a low molecular weight amphiphilic polymer can be synthesized with the aid of a living polymerisation mechanism (Davis & Matyjaszewski, 2000).

The t-butyl acrylate block can be hydrolysed in the presence of a strong acid such as HCl (Davis & Matyjaszewski, 2000; Davis *et al.*, 2000). Alternatively, trifluoroacetic acid can be used as the strong acid (Burguière *et al.*, 2000).

A method that uses a combination of conventional radical polymerisation and ATRP has been used to synthesise an n-butyl acrylate macroinitiator first and then to copolymerise with styrene (Destarac & Boutevin, 1998; Destarac & Boutevin, 1999).

The poly(n-butyl acrylate) macroinitiator is used to initiate ATRP of styrene. Since 1,1,1-trichloroalkanes are reportedly efficient initiators for ATRP of styrene catalysed with CuCl and 2,2'-Bipyridine (2Bpy), 2,2,2-trichloroethyl pivalate was tested and showed good initiation efficacy. Therefore, the ATRP of styrene with poly(n-butyl acrylate) macroinitiator can be carried out in the presence of 2,2,2-trichloroethyl pivalate and catalysed by CuCl and 2Bpy. The reaction shows satisfactory monomer conversion and results in a polymer with a good polydispersity index (Destarac & Boutevin, 1998).

Block copolymers of styrene and butyl acrylate have also been synthesised by a combination of living anionic polymerisation (LAP) and ATRP. This method entails the synthesis of polystyrene containing a 2-bromoisobutyryl end group, which is synthesised by LAP. This functionalised polystyrene is a sufficient macroinitiator for the ATRP of butyl acrylate (Acar & Matyjaszewski, 1998).

A nitroxide functionalised poly(n-butyl acrylate) synthesised by normal free radical methods can also be used to initiate styrene polymerisation thus attaching a polystyrene block onto the poly(n-butyl acrylate) block. In addition, since the termination of the nitroxide functionalised poly(n-butyl acrylate) radicals proceeds predominantly by coupling, difunctionalised poly(n-butyl acrylate) macroinitiators are

formed. This allows for the formation of triblock copolymers of poly(styrene-butyl acrylate-styrene) (Li, Howell, Dineen & Priddy, 1997).

2.2 SURFACE-ACTIVE AGENTS (SURFACTANTS)

A surfactant is an agent, which is active at an interface and characteristically contains both a water-soluble group (hydrophilic) and water-insoluble group (hydrophobic). For groups to have an affinity for water they must either have an electrically charged component or they must participate in hydrogen bonding.

Typically there are two types of surfactants; ionic and non-ionic surfactants (Figure 4). Ionic surfactants are further sub-divided into anionic, cationic and amphoteric surfactants. Non-ionic surfactants interact with water by means of hydrogen bonding (Piirma, 1992: 55) and are especially useful in applications that cannot tolerate the more commonly used non-polymeric anionic or cationic surfactants (Noshay & McGrath, 1977: 75). Polymeric surfactants can be either ionic or non-ionic, depending on the presence of the relevant groups, which lead to the classification.

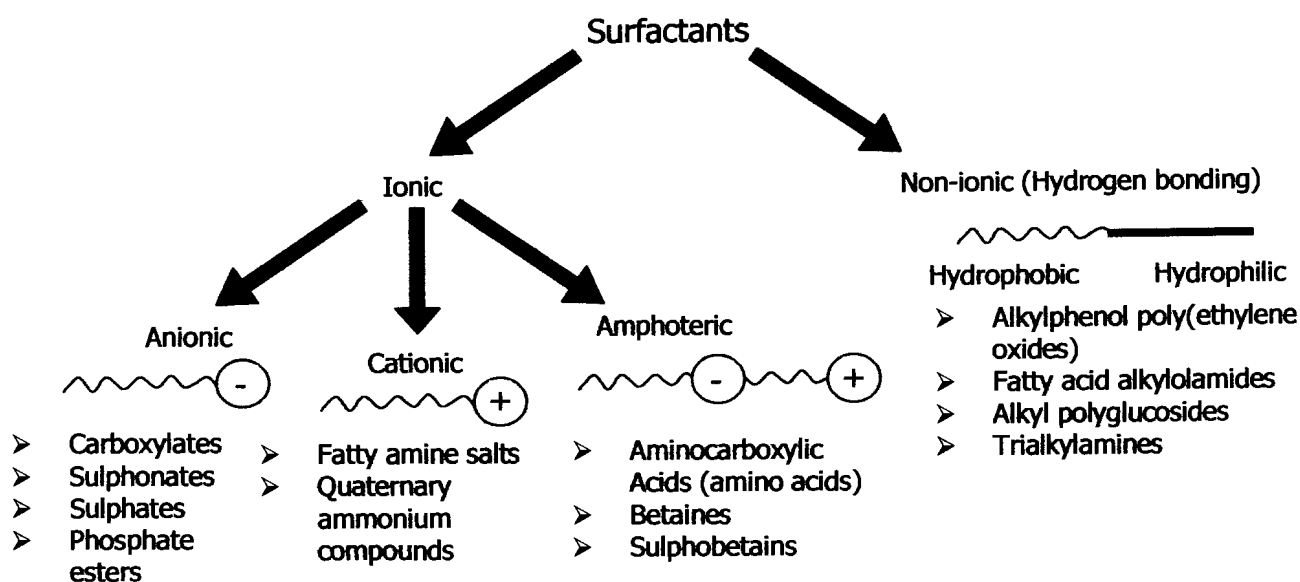


Figure 4: Classification of surfactants into ionic and non-ionic groups and examples of surfactants in the respective groups (Kosswig, 1994: 751).

The interface between two phases at which a surfactant acts is often so thin, that its thickness is sometimes neglected. However, it is the rapid change of density and other physical properties across the interface that gives dispersions their most important quality. An interface between two phases can be observed in a dispersion of one phase in another (Miller & Neogi, 1985: 1).

Dispersions consist of finely subdivided systems of dispersed phase in a dispersion medium, thus creating a high specific surface area. These individual systems play a vital role in determining the physical properties of the dispersion as a whole. The most common type of dispersion is one liquid dispersed in another and is called an emulsion (Piirma, 1992: 1). A solid dispersed in a liquid is known as a suspension (Miller & Neogi, 1985: 91). However, if the solid is a polymer, the dispersion is called a polymer colloid (Piirma, 1992: 1). Also, when a gas is dispersed in a liquid, it is known as a foam and when a liquid or solid is dispersed in a gas, it is known as an aerosol (Miller & Neogi, 1985: 91) (Table 1).

Table 1: Dispersed phases and dispersion media of different dispersions.

Dispersion Type	Dispersed Phase	Dispersion Medium
Emulsion	Liquid	Liquid
Suspension	Solid	Liquid
Polymer Colloid	Polymer	Liquid
Foam	Gas	Liquid
Aerosol	Liquid/Solid	Gas

Most dispersions are thermodynamically unstable and the dispersed phase would prefer to revert to a single bulk phase so as to reduce the free energy of the system. Whether a dispersion remains stable depends essentially on the interaction between the particles or drops of the dispersed phase (Miller & Neogi, 1985: 92). External intervention, such as surfactants, may be required to introduce stability to a dispersion at the interfacial level.

The surface properties exhibited by any type of particle originate from the forces at the surface of the particular material. These surface forces are caused by the

summation of the interatomic forces acting between the atoms of the material, the particles themselves and the medium in which they exist. The nature of these surface forces determines the type of inter-particle interaction (Garbassi, Morra & Occhiello, 1996: 3). They play an important role in the stability of a dispersion or colloid, especially since the surface area to volume ratio in these systems is so high (Piirma, 1992:2).

Particles, however, are in constant motion and collide with each other and the vessel walls. This is called Brownian motion, and owing to the attractive van der Waals forces between the particles, these collisions tend to result in particle aggregation. It is therefore necessary to provide particles with repulsive interactions that will counteract these forces of attraction (Piirma, 1992: 2).

Stability can be provided to particles by surrounding them with an electrical double layer (electrostatic stabilisation), by chemically attaching polymeric materials to the surface of the particles (steric stabilisation) or by having a free polymer in the dispersion medium (depletion stabilisation). The last two modes of stabilisation are often combined under polymeric stabilisation (Piirma, 1992: 3).

2.2.1 ELECTROSTATIC STABILISATION

Particles in a dispersion may be stabilized if electrical interaction forces are introduced by means of an electrical charge on the particle surface. It has been found that solid surfaces electrify in the presence of an electrolyte solution. This occurrence is due to an unequal adsorption of the charged ions onto the particle surface, giving it a net positive or negative charge (Miller & Neogi, 1985: 99).

Electrostatic stabilisation of particles is to date the most effective manner of counteracting the inherent attractive van der Waals forces between the particles, especially for dispersions of inorganic particles in aqueous media. In non-aqueous media, the low dielectric constant of the medium results in the depletion of any electrical interaction and the dominance of the van der Waals forces. In these circumstances, an adsorbed layer of polymeric molecules (steric stabilisation) provides a viable method of stabilisation (Schofield, 1990: 36).

Electrostatic stabilisation involves the introduction of a potential energy barrier to the particles via Coulomb repulsion (Piirma, 1992:4). In liquid dispersion media, the particles can acquire a charge by either ionising suitable groups (carboxyl, sulphate or amino groups) or by specific absorption of ions (ionic surfactants) (Garbassi *et al.*, 1996: 14). Electroneutrality is maintained by the presence of counter ions in the surrounding medium and creates an electrical double layer (Piirma, 1992:4). The electrical double layer refers to the concentration of counter ions in the dispersion medium, which is higher at the particle surface than in the bulk medium (Garbassi *et al.*, 1996: 15). The thickness of this double layer is dependant on the ionic strength of the dispersion medium (Piirma, 1992:4). Figure 5 below shows the electrical double layer (Lafuma, 2000).

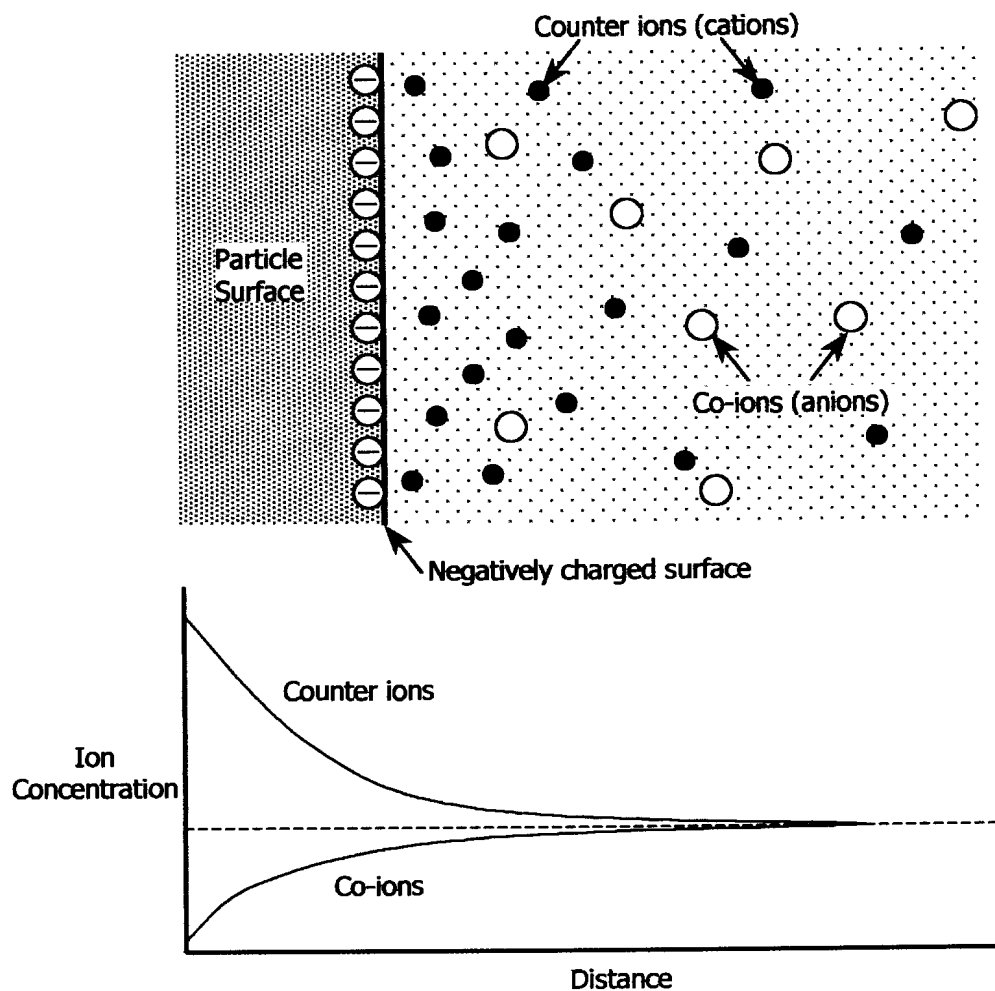


Figure 5: Diagrammatic and graphical representation of the electrical double layer.

2.2.2 POLYMERIC STABILISATION

Polymeric stabilisation of dispersions includes two recognised mechanisms: steric stabilisation and depletion stabilisation. Steric stabilisation prevents particles from coagulating by means of adsorbed macromolecules. Depletion stabilisation, however, is provided by means of unattached polymer molecules in the dispersion phase, such as homopolymers which are soluble in the dispersion medium but do not contain anchoring moieties for attachment to the particles (Piirma, 1992:5).

Steric Stabilisation

As previously stated, steric stabilisation involves the prevention of coagulation by attaching macromolecules to the particle surface. These steric effects have a thermodynamic origin and do not require an electrostatic charge. Homopolymers are ineffective in imparting steric stabilisation to a system as they tend to preferentially associate to either the solvent or the particle surface. For effective steric stabilisation the stabilising entity needs to have both of these characteristics, thus being able to act at the interface between the dispersed and continuous phase (Schofield, 1990: 41). The most effective steric stabilisers have been found to be amphiphilic block or graft copolymers. These copolymers have one part of the copolymer molecule soluble in the dispersion medium and the other part soluble or chemically compatible with the dispersed phase (Piirma, 1992:6).

In addition to the chemical morphology of the polymeric dispersant, the size of the polymer plays an important role in the stabilisation process. High molecular mass polymeric surfactants tend to not enhance stabilisation and even have the possibility of promoting particle agglomeration and subsequent flocculation. Polymeric chains containing solvent soluble segments need only have 50 to 100 carbon atoms in the backbone to supply an effective barrier (Schofield, 1990: 41).

During steric stabilisation, segments of the adsorbed macromolecule reach out into the dispersion medium and interact with the stabilising moieties attached on an adjacent particle. For effective stabilisation, these interacting groups should be mutually repulsive in order to maintain a sufficient distance between the particles. These macromolecules need to be attached to the particle surface strongly enough to

prevent desorption from the surface when particles undergo Brownian collisions. In addition, complete surface coverage helps prevent escape. Figure 6 below shows the interaction that occurs during steric stabilisation (Piirma, 1992:6).

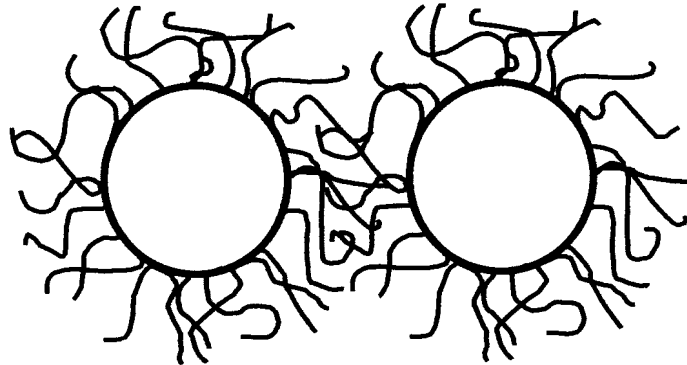


Figure 6: Schematic representation of steric stabilisation.

Steric stabilisation has a number of advantages over electrostatic stabilisation (Piirma, 1992:8):

- Steric stabilisation is equally effective in aqueous and non-aqueous systems at high and low solids content
- Sterically stabilised systems are insensitive to the presence of electrolytes.

In steric stabilisation, stability is imparted by the interaction of the adsorbed macromolecular chains on adjacent particles. Upon contact of the particles, the concentration of these stabilising chains in the interaction zone increases considerably. Since the final concentration of the stabilising groups is higher than their initial concentration, the free energy of the system is increased due to the mixing of the polymeric segments. This free energy of mixing gives rise to the repulsive force, which imparts stability (Piirma, 1992:9).

Surfactant molecules on colloidal particles may undergo orientational changes, lateral movements, or desorption of surfactant to relieve the stresses resulting from the repulsive force thus decreasing the free energy of mixing of the adsorbed segments. These changes may however result in a "bare spot" on the particle surface thus

creating a site for particle coalescence. Adding an excess of polymeric surfactant will allow for complete coverage of the particles and reduce instability. In addition, careful choice of the surfactant and ensuring high compatibility with the dispersed phase will minimise desorption of the polymeric surfactant and stability will be enhanced (Piirma, 1992:9).

Depletion Stabilisation

Depletion stabilisation is provided by unattached polymer molecules in the dispersion phase. These molecules may be homopolymers which are soluble in the dispersion medium and do not contain any possible anchoring groups. It has been known that the introduction to a dispersion of a polymer that is soluble in the continuous phase can induce flocculation. However, flocculation is reversible and can be explained as a depletion effect. When two rigid spheres are placed in a solution of spherically shaped molecules and when the distance between them is smaller than the spherical molecules, only pure solvent will exist between the rigid spheres. The depletion of the soluble spheres from the region between the rigid spheres and the concentration of the solute outside this region creates an osmotic pressure. The solution therefore exerts an inward force between the rigid spheres resulting in their stabilisation (Piirma, 1992:12).

3. Experimental

3.1 PLANNING

3.1.1 BLOCK COPOLYMER SYNTHESIS

As described in the previous chapter there are various methods that can be used to synthesise block copolymers. However, due to the reliability and versatility of the ATRP method, it was decided to proceed with the synthesis using this method. It was proposed to synthesise block copolymers with the following morphologies (Figure 7) (• hydrophobic polystyrene, - hydrophilic poly(acrylic acid), molecular masses are given below each morphology):

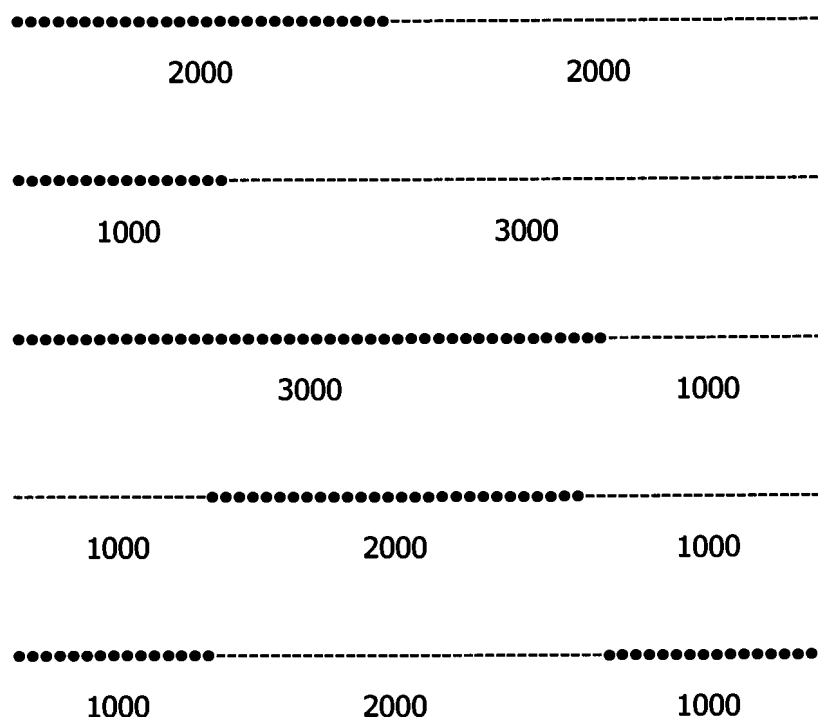


Figure 7: Proposed morphologies of poly (styrene-co-acrylic acid) block copolymers.

The block copolymers would be synthesised using both the method in which the poly(*t*-butyl acrylate) block is used as the macroinitiator and the method which uses the functionalised polystyrene as the macroinitiator.

The molecular mass of the block copolymers was standardised at a molecular mass of 4000 (Bognolo, 2000). The low molecular mass amphiphilic polymer chain will act as a dispersant and thus avoid the possibility of resulting in the flocculation of the particles with larger polymers. This compares well with the molecular mass suggested by Schofield (Schofield, 1990).

3.1.2 SURFACTANT ASSISTED MICRO-MIXING

The poly(styrene-co-acrylic acid) block copolymers can be used to emulsion polymerise styrene, thus preparing a dispersion of polystyrene particles stabilised by acrylic acid containing surfactants. It was also required to prepare wax emulsions stabilised by surfactants containing the ethoxylate entity, such that the polystyrene and wax emulsion prepared may be mixed and the interaction between the surfactants investigated. Low melting point wax was proposed to be emulsified using poly(ethylene oxide) – poly(propylene oxide) (PEO-PPO) surfactants, which are amphiphilic in nature (Tadros, 1987: 109). The interaction proposed was shown in Figure 2.

The experimental model described above, however, was not successful for reasons that will be explained under Results and Discussion (Chapter 4). It was, therefore, proposed to prepare a poly(acrylic acid) (commercially obtained) stabilised melamine dispersion to replace the polystyrene emulsion. The melamine particles would substitute the polystyrene particles, but the presence of the poly(acrylic acid) group would still be maintained. Due to the ability of the amine groups of melamine and the acid groups of the poly(acrylic acid) to interact via hydrogen bonding, it is possible to disperse the melamine particles with the water soluble poly(acrylic acid). The molecular mass of the poly(acrylic acid) dispersant used should be within the same range as that of the poly(styrene-co-acrylic acid) block copolymer synthesised. The limiting concentration of poly(acrylic acid) should be determined, i.e. the minimum amount of poly(acrylic acid) required to stabilise the melamine dispersion. The poly(acrylic acid) stabilised melamine dispersion prepared and a PEO stabilised wax

emulsion should thereafter be mixed in a 1:1 volume ratio in order to determine the presence of an interaction between the acrylic acid group and the ethylene oxide group.

In addition, the proposed PEO-PPO stabilised wax emulsion was replaced with an industrially available wax emulsion, which is stabilised by a mixture of nonylphenoxyethoxy surfactants (Results and Discussion, Chapter 4). The presence of the ethoxy group still allows for the investigation of the possible interaction between the acrylic acid group of the poly(acrylic acid) stabiliser and the ethoxy group of the nonylphenoxyethoxy surfactant. Figure 8 below shows the proposed interaction between the two stabilising surfactants.

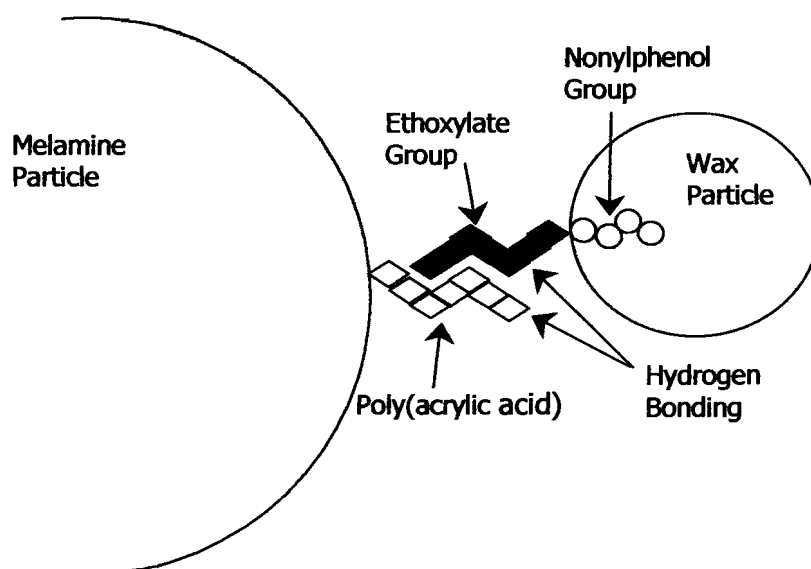


Figure 8: Schematic representation of hydrogen bonding between the poly(acrylic acid) and the ethoxy group of the nonylphenoxyethoxy surfactant.

3.2 MATERIALS

3.2.1 BLOCK COPOLYMER SYNTHESIS

- Styrene (Aldrich, 99%)
- CaH₂ (Aldrich, 90-95%)
- t – butyl acrylate (Aldrich, 98%)

- CaCl_2 (Unilab, 4-8 mesh).
- CuBr (Aldrich, 98%)
- CuBr_2 (BDH, 98%)
- N,N,N',N'',N'''-pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%)
- Methyl 2-bromopropionate (Aldrich, 98%)
- 2-Bromoethylbenzene (BEB) (Aldrich, 97%)
- Dimethyl-2,6-dibromoheptanedioate (DMDBHD) (Aldrich, 97%)
- NaOH (BDH, 99%, pellets)
- Trifluoroacetic acid (TFA) (BDH, 99%)

3.2.2 SURFACTANT ASSISTED MICRO-MIXING

Polystyrene Emulsion Polymerisation

- NaHCO_3 (Aldrich 90-95%)
- $\text{K}_2\text{S}_2\text{O}_8$ (Sigma Aldrich, 99%)

Melamine Dispersion

- Melamine (Degussa, 99%)
- Poly(acrylic acid) – Goodrite K732 (Carst and Walker) (MW ~5100)

Wax Emulsion

- Paraffin Wax (Melting point 57-60°C, Merck)
- Synperonic A2 (Uniquema)
- Synperonic A7 (Uniquema)
- Synperonic P85 (Uniquema)
- NP9 (Uniquema)

Micro-mixing

- Atebin A1 Micro (Böhme Africa, Appendix 1)

3.3 METHOD

3.3.1 BLOCK COPOLYMER SYNTHESIS

Reagent Preparation

Styrene was dried overnight in CaH₂ at room temperature and thereafter distilled at 60°C under vacuum. Molecular sieves were placed in the distillate to remove any moisture. t – Butyl acrylate was extracted three times with an equal volume of 5% NaOH and thereafter once with an equal volume of distilled water. The t – butyl acrylate was dried by adding anhydrous CaCl₂. The t – butyl acrylate was thereafter distilled at 60°C under vacuum and molecular sieves were placed in the distillate. CuBr, N,N,N',N'',N'''-pentadimethyldiethylenetriamine (PMDETA), methyl 2-bromopropionate (MBP), 2-bromoethyl-benzene (BEB) and dimethyl-2,6-dibromoheptanedioate (DMDBHD) were all used as received.

Synthesis and Characterisation of the Block Copolymers: A. Poly(t-butyl-acrylate) Macroinitiators

A poly(t-butyl acrylate) monofunctional macroinitiator with a molecular mass of ~2000 was required to be synthesized. One difunctional poly(t-butyl acrylate) macroinitiator of ~2000 molecular mass was also required to be synthesized.

To synthesize a macroinitiator of a required size the following formula, applicable to controlled free radical polymerisation processes, was used to determine the required amount of initiator corresponding to the amount of monomer used (Summers, 2001):

$$\text{Molecular mass} = \frac{\text{gram monomer}}{\text{mol initiator}} \quad (\text{Eq 3-1})$$

Poly(t-butyl acrylate) Macroinitiator Synthesis

The synthesis of the poly(t-butyl acrylate) macroinitiators was carried out via ATRP. CuBr, CuBr₂, t-butyl acrylate and PMDETA were added to a dry Schlenk flask and stirred to allow for the formation of the Cu/ligand complex. The complexation was

complete when the solution turned from colourless to green. The initiator was thereafter added and the flask was sealed with a rubber septum. Methyl 2-bromopropionate (MBP) and dimethyl-2,6-dibromoheptanedioate (DMDBHD) were the initiators used for the synthesis of the monofunctional polystyrene macroinitiator and the difunctional polystyrene macroinitiator respectively. The contents of the flask were subjected to three freeze-thaw cycles under vacuum to remove oxygen from the reaction mixture and then left under nitrogen. The freeze-thaw cycles must be carried out immediately after initiator addition to minimize the probability of oxygen interfering with the initiation step. The reaction was allowed to take place overnight at 60°C. Table 2 gives a detailed description of the amounts and molar ratios of reactants used for each poly(*t*-butyl acrylate) macroinitiator synthesis.

Table 2: Reagent amounts and ratios for poly(*t*-butyl acrylate) macroinitiator synthesis via ATRP.

Experiment [#]	M (ml)	I (ml)	CuBr (g)	CuBr ₂ (g)	L (ml)	M:I:Cu:Cu ₂ :L*	Solvent	Mn (theo) ⁺
1P(<i>t</i> BA)A	5.8	0.22	0.140	0.012	0.22	20:1:0.5:0.03:0.5	Bulk	2000
2P(<i>t</i> BA)B	2.3	0.17	0.029	-	0.04	20:1:0.25:0:0.25	Bulk	2000

[#] The first digit is associated with the number of functionalities on the macroinitiator

* Molar ratios: *t*-butyl acrylate monomer (M), initiator (I), CuBr catalyst (Cu), CuBr₂ co-catalyst (Cu₂) & PMDETA ligand (L)

⁺ Molecular mass calculated by Eq 3-1

The poly(*t*-butyl acrylate) macroinitiators were not used in the synthesis of the block copolymers for reasons that will be explained in the Results and Discussion chapter, therefore no molecular mass analyses were carried out.

Synthesis and Characterisation of the Block Copolymers: B. Polystyrene Macroinitiators

Polystyrene monofunctional macroinitiators with molecular masses of ~1000, ~2000 and ~3000 were required to be synthesized. One difunctional polystyrene macroinitiator of ~2000 molecular mass was also required to be synthesized.

To synthesize a macroinitiator of a required size, equation 3-1 was used to determine the required amount of initiator corresponding to the amount of monomer used (Summers, 2001).

Polystyrene Macroinitiator Synthesis

The synthesis of the styrene macroinitiators was carried out via ATRP. CuBr, styrene and PMDETA were added to a dry Schlenk flask and stirred to allow for the formation of the Cu/ligand complex. The complexation was complete when the solution turned from colourless to green. The addition of a solvent such as acetone was optional and it was dependent on the viscosity of the reaction mixture and the ability for proper mixing to take place. The initiator was thereafter added and the flask was sealed with a rubber septum. 2-Bromoethylbenzene (BEB) and dimethyl-2,6-dibromoheptanedioate (DMDBHD) were the initiators used for the synthesis of the monofunctional polystyrene macroinitiator and the difunctional polystyrene macroinitiator respectively. The contents of the flask were subjected to three freeze-thaw cycles under vacuum to remove oxygen from the reaction mixture and then left under nitrogen. The freeze-thaw cycles must be carried out immediately after initiator addition to minimize the probability of oxygen interfering with the initiation step. The reaction was allowed to take place overnight at 100°C. Table 3 gives a detailed description of the amounts and molar ratios of reactants used for each polystyrene macroinitiator synthesis.

Table 3: Reagent amounts and ratios for polystyrene macroinitiator synthesis via ATRP.

Experiment [#]	M (ml)	I (ml)	CuBr(g)	L (ml)	M:I:Cu:L*	Solvent	Mn (theo) ⁺
1PSA	11	0.62	0.135	0.20	21:1:0.2:0.2	Bulk	2000
2PSB	11	1.58	0.131	0.20	13:1:0.1:0.1	Bulk	2000
1PSC	11	1.25	0.260	0.38	10:1:0.2:0.2	Bulk	1000
1PSD	16.5	0.68	0.140	0.20	29:1:0.2:0.2	Bulk	3000
1PSE	11	1.24	0.273	0.38	11:1:0.2:0.2	Bulk	1000
1PSF	16.5	0.67	0.145	0.21	29:1:0.2:0.2	Bulk	3000

[#] The first digit is associated with the number of functionalities on the macroinitiator

* Molar ratios: styrene monomer (M), BEB initiator (I), CuBr catalyst (Cu) & PMDETA ligand (L)

⁺ Molecular mass calculated by Eq 3-1

Poly(styrene-co-t-butyl acrylate) Block Copolymer Synthesis

The synthesis of the block copolymers was carried out via ATRP. The polystyrene macroinitiators were used to initiate the growth of the t-butyl acrylate (tBA) blocks. However, it must be noted that for the difunctional initiator there are two moles of initiation sites per one mole of polystyrene macroinitiator. Equation (3-1) was used to determine the amount of macroinitiator required to copolymerise tBA to a specific size. The polystyrene macroinitiator and the CuBr were added to a dry Schlenk flask. The PMDETA was added and the mixture was immediately frozen to prevent the initiation of the polymerisation in open atmosphere. Acetone was added to the reaction mixture in order to facilitate the proper mixing of the reagents. The flask was thereafter sealed with a rubber septum and subjected to three freeze-thaw cycles under vacuum to remove oxygen from the reaction mixture and then left under nitrogen. Upon thawing of the reaction mixture the Cu/ligand complex was allowed to form. The complexation was complete when the solution turned from colourless to green. The reaction was allowed to take place overnight at 60°C. Table 4 gives a detailed description of the amounts and molar ratios of reactants used for each poly(styrene-co-t-butyl acrylate) block copolymer synthesis.

Table 4: Reagent amounts and ratios for poly(styrene-co t-butyl acrylate) block copolymer synthesis via ATRP.

Experiment [#]	M (ml)	MI (g)	CuBr (g)	L (ml)	M:MI:Cu:L*	S/M [%]	Mn (theo) ⁺
1PS-P(tBA)A	4.45	3.0	0.109	0.16	20:1:0.5:0.5	0.25	4000
2P(tBA)-PS-P(tBA)B	4.45	3.0	0.108	0.16	20:1:0.5:0.5	0.25	4000
1PS-P(tBA)C	3.9	2.0	0.096	0.14	20:1:0.5:0.5	0.26	4000
1PS-P(tBA)D	2.5	3.5	0.102	0.15	12:1:0.5:0.5	0.24	4000
1PS-P(tBA)E	3.9	2.0	0.097	0.14	13:1:0.3:0.3	0.26	4000
1PS-P(tBA)F	2.5	3.5	0.101	0.15	15:1:0.6:0.6	0.24	4000

[#] The first digit is associated with the number of functionalities on the macroinitiator. The capital letter suffix reflects the PS macroinitiator used.

* Molar ratios: t-butyl acrylate monomer (M), macroinitiator (MI), CuBr catalyst (Cu) & PMDETA ligand (L)

[%] Volumetric ratio of acetone solvent (S) to t-butyl acrylate monomer (M)

⁺ Molecular mass calculated by Eq 3-1

Hydrolysis

Hydrolysis of the t-butyl acrylate block was attempted in acidic (HCl) and basic conditions (NaOH – saponification) without success. In both of these hydrolysis procedures the block copolymer was dissolved in THF, the acid or base was added and the mixture was thereafter stirred continuously and allowed to reflux overnight. Finally, the poly(styrene-co-t-butyl acrylate) block copolymers were hydrolysed to poly(styrene-co-acrylic acid) block copolymers in the presence of TFA catalyst in dichloromethane at room temperature for 24 hours. The solvent was evaporated under vacuum and the polymer was vacuum dried.

Analytical Techniques

The molecular mass and molecular mass distribution of the polystyrene macroinitiators and the block copolymers were determined by size exclusion chromatography (SEC) using tetrahydrofuran (THF) as eluent, a phenogel column (500Å pore size, 3000 x 7.8 mm), a refractive index detector and polystyrene standards. The molecular mass and molecular mass distribution of the polystyrene macroinitiators and the block copolymers synthesised was also determined by matrix assisted laser desorption ionisation time-of-flight mass spectrometry (MALDI-TOF-MS) (Voyager-DE STR). A 2,5-dihydroxybenzoic acid matrix was used in the analysis. No salt solution was added to charge the sample as it was observed that sodium (from the glassware used during the polymer synthesis) and copper (from the metal halide catalyst) were inherently present in the polymer and therefore provided sufficient charging for the analysis procedure to occur. The matrix and polymer were premixed in a 4:1 ratio with the concentrations of 40 mg/ml and 2.6 mg/ml in THF respectively.

The poly(t-butyl acrylate) and polystyrene macroinitiators and block copolymers synthesised were characterised by ¹H-NMR using a 300MHz Bruker ARX300 spectrometer. Deuterated trichloromethane was used as the solvent for the polystyrene macroinitiators and the unhydrolysed block copolymers. Deuterated dimethylsulphoxide was used as the solvent for the hydrolysed block copolymers. The deuterated trichloromethane did not solubilise the hydrolysed block copolymers effectively for ¹H-NMR analysis.

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3.3.2 SURFACTANT ASSISTED MICRO-MIXING

Polystyrene Emulsion Polymerisation

Styrene was emulsion polymerised by making use of the block copolymers synthesised in order to prepare a polystyrene particle dispersion.

0.05g of 1PS-P(tBA)A block copolymer solution (2.2×10^{-4} mol/l), 0.05g of NaHCO_3 solution (1.2×10^{-2} mol/l) and 5g of styrene were placed in a round-bottomed flask, immersed in an oil bath at 70°C and bubbled with nitrogen. Proper mixing of the reagents was continuously ensured. 0.05g of $\text{K}_2\text{S}_2\text{O}_8$ initiator solution (3.7×10^{-3} mol/l) was thereafter added to the reaction mixture and the reaction was allowed to take place overnight.

Melamine Dispersion

10 % Melamine dispersions were prepared by using an increasing amount of poly(acrylic acid) (PAA) dispersant (Goodrite K732) so as to determine the point at which a stable dispersion is obtained. Stability was determined by leaving the dispersions overnight at room temperature without agitation. If a sediment was observed, the dispersion was deemed unstable. A 10% poly(acrylic acid) solution was prepared and used to introduce the poly(acrylic acid) dispersant to the melamine dispersion. Table 5 shows the different amounts of poly(acrylic acid) used.

Table 5: Determination of the minimum amount of poly(acrylic acid) required for a stable 10% melamine dispersion.

Experiment	Distilled Water (g)	Melamine (g)	10% PAA Solution (g)	PAA : Melamine* %
1	10.01	1.11	0.57	5.14
2	10.05	1.13	0.70	6.20
3	10.80	1.20	0.86	7.17
4	10.04	1.12	0.87	7.77
5	10.02	1.11	0.90	8.11
6	10.02	1.11	0.99	8.92
7	10.08	1.13	1.14	10.09
8	10.01	1.12	1.35	12.05
9	10.01	1.12	1.69	15.09
10	11.21	1.24	0	0

$$* \frac{\text{Mass 10\% PAA Solution}}{\text{Mass Melamine}} \times \frac{100}{10}$$

The prepared dispersions were gently mixed in an end-over-end tumbler for 48 hours to ensure reaction of the melamine with the poly(acrylic acid) dispersant. In addition, a control was prepared without the presence of the poly(acrylic acid) dispersant so as to ensure that the melamine and wax do not inherently interact upon mixing of the melamine dispersion and wax emulsion. Table 6 shows the compositions of the melamine dispersions prepared for micro-mixing purposes.

Table 6: Composition of melamine dispersion prepared for the micro-mixing experiments.

Experiment	Distilled Water (g)	Melamine (g)	10% PAA Solution (g)	PAA:Melamine* %
A	10.435	1.159	0	0
B	10.335	1.156	0.475	4.11
C	10.567	1.181	0.713	6.04
D	10.332	1.183	0.953	8.06
E	10.458	1.170	1.174	10.03

$$* \frac{\text{Mass 10\% PAA Solution}}{\text{Mass Melamine}} \times \frac{100}{10}$$

Wax Emulsion

Aqueous wax emulsions were prepared using low melting point (57-60°C) wax and low molecular mass PEO-PPO surfactants. The water and surfactants were heated to 80°C and thereafter the wax was added and allowed to melt. Mixing becomes easier when the viscosity of the materials are in the same order of magnitude. As the ratio of the two viscosities approaches the value of 1, the shear rate required tends towards a minimum (Grace, 1982). A high-speed shear mixer was used to emulsify the wax. The shearing action ensures good mixing of the materials and prevents deagglomeration of the wax particle formed. The materials were mixed for 2 hours. Table 7 shows the amounts of material used for the wax emulsion preparation. In addition to the use of low molecular mass ethylene oxide based surfactants, it was attempted to use a mixture of low molecular mass (Synperonic A2) and higher molecular mass (Synperonic A7) ethylene oxide containing surfactants so as to allow for better surface coverage of the wax particles and subsequently possibly improve dispersion.

Table 7: Amounts of material used for the wax emulsion preparation.

Exp	Distilled Water (g)	Wax (g)	Wax %	Surfactant [#]	Surfactant (g)	Surfactant:Wax %
1	50.79	50.01	48.88	NP9	1.52	3.03
2	75.01	75.01	47.62	NP9	7.51	10.01
3	120.01	30.01	19.60	NP9	3.09	10.28
4	120.15	30.06	19.41	NP9	4.66	15.49
5	120.93	30.00	19.49	A7	3.03	10.11
6	120.90	30.00	19.49	NP9	3.00	10.00
7	121.22	30.04	19.46	A2	1.23	10.26
				A7	1.86	
8	120.02	30.06	18.54	A2	4.83	40.12
				A7	7.23	
9	120.19	30.02	18.84	A2	3.64	30.31
				A7	5.46	
10	120.31	10.07	7.53	A2	1.36	33.37
				A7	2.00	
11	102.05	25.03	17.60	A2	6.04	60.41
				A7	9.08	
12	103.23	8.38	7.23	A2	1.70	50.60
				A7	2.54	
13	100.30	8.35	7.40	A2	1.68	50.30
				A7	2.52	
14	100.35	8.38	6.26	A2	10.01	299.16
				A7	15.06	
15	100.42	8.41	6.91	A2	5.01	152.08
				A7	7.78	
16	100.68	2.15	1.97	A2	2.51	298.60
				A7	3.91	
17	104.34	1.05	0.98	A2	0.61	138.10
				A7	0.84	

[#] NP9 – Nonylphenoethoxylate surfactant, A2 – Synperonic A2, A7 – Synperonic A7

Micro-mixing

The micro-mixing was based on a 1:1 volume melamine: volume wax. The wax emulsion was added to the melamine dispersion, mixed and the mixture was subsequently centrifuged for 20 minutes at 3000 rpm. The supernatant was removed and the sediment obtained from the micro-mixing was dried and prepared for analysis (SEM). Table 8 below shows the amount of melamine dispersion mixed with wax emulsion in the micro-mixing experiments.

Table 8: Amounts of melamine dispersion mixed with wax emulsion in the micro-mixing experiments.

Experiment	Melamine Dispersion (g)	Wax Emulsion (g)
MMA	11.594	2.583
MMB	11.966	2.677
MMC	12.461	2.777
MMD	12.468	2.795
MME	12.802	2.885

The supernatant removed after centrifuging was oven-dried at 50°C overnight. This temperature was chosen so that the wax would not volatilise and thus influence the experimental results. In addition, the melting point of the wax is between 57°C and 60°C. The wax obtained was weighed to determine whether the increase in the amount of poly(acrylic acid) dispersant used, has an influence on the amount of ethylene oxide stabilised wax which interacts with the poly(acrylic acid).

Analytical Techniques

The wax, melamine and sediment particles were viewed using scanning electron microscopy (SEM). Samples of the wax emulsion were placed on graphite stubs which were subsequently freeze dried in liquid propane at -180°C with a Reichert KF 80 freeze plunger. The frozen samples were transferred under liquid nitrogen into slots in a copper block (63 x 63 x 15 mm). The copper block was kept completely immersed in liquid nitrogen in a plastic container, thus keeping the material under nitrogen atmosphere and preventing the condensation of moisture onto the sample. The copper block was thereafter transferred to a Fisons high vacuum unit where the evacuation started immediately. Freeze-drying was carried out over 2 days, over which the temperature steadily increased back to room temperature. The samples were coated with chromium in a Gatan Ion beam coater, model 681. The melamine and sediment particles were placed on the polished side of graphite stubs using double-sided carbon tape and the excess particles were removed. Samples were coated with chromium, however, charging of the particles was observed and the sample was thereafter coated with ruthenium tetroxide. All the particles were viewed with a JEOL 6000F in-lens field emission scanning electron microscope.

4. Results and Discussion

4.1 BLOCK COPOLYMER SYNTHESIS

4.1.1 POLY(T-BUTYL ACRYLATE) MACROINITIATOR

The synthesis of the block copolymer was attempted by first synthesising a poly(*t*-butyl acrylate) macroinitiator. The mono- and difunctional poly(*t*-butyl acrylate) macroinitiators (1P(*t*BA)A and 2P(*t*BA)B) synthesised however, were difficult to isolate as they both precipitated out as a highly viscous liquid. This is due to their low molecular mass (~2000) and the lower glass transition temperature (T_g) of poly(*t*-butyl acrylate). The bulky *t*-butyl acrylate group of the poly(*t*-butyl acrylate) inhibits the polymer chains from packing too closely and therefore results in a polymer with a higher free volume and subsequently a lower T_g . It was therefore decided to continue the block copolymer synthesis by first preparing the polystyrene macroinitiators. The results of the polystyrene macroinitiator synthesis will be presented in chapter 4.1.2.

The $^1\text{H-NMR}$ spectrum of 1P(*t*BA)A is shown in Appendix 2.

4.1.2 POLYSTYRENE MACROINITIATOR

The polystyrene mono- and difunctional macroinitiators were successfully isolated by precipitation. A white powder-like solid precipitated out, which upon drying became light and fluffy. The molecular mass and the molecular mass distributions of the polystyrene macroinitiators were analysed using SEC and MALDI-TOF MS. This was to confirm that the required molecular mass was obtained at a satisfactory PDI. Table 9 below gives a detailed description of the results obtained for the molecular mass and molecular mass distributions of the polystyrene macroinitiators synthesised.

Table 9: Molecular mass and molecular mass distribution for polystyrene macroinitiators synthesis via ATRP; SEC and MALDI-TOF MS results thereof.

Experiment [#]	Mn (theo) ^x	SEC [†]		MALDI-TOF MS ^{††}	
		Mn (exp)	PDI [%]	Mn (exp)	PDI [%]
1PSA	2000	2072	1.21	2198	1.09
2PSB	2000	2333	1.10	2369	1.07
1PSC	1000	1510	1.06	1580	1.06
1PSD	3000	2510	1.26	2762	1.05
1PSE	1000	1652	1.09	1614	1.07
1PSF	3000	3016	1.13	3014	1.04

[†] Size Exclusion Chromatography – Polystyrene standard

^{††} Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

[#] The first digit is associated with the number of functionalities on the macroinitiator

^x Molecular mass calculated by Eq 3-1

[%] Polydispersity index

From the data given in Table 9, the polystyrene macroinitiators were reliably synthesized via ATRP. The molecular masses and molecular mass distributions obtained were satisfactory relative to the values required. In addition, the results from the SEC and MALDI-TOF MS compare well with each other. The MALDI-TOF MS spectra of the polystyrene macroinitiators are shown in Appendix 3.

The PDI of the MALDI-TOF MS analysis is lower than that of SEC, since the 2,5-dihydroxybenzoic acid matrix used overlaps with some of the low molecular mass polystyrene peaks and this region was avoided during molecular mass determination. Also, by avoiding the low molecular mass matrix, the molecular masses obtained by MALDI-TOF MS are higher than those obtained by SEC. A typical MALDI-TOF MS spectrum for the polystyrene macroinitiators is shown in Figure 9.

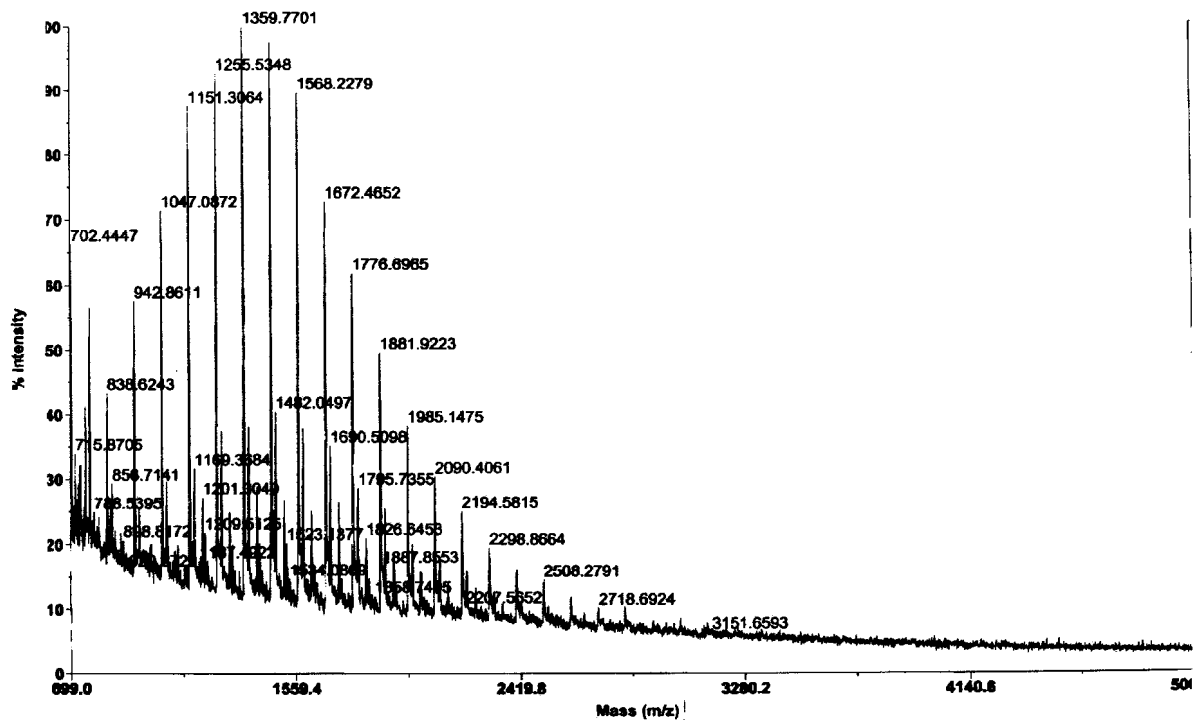


Figure 9: MALDI-TOF MS spectrum of 1PSC showing the distribution of molecular masses.

In the MALDI-TOF-MS analysis compensation is needed to be made for the presence of the cation which is attached to the polymer chain. The purpose of the cation is to charge the polymer chain such that when a current is placed across the sample tube the chains can fly to the detector. The origin of the cation can either be inherently present in the sample, as in this case, or introduced during sample preparation by means of a salt solution.

The segment of the spectrum shown in Figure 10 is for the polystyrene macroinitiator 1PSC, and it can be seen that the series of peaks is repeated. The first four peaks are repeated at an interval of 104, which is the molecular mass of one styrene unit. The reason why we see four peaks in a series is due to the state in which the polymer chain exists. For example, the cation present on the polymer fragment or perhaps the loss of a fragment due to it being abstracted by the laser modifies the state of the polymer chain.

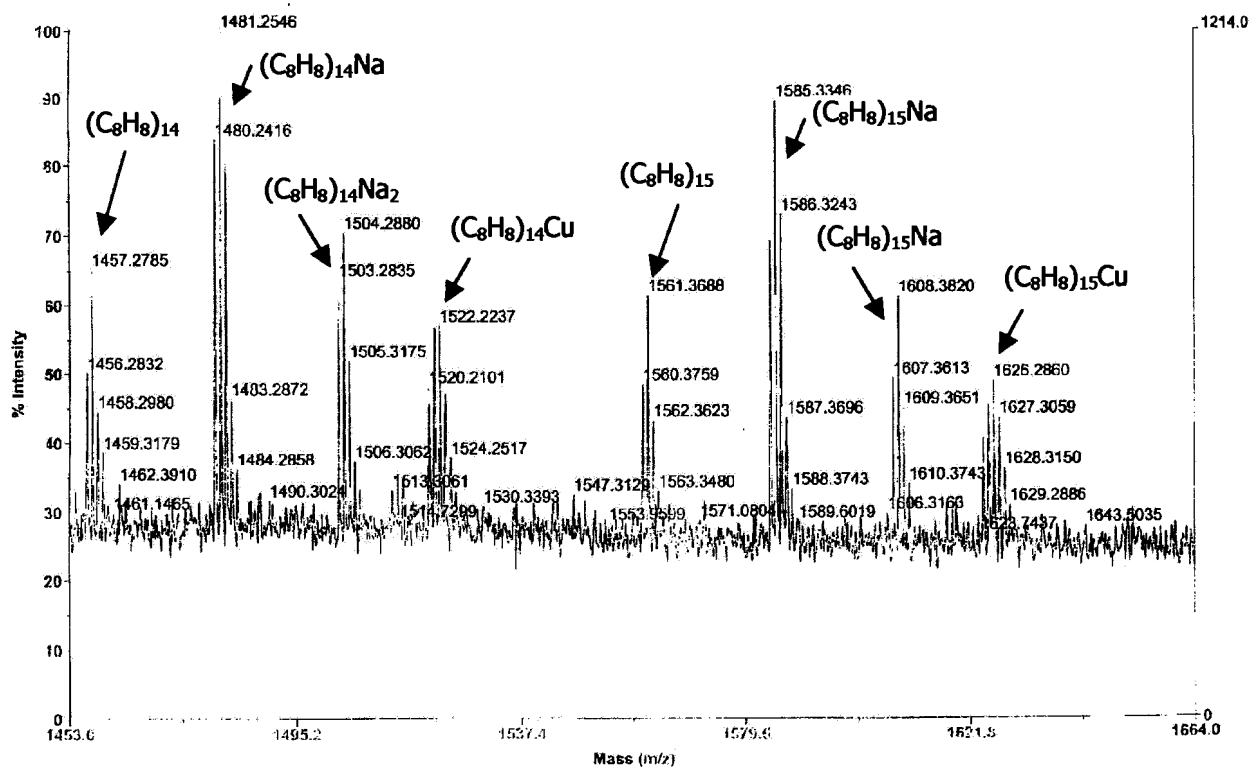


Figure 10: Segment of the MALDI-TOF MS spectrum of 1PSC showing the repetition of chain configuration peaks.

A closer look at each peak allows for the identification of the form in which the polymer chain exists. Figure 11 shows that the series of peaks obtained from the sample versus a theoretically obtained spectrum of (C₈H₈)₁₄Cu compare well with each other.

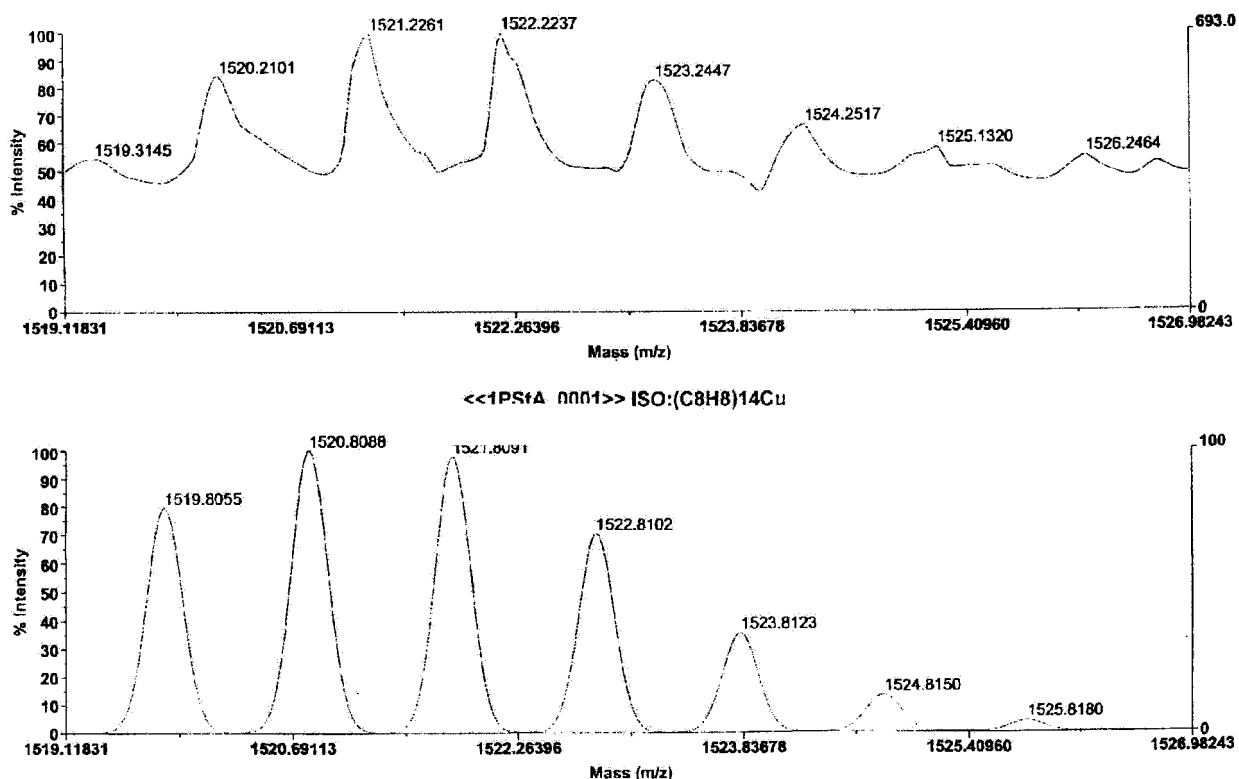


Figure 11: The top spectrum is the series of peaks in the region of 1522 for 1PSC. The bottom spectrum shows the theoretically resultant peaks from a $(C_8H_8)_{14}Cu$ chain segment. The two spectra correspond well.

Other peaks may correspond to the sodium cation and any other cation introduced or present in the system, even possibly to a polymer chain, which has a fragment, abstracted. Fragments include hydrogen, methyls and others. In our analysis samples the terminal bromine found on the polymer chains inherent to the ATRP process were found to be readily abstracted and all peaks observed showed the absence of bromine. The copper is inherently in the system due to the copper halide catalyst used in the synthesis and the sodium originates from the glassware used. The introduction of another cation such as silver will introduce more peaks and it is found that due to the presence of the copper and sodium it is not necessary to introduce other cations to charge the polymer chain.

The $^1\text{H-NMR}$ spectra of the monofunctional macroinitiator (1PSA) and the difunctional macroinitiator (2PSB) are shown in Figure 12 and Figure 13 respectively. The protons responsible for specific peaks in the $^1\text{H-NMR}$ spectrum are shown relative to the structure of the polystyrene macroinitiator (Skoog & Leary, 1992: 328). $^1\text{H-NMR}$ spectra of the other macroinitiators are shown in Appendix 4. The peaks observed for all the monofunctional polystyrene macroinitiators will be the same, only the intensity will vary due to the change in the molecular mass. The difunctional polystyrene macroinitiator will also show the same structural peaks with the addition of the peaks due to the difunctional initiator used for the macroinitiator synthesis.

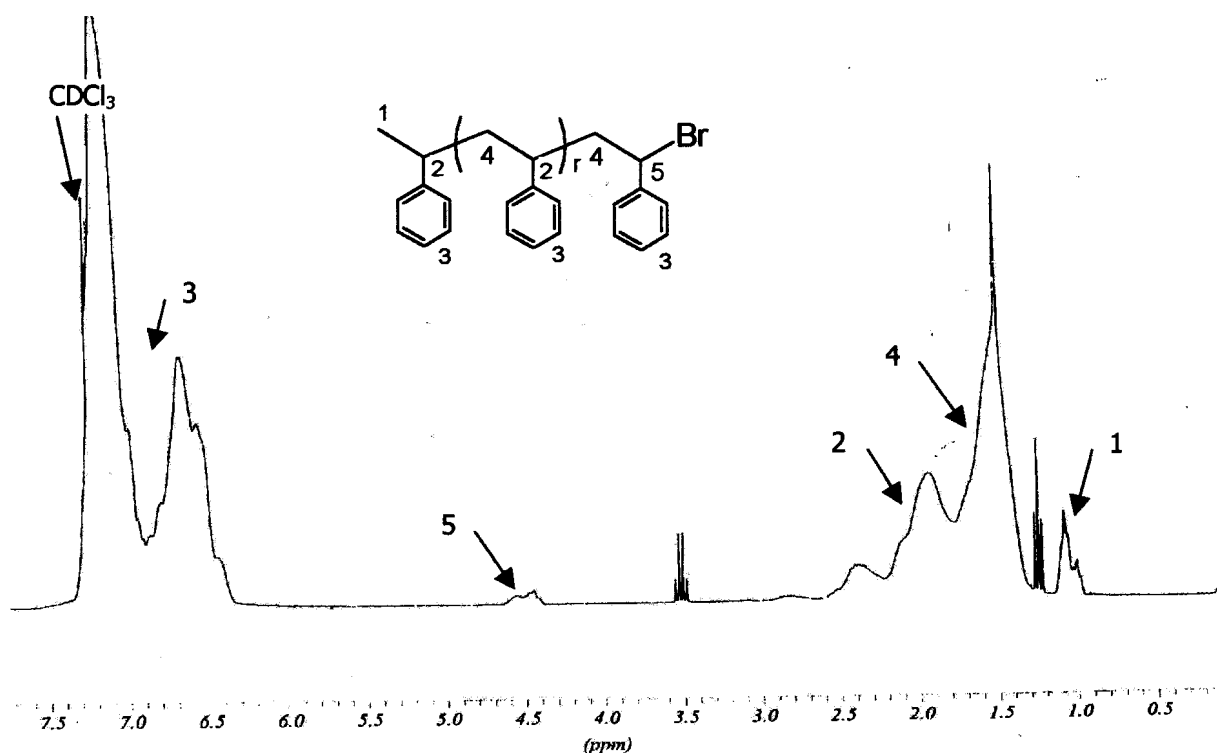


Figure 12: $^1\text{H-NMR}$ spectrum of monofunctional polystyrene macroinitiator 1PSA. Peak contributions are numbered. The solvent (CDCl_3) peak occurs at 7,29 ppm.

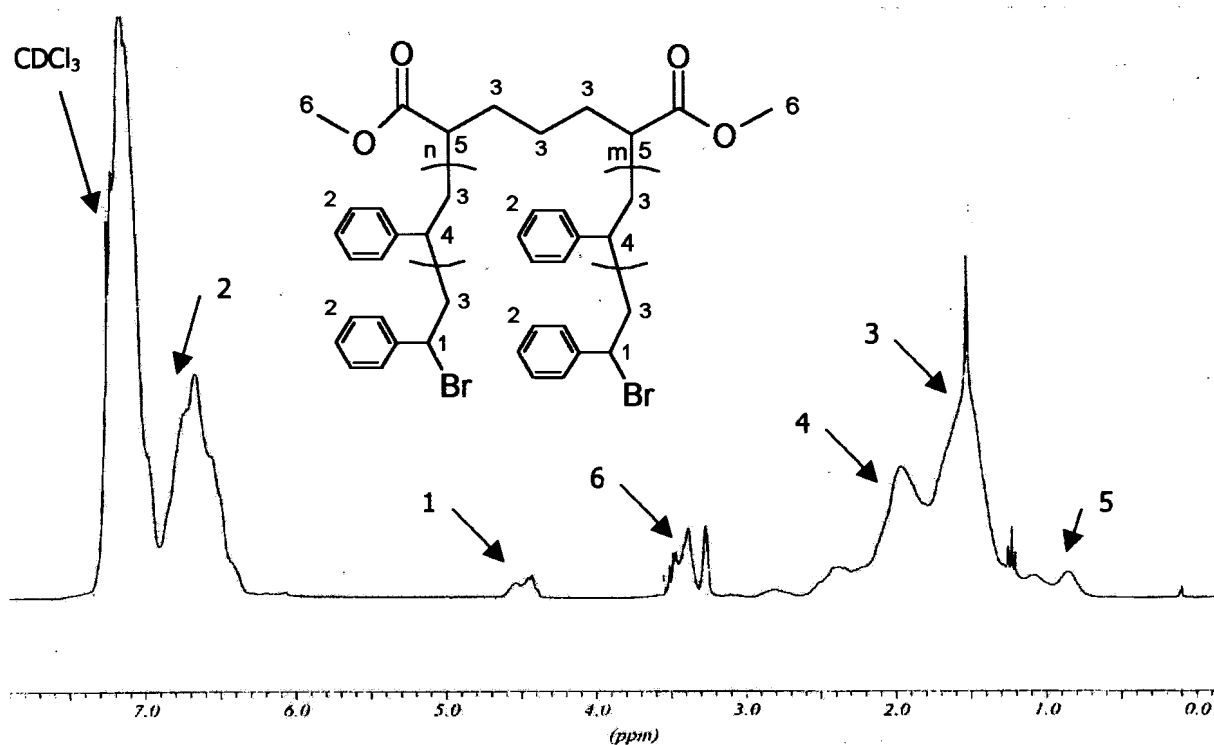


Figure 13: ¹H-NMR spectrum of difunctional polystyrene macroinitiator 2PSB. Peak contributions are numbered. The solvent (CDCl₃) peak occurs at 7,29 ppm.

4.1.3 POLY(STYRENE-CO-T-BUTYL ACRYLATE) BLOCK COPOLYMER

The poly(styrene-co-t-butyl acrylate) block copolymer precipitated out as a sticky solid, which upon drying became a brittle powder. The molecular mass and the molecular mass distributions of the polystyrene macroinitiators were analysed using SEC and MALDI-TOF MS. This was to confirm that the required molecular mass was obtained at a satisfactory PDI. Table 10 below gives a detailed description of the results obtained for the molecular mass and molecular mass distributions of the polystyrene macroinitiators synthesised.

Table 10: Molecular mass and molecular mass distribution for poly(styrene-co-t-butyl acrylate) block copolymers synthesised via ATRP; SEC and MALDI-TOF MS results thereof.

Experiment [#]	Initiator	Mn (theo) ^x	SEC [†]		MALDI-TOF MS ^{††}	
			Mn (exp)	PDI [%]	Mn (exp)	PDI [%]
1PS-P(tBA)A	1PSA	4000	4251	1.28	4317	1.34
2P(tBA)-PS-P(tBA)B	2PSB	4000	4375	1.76	4263	1.30
1PS-P(tBA)C	1PSC	4000	3783	1.18	3735	1.24
1PS-P(tBA)D	1PSD	4000	4090	1.17	33868	1.29
1PS-P(tBA)E	1PSE	4000	3014	1.11	3461	1.24
1PS-P(tBA)F	1PSF	4000	4078	1.10	3918	1.29

[†] Size Exclusion Chromatography – Polystyrene standard

^{††} Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry

[#] The first digit is associated with the number of functionalities on the macroinitiator

^x Molecular mass calculated by Eq 3-1

[%] Polydispersity index

As with the polystyrene macroinitiators the block copolymers show satisfactory results with respect to molecular mass and molecular mass distribution. Again the two analyses compare well with each other, however it is more difficult to identify the cation peaks in the MALDI-TOF MS block copolymer spectra. With the introduction of the second block the system has become two-dimensional as the number of units in both blocks influences the peaks, therefore some overlapping does occur and the peak series are not as distinguishable. The molecular mass analysis however can still be carried out. Figure 14 shows a typical MALDI-TOF MS spectrum with the molecular mass distribution of the block copolymer being rather evident in the existence of the spectrum "hump". The MALDI-TOF MS spectra of the remaining block copolymers are shown in Appendix 5.

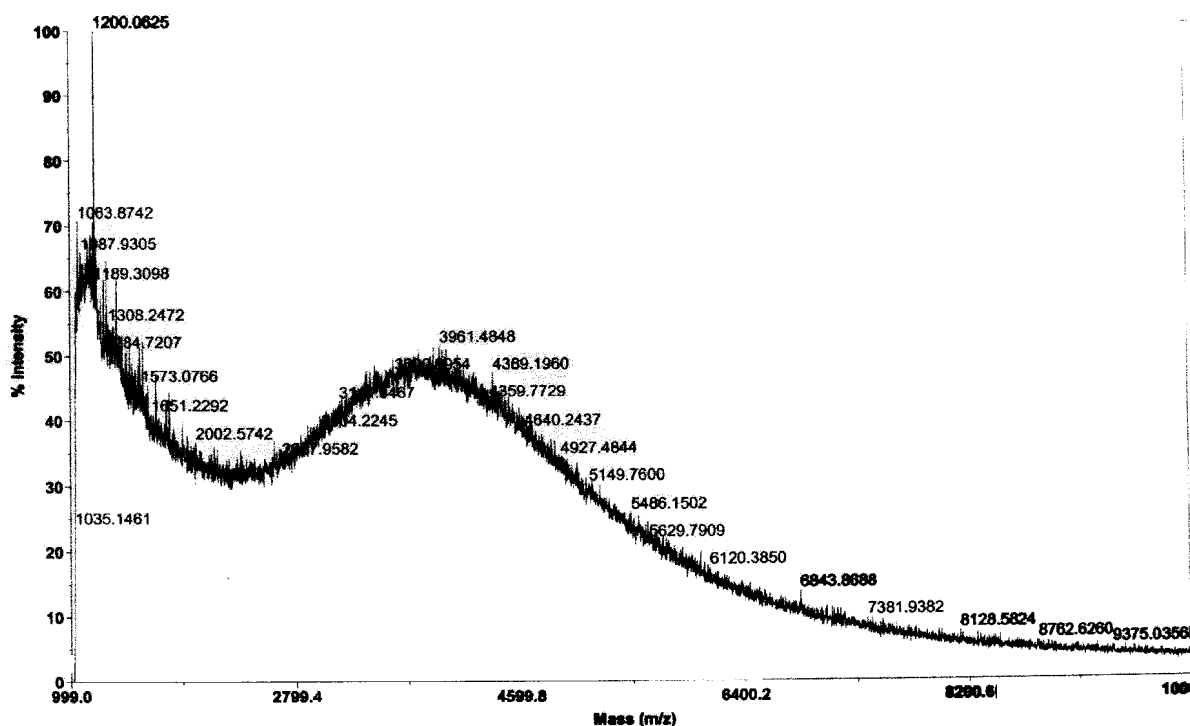


Figure 14: MALDI-TOF MS spectrum of 1PS-P(tBA)C showing the characteristic "hump" of molecular mass distribution. The individual peaks are difficult to differentiate.

The $^1\text{H-NMR}$ spectrum of the diblock copolymer (1PS—P(tBA)A) and the triblock copolymer (2P(tBA)-PS-P(tBA)B) are shown in Figure 15 and Figure 16 respectively. $^1\text{H-NMR}$ spectra of the other block copolymers are shown in Appendix 6. The protons responsible for specific peaks in the $^1\text{H-NMR}$ spectrum are shown relative to the structure of the poly(styrene-co-t-butyl acrylate) block copolymer (Skoog & Leary, 1992: 328).

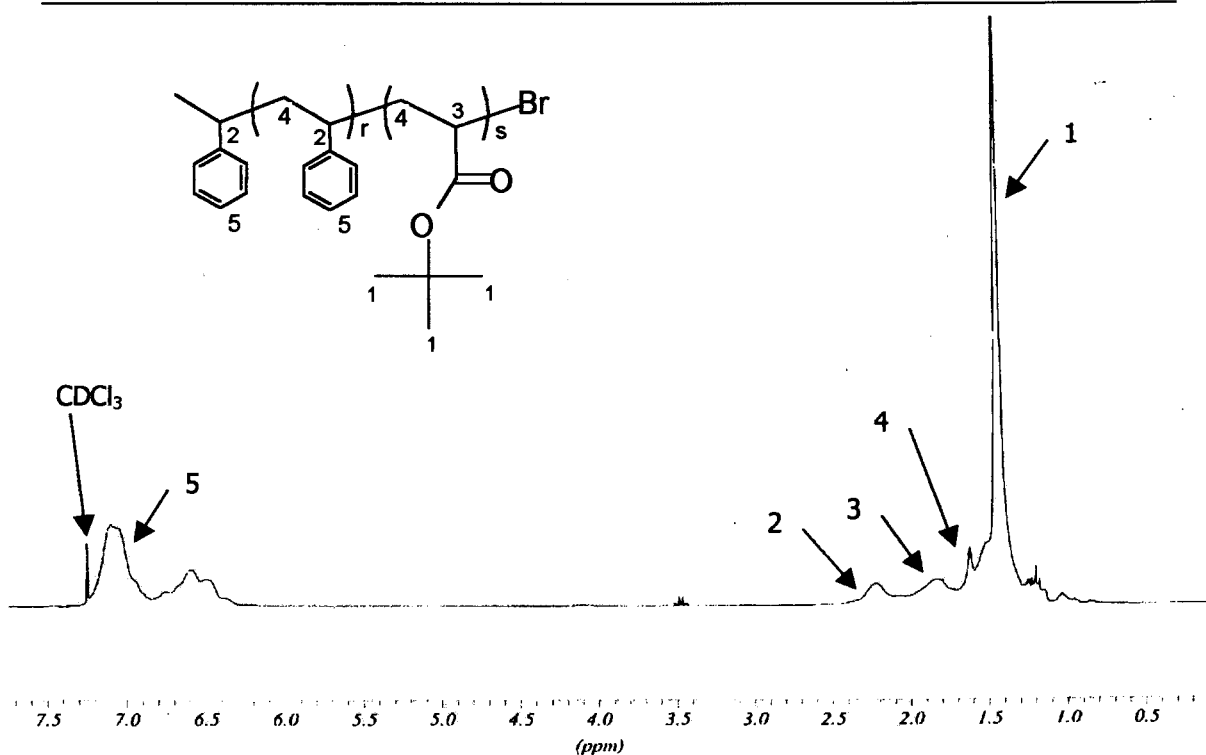


Figure 15: $^1\text{H-NMR}$ spectrum of polystyrene-co-poly(*t*-butyl acrylate) diblock copolymer 1PS-P(*t*BA)A. The solvent (CDCl_3) peak occurs at 7,29 ppm.

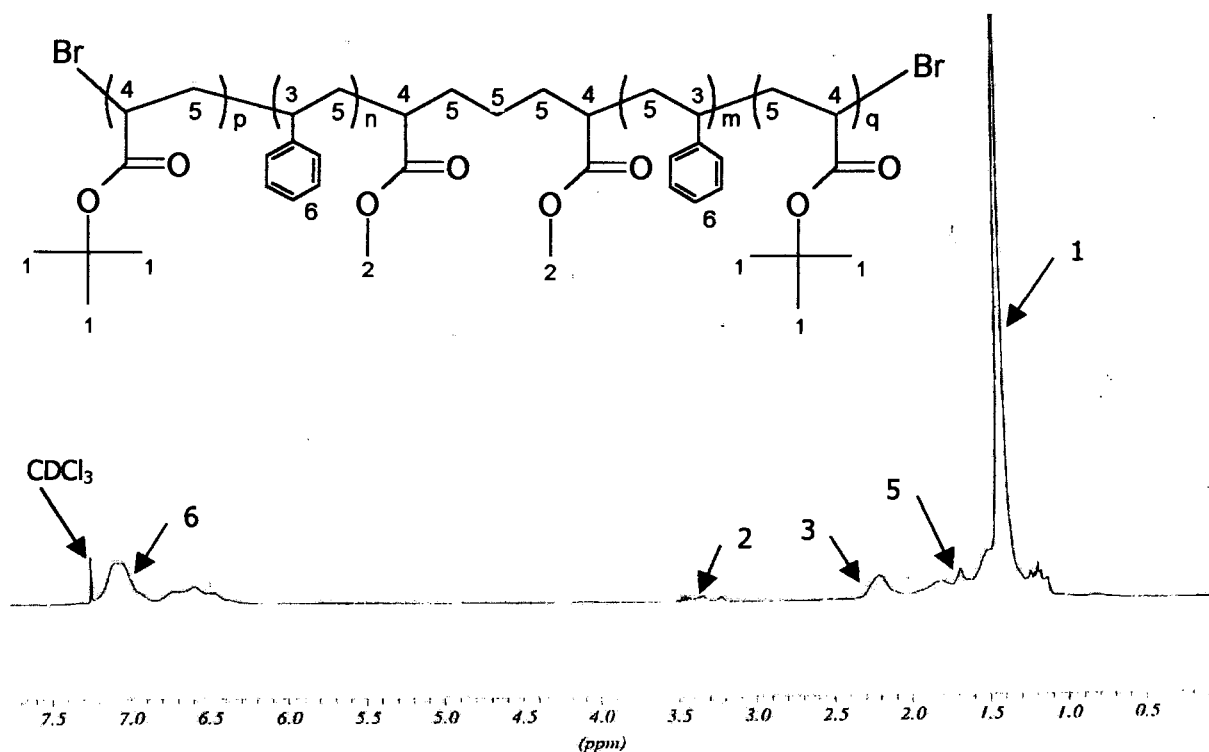


Figure 16: $^1\text{H-NMR}$ spectrum of polystyrene-co-poly(*t*-butyl acrylate) triblock copolymer 2P(*t*BA)-PS-P(*t*BA)B. The solvent (CDCl_3) peak occurs at 7,29 ppm.

4.1.4 POLY(STYRENE-CO-ACRYLIC ACID) BLOCK COPOLYMER

The poly(styrene-co-acrylic acid) block copolymer was synthesised by the hydrolysis of the poly(styrene-co-t-butyl acrylate) block copolymer. Hydrolysis was first attempted in acidic conditions using HCl (see Method chapter 3.3.1). The $^1\text{H-NMR}$ spectrum of the resulting polymer is shown below in Figure 17. The dominant peak at 1.4ppm due to the presence of the CH_3 - group of t-butyl acrylate does not disappear and therefore hydrolysis was not successful.

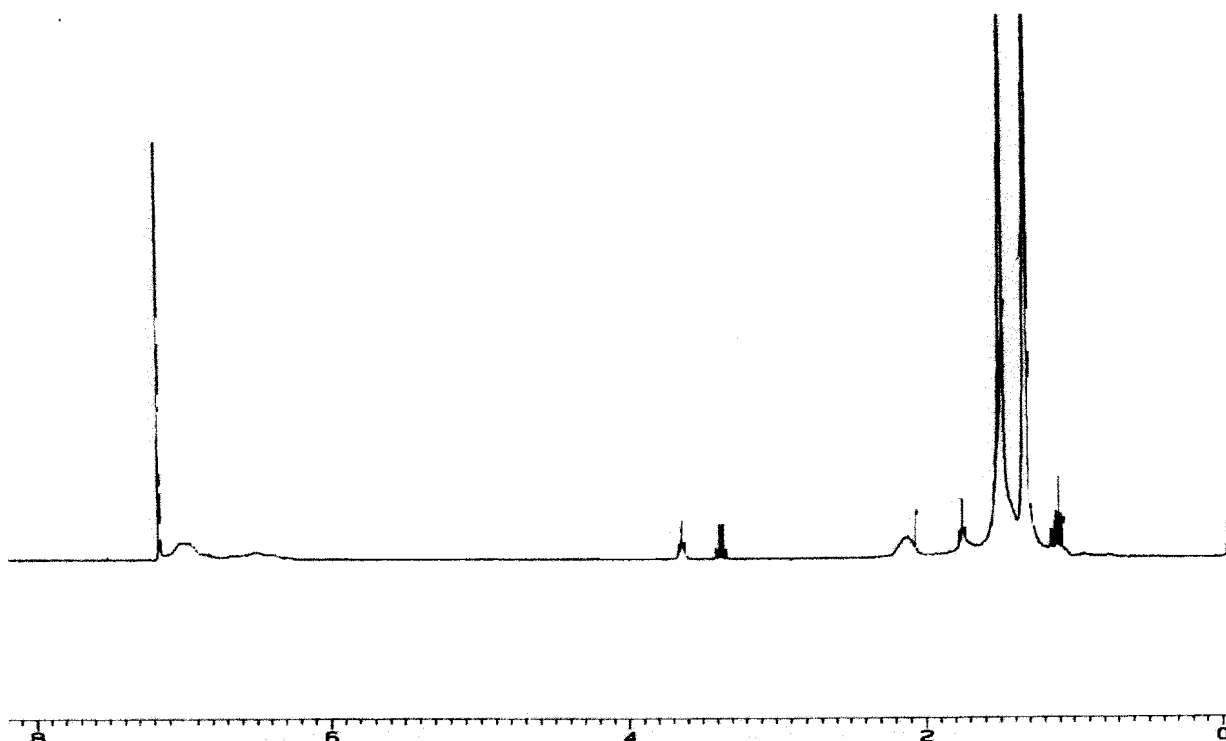


Figure 17: $^1\text{H-NMR}$ spectrum of poly(styrene-co-t-butyl acrylate) (1PS-P(tBA)C) hydrolysed in an acidic medium (HCl).

The attempt to hydrolyse in a basic medium was also not successful. Again the dominant CH_3 - proton peak does not disappear, thus indicating that the hydrolysis was not completed. Figure 18 shows the $^1\text{H-NMR}$ spectrum of the block copolymer after attempting to hydrolyse with NaOH.

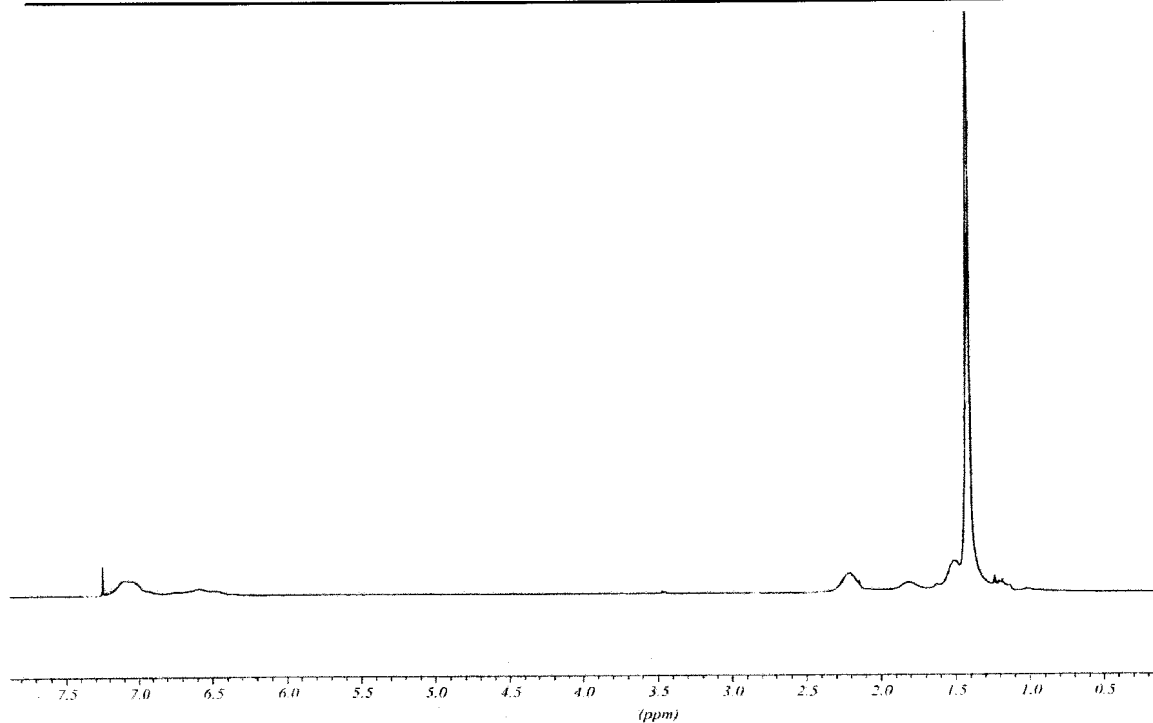


Figure 18: ¹H-NMR spectrum of poly(styrene-co-t-butyl acrylate) (1PS-P(tBA)C) hydrolysed in a basic medium (NaOH).

The hydrolysis using TFA as the catalyst proved to be successful. The dominant peak at 1.4 ppm disappears, thus indicating the removal of the CH₃- group (i.e. t-butyl acrylate). The spectrum only shows the backbone protons in the region of 1-2.5ppm, the solvent (DMSO) peak at 2.5ppm and the styrene protons at 6.3-7.3ppm. Figure 19 shows the ¹H-NMR spectrum of the poly(styrene-co-acrylic acid).

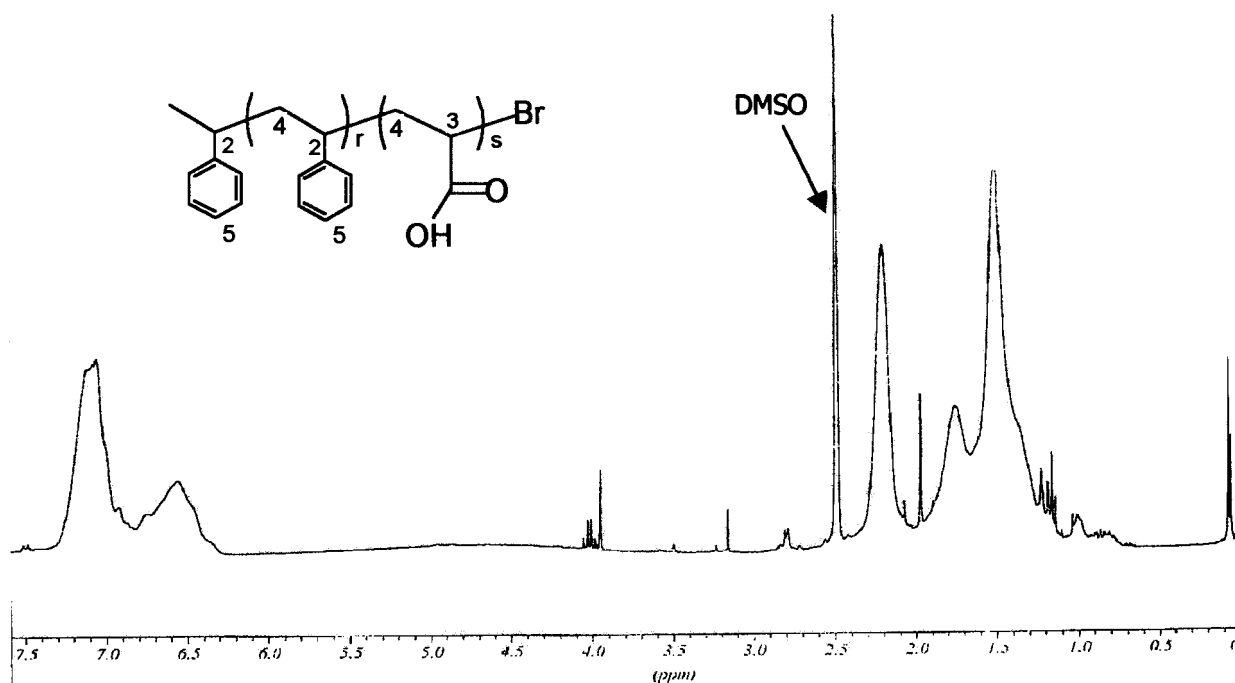


Figure 19: $^1\text{H-NMR}$ spectrum of the poly(styrene-co-acrylic acid) (1PS-P(tBA)C) block copolymer showing the elimination of the t-butyl acrylate peak upon hydrolysis. The peaks from 1,0-2,5ppm are representative of the backbone protons. The large peak at 2,5ppm is the deuterated dimethylsulphoxide (DMSO) solvent.

4.2 SURFACTANT ASSISTED MICRO-MIXING

4.2.1 POLYSTYRENE EMULSION POLYMERISATION

The polystyrene emulsion was not used in the micro-mixing experiments due to the fact that the polystyrene particles are stabilised by the sodium salt of the poly(styrene-co-acrylic acid) block copolymer. The sodium salt of the block copolymer allows for more water solubility of the polymer thus making it ideal for the emulsion polymerisation of styrene in an aqueous medium. The presence of the sodium, however, eliminates the $-\text{OH}$ of the carboxylic acid group and subsequently removes the entity which allows for the required hydrogen bonding between the surfactants used in surfactant assisted micro-mixing. The styrene polymerisation was attempted with the 1PS-P(tBA)A block copolymer but due to insufficient stabilisation a dispersion of polystyrene particles was not obtained. Therefore, the polystyrene emulsion was replaced with the melamine dispersion.

4.2.2 MELAMINE DISPERSION

It was determined that in the region of 6.20-7.17% poly(acrylic acid) dispersant relative to melamine the 10% melamine dispersion becomes stable. Table 11 shows the percentage of poly(acrylic acid) relative to melamine that was used to determine the stability of the 10% melamine dispersions prepared.

Table 11: Determination of the minimum amount of poly(acrylic acid) (PAA) (Goodrite K732) required for a stable 10% melamine dispersion.

Experiment	PAA : Melamine* %	Stable
1	5.14	No
2	6.20	No
3	7.17	Yes
4	7.77	Yes
5	8.11	Yes
6	8.92	Yes
7	10.09	Yes
8	12.05	Yes
9	15.09	Yes
10	0	No

$$* \frac{\text{Mass 10\% PAA Solution}}{\text{Mass Melamine}} \times \frac{100}{10}$$

SEM was used to investigate the surface of the melamine particles prior to their use in the micro-mixing experiments. Figure 20 (a) and (b) shows that the surface of the melamine particles has imperfections that are smaller than 0.5 μm and occur throughout the surface.

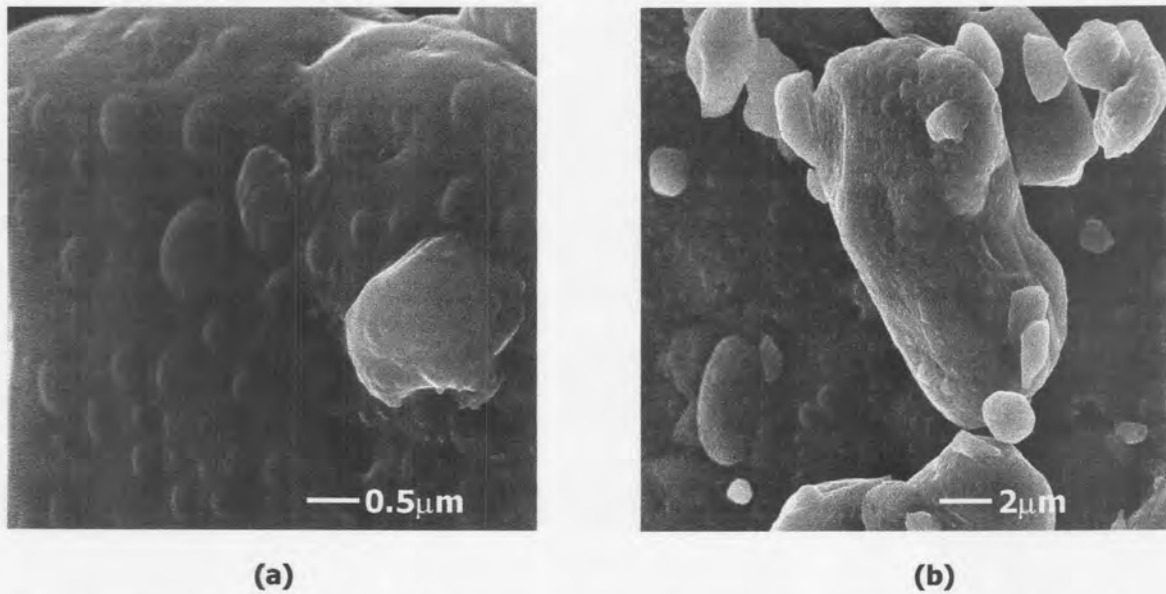


Figure 20 (a), (b): Melamine particles prior to use in micro-mixing experiments showing surface imperfections.

4.2.3 WAX EMULSION

The wax emulsions prepared as described in Table 7 resulted in wax emulsions that were not stable. In addition, the particles obtained were not uniform in size or shape as shown in the SEM analysis (Figure 21) of the wax emulsions prepared.

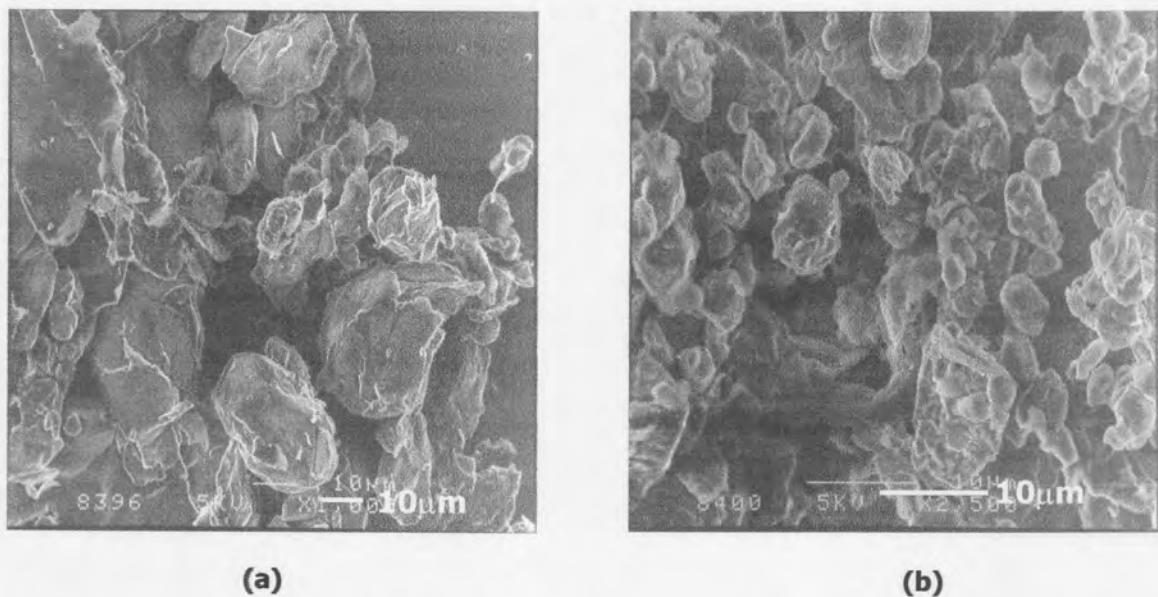


Figure 21 (a), (b): Wax particles in the wax emulsions prepared in Experiment 14 and 17 respectively.

Due to the inability to prepare stable wax emulsions with uniform particle sizes a commercial wax emulsion was used for the surfactant assisted micro-mixing experiments. Figure 22 (a) and (b) shows the wax particles (100-300nm) in Atebin A1 Micro wax emulsion. Wax particles are observed to occur in a matrix of continuous phase.

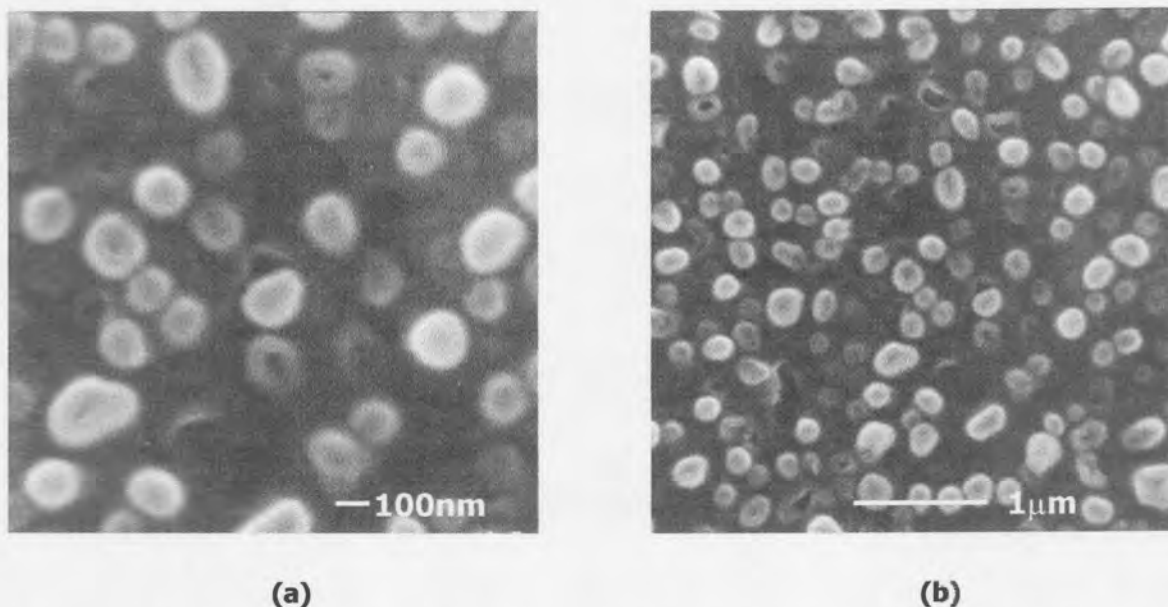


Figure 22 (a), (b): Wax particles stabilized by nonylphenoethoxylate surfactant (Atebin A1 Micro, Böhme Africa) surrounded by emulsion continuous phase.

4.2.4 MICRO-MIXING

Upon mixing of the melamine dispersion and the wax emulsion the melamine particles were observed to flocculate out almost immediately. The addition of the wax emulsion to the melamine dispersion influenced the stability of the melamine dispersion. From the SEM analysis it can be determined as to whether it is the interaction of the poly(acrylic acid) (PAA) and the ethylene oxide stabilisers that result in the flocculation.

The control melamine dispersion (Experiment MMA, Table 6) prepared, i.e. melamine dispersion without PAA stabilisers, was mixed with the wax emulsion so as to observe whether the melamine and wax particles have an inherent interaction. This was to ensure that if an interaction was observed between the PAA stabiliser and the ethoxylate surfactant, it could not be attributed to an existing interaction between the

melamine particles and the ethoxylate surfactant, which stabilises the wax emulsion. Figure 23 below shows the SEM analysis of the melamine particles of the control. The surface morphology is as that shown in Figure 20 for the melamine prior to use in the micro-mixing experiments. No wax particles can be observed on the surface of the melamine particles and it can be concluded that the melamine and the wax particles do not interact in the absence of the PAA dispersant although they were in contact.

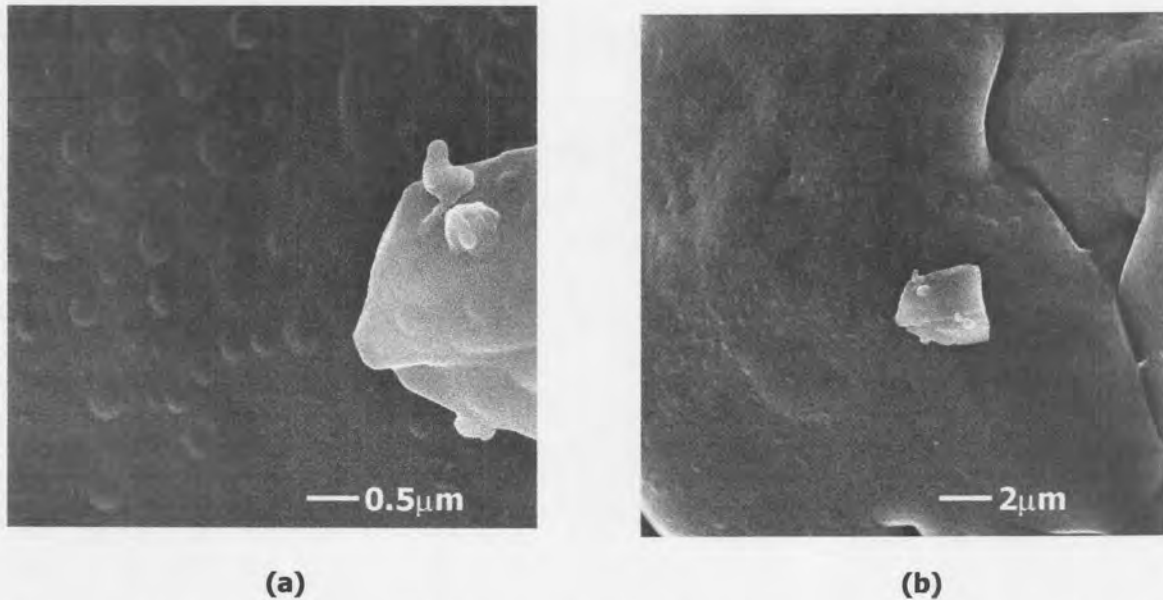


Figure 23 (a), (b): Melamine particle surface of melamine dispersion not stabilized by poly(acrylic acid) and micro-mixed with wax emulsion (Atebin A1 Micro, Böhme Africa).

Figure 24 (a) and (b) shows the surface of a melamine particle treated with poly(acrylic acid) (8% PAA relative to melamine on a mass basis). As it can be seen the surface of the melamine particle is covered with particles that are smaller than the "humps" observed in Figure 20 and Figure 23. In addition, these particles are in the same size range as that observed for the wax particles in Figure 22. The presence of the wax particles on the treated surface indicates that there exists an interaction between the poly(acrylic acid) and the ethoxylate groups of the wax emulsion surfactant (possibly hydrogen bonding) such that the wax particles become attached to the melamine surface and cause particle sedimentation.

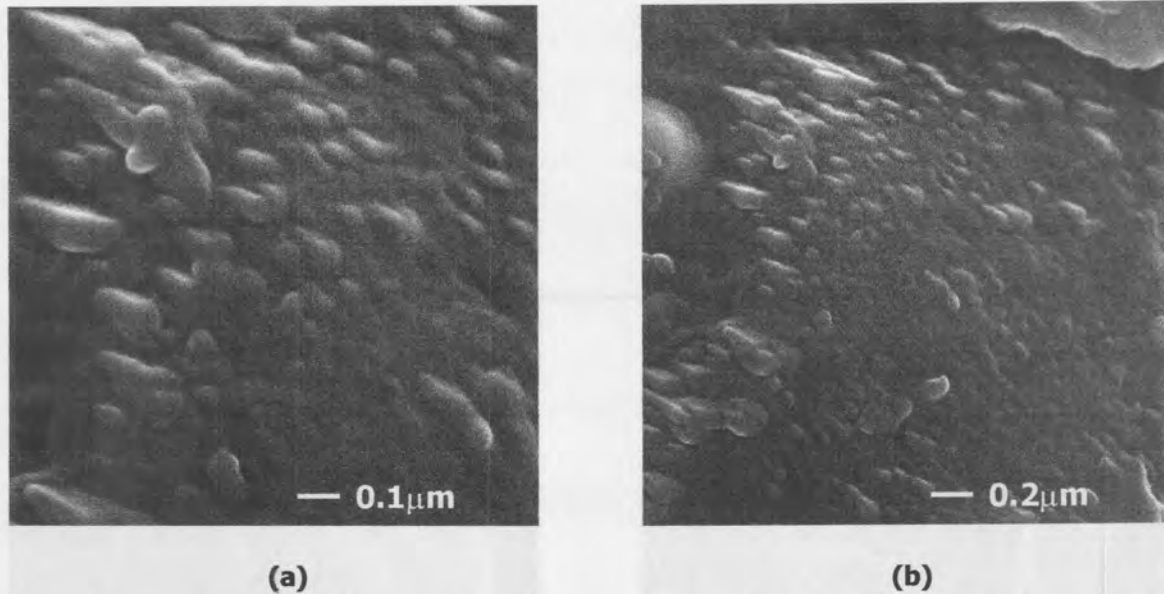


Figure 24 (a), (b): Surface of melamine particle treated with poly(acrylic acid) and subsequently micro-mixed with wax emulsion. Wax particles on melamine particle surface.

Figure 25 (a) and (b) shows an area of a treated melamine particle surface with no observable wax particles. However, on comparison of Figure 23 (a) and (b) with Figure 25 (a) and (b), the melamine surface shows distinct differences with respect to surface texture. The "humps" observed in Figure 23 (a) and (b) are not discernable in Figure 25 (a) and (b). This is possibly attributable to the interaction of free alkyl phenol ethoxylate surfactant found in the matrix of continuous phase as was observed in Figure 22 (a) and (b). The interaction of the poly(acrylic acid) treated melamine with the matrix film results in a change in melamine particle surface texture.

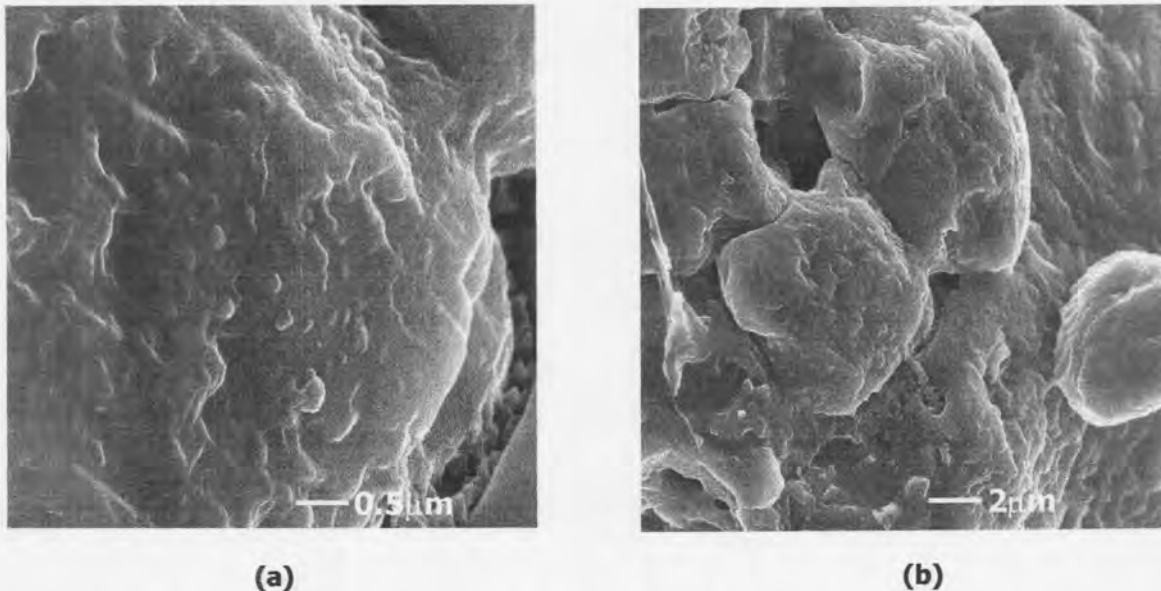


Figure 25 (a), (b): Surface of melamine particle treated with poly(acrylic acid) and subsequently micro-mixed with wax emulsion showing a change in surface texture of the melamine particle attributable to the continuous phase in the wax emulsion.

From the discussion above, although an interaction is evident from the SEM analysis it cannot as such be called particle micro-mixing. Due to the considerable difference in particle size between the melamine and wax particles, the phenomenon will be referred to as particle coating.

In addition to the analysis carried out by using SEM, it was attempted to determine the effect of increasing the poly(acrylic acid) dispersant on the amount of wax that would interact. Upon mixing of the melamine dispersion and the wax emulsion, the melamine particles almost immediately started to precipitate out and after centrifuging the dispersion the supernatant was removed. After drying the supernatant, it was weighed and used to determine the amount of wax particles that did interact with the melamine particles. It was assumed that no melamine was present in the supernatant after centrifuging.

The graph below (Figure 26) shows the amount of wax in grams that interacted with the melamine particles, based on 30% solids in the original wax emulsion (Atebin A1 Micro), relative to the poly(acrylic acid) dispersant : melamine ratio. The amount of wax that interacted decreases towards a minimum at approximately 8% poly(acrylic acid) dispersant : melamine ratio. A stability bar is included to show the amount of poly(acrylic acid) that is required to stabilise the melamine without the presence of the

wax emulsion for comparison purposes, i.e. the results shown in Table 11. It has been included as it is possible that the wax interaction can be explained relative to the degree of stability of the melamine particles in the dispersion.

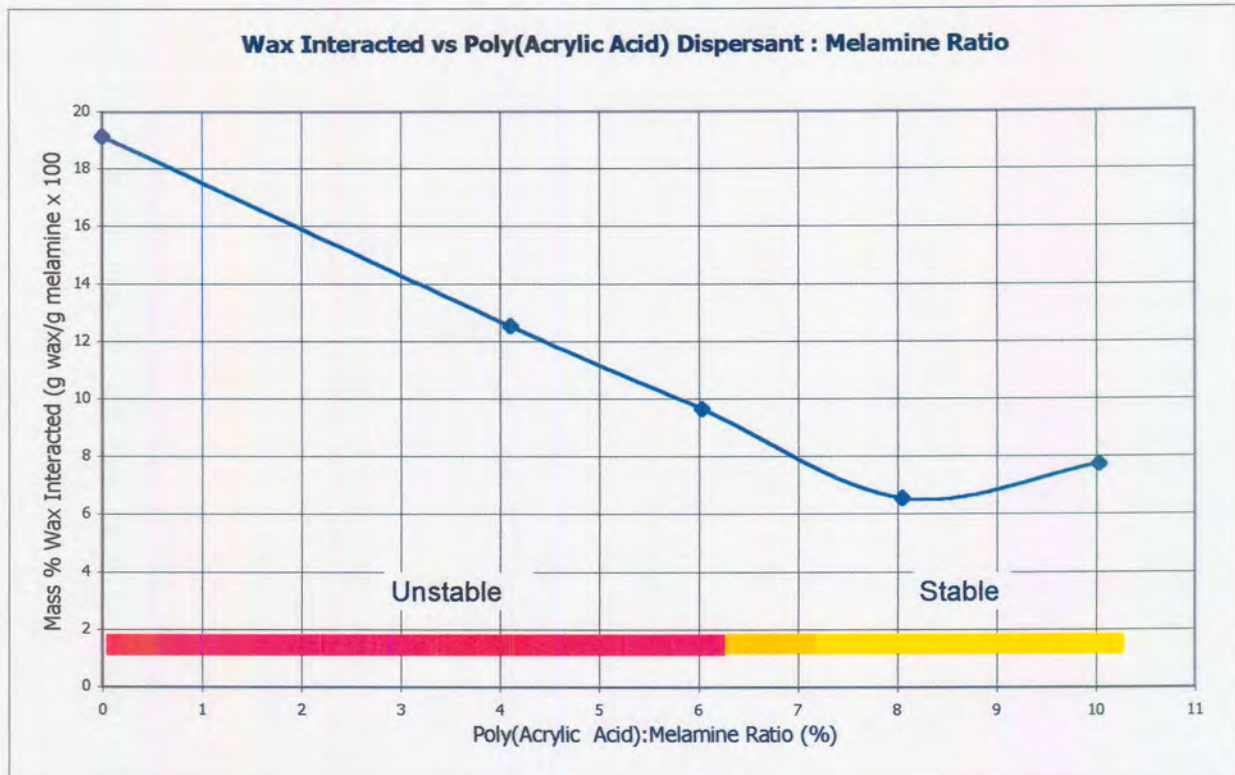


Figure 26: Wax residue vs poly(acrylic acid) : melamine ratio showing an decrease in wax interacted up to 8% poly(acrylic acid) : melamine ratio, above which the interaction seems to increase. A stability bar is included to show the amount of poly(acrylic acid) that is required to stabilise the melamine without the presence of the wax emulsion.

The decrease in the wax interaction was rather a surprise to the author, as it was expected that with an increase in poly(acrylic acid) content more ethylene oxide stabilised wax particles would interact with the poly(acrylic acid). Noting that our micro-mixing basis was 1:1 wax : melamine based on volume, this means that on a surface area basis there is an excess of wax particles, since smaller particles have a higher surface area to volume area.

A possible explanation in the decrease in wax interacted could be attributed to the occlusion of wax particles amongst the melamine particles. The control experiment, i.e. 0% poly(acrylic acid) : melamine ratio, showed the highest wax interaction

although there was no poly(acrylic acid) to interact with. Since the melamine particles are not stabilised they may be present in the form of small flocs, which trap the wax particles in the available spaces between the particles.

With an increase in the poly(acrylic acid) the melamine particles begin to become dispersed and therefore start moving further apart and subsequently trap fewer wax particles in the spaces available. This occurs in the area of the red stability bar in Figure 26, where most of the poly(acrylic acid) is used to coat the melamine surface and thus assist to stabilise the dispersion. Fewer wax particles become occluded in the melamine inter-particle spaces and therefore more remain suspended in the supernatant. This is not to say however, that no hydrogen bond interaction occurred between the ethylene oxide and poly(acrylic acid) since from the SEM analysis, wax particles were observed on the melamine surface. However, due to the excess of wax present there were wax particles available to become occluded.

Above a poly(acrylic acid) content of 8% relative to the melamine, i.e. the yellow stability bar in Figure 26, the poly(acrylic acid) has managed to act in such a way as to stabilise the melamine particles and it seems as though the wax interaction is beginning to increase. It is understood that in this region, since the melamine dispersion has been stabilised by the dispersant, wax particles are no longer able to become occluded and therefore a rise in the amount of wax that interacts with the poly(acrylic acid) may be observed at a higher poly(acrylic acid) content, i.e. above 8% poly(acrylic acid) dispersant : melamine (mass basis).

5. Conclusions and Recommendations

Low molecular mass polystyrene macroinitiators were successfully synthesised. The use of ATRP allowed for the synthesis of the low molecular mass macroinitiators with low polydispersity indices. SEC and MALDI-TOF MS analyses gave results that compared well with each other. ¹H-NMR confirmed the preparation of the polystyrene macroinitiators with spectrum peaks corresponding well with the structure of the polystyrene macroinitiators.

Due to the successful synthesis of the polystyrene macroinitiators, their use in the synthesis of the poly(styrene-co-t-butyl acrylate) block copolymer synthesis was reliable. Although some of the polydispersities obtained showed some deviation from the ideal value of 1, the molecular masses and polydispersities were acceptable for the micro-mixing purposes. Again the SEC and MALDI-TOF MS molecular mass analyses compared well with each other. In addition, the ¹H-NMR spectra of the block copolymers showing the dominant peak at 1.4ppm due to the t-butyl group, and the characteristic benzene peaks between 6.5 and 7.3ppm, confirmed the synthesis of the block copolymers.

Hydrolysis of the poly(t-butyl acrylate) block did not prove successful in the presence of HCl or NaOH, since the prominent t-butyl-group peak at 1.4ppm was still present. Hydrolysis in the presence of TFA was however successful in producing the amphiphilic poly(styrene-co-acrylic acid) block copolymer.

The amphiphilic block copolymer synthesised could not be used to emulsion polymerise styrene, since the block copolymer is not as water soluble as its ionised counterpart. The necessity to substitute the polystyrene emulsion gave rise to a poly(acrylic acid) stabilised melamine dispersion, which resulted in a stable dispersion with a poly(acrylic acid) : melamine ration of 8% based on mass.

In addition, the attempted wax emulsions using PEO containing surfactants were not successful as the emulsions were not stable and the particles formed were not uniform in shape or size. A commercially available wax emulsion allowed for the investigation of the poly(acrylic acid) – polyethylene oxide surfactant interaction. Subsequently

upon mixing of the poly(acrylic acid) melamine dispersion and the poly(ethylene oxide) stabilised wax emulsion, wax particles were found to adhere to the melamine particles. Since this phenomenon was not observed in the melamine dispersion not stabilised by poly(acrylic acid) it is fair to conclude that the phenomenon observed can be attributed to the interaction (hydrogen bonding) between the poly(acrylic acid) dispersant and the poly(ethylene oxide) containing surfactant.

The amount of wax particles that interact with the melamine seemed to decrease with an increase in the amount of poly(acrylic acid) dispersant used. This was contrary to what was expected, but can be attributed to the occlusion of wax particles between the melamine particles during the unstable dispersion phase of the melamine particles. As the melamine dispersion becomes more stable with the addition of poly(acrylic acid) dispersant, the amount of wax occluded decreases. It was observed that above 8% poly(acrylic acid) dispersant relative to melamine on a mass basis, the amount of wax interacted seemed to increase. It was postulated that this increase occurs once the melamine dispersion was stabilised and therefore more surface interaction between the wax and melamine is permitted. It is therefore recommended to investigate as to whether this increase continues past 8% poly(acrylic acid) : melamine ratio.

The micro-mixing observation could be applicable to other systems. However, each system is individual in nature with respect to the type of particles, size of particles and type of interacting surfactants used. Therefore a degree of refinement is required for each application in order to determine the ideal combination of the abovementioned factors. More accurate analytical techniques need to be made use of to quantify the phenomena observed in this investigation. In addition, although amphiphilic block copolymers were synthesised, their specific application in particle micro-mixing was not investigated. It is therefore recommended to investigate the possibilities of applying amphiphilic block copolymers, in conditions of micro-mixing.

6. References

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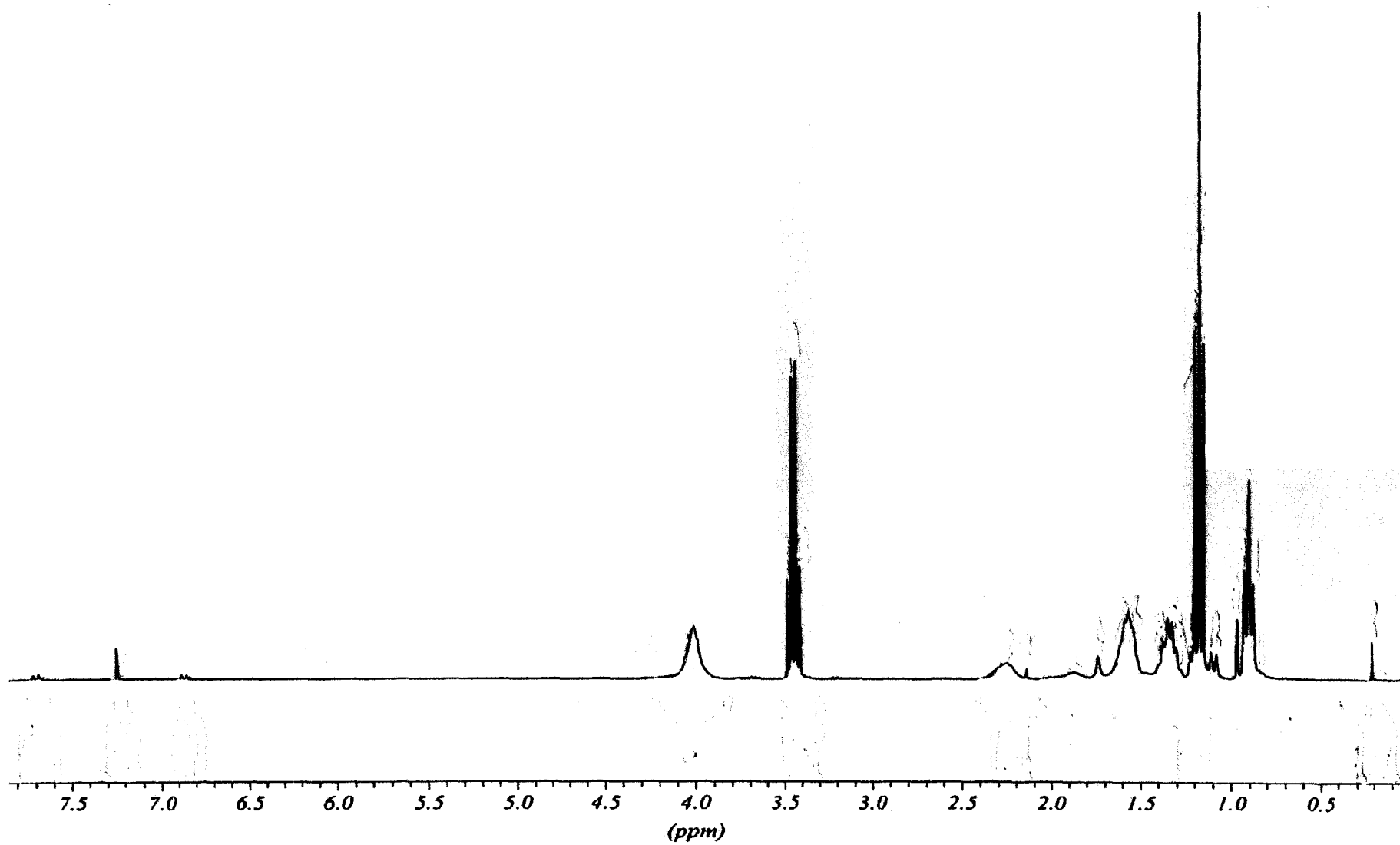


Appendix 1

Atebin A1 Micro Datasheet

Appendix 2

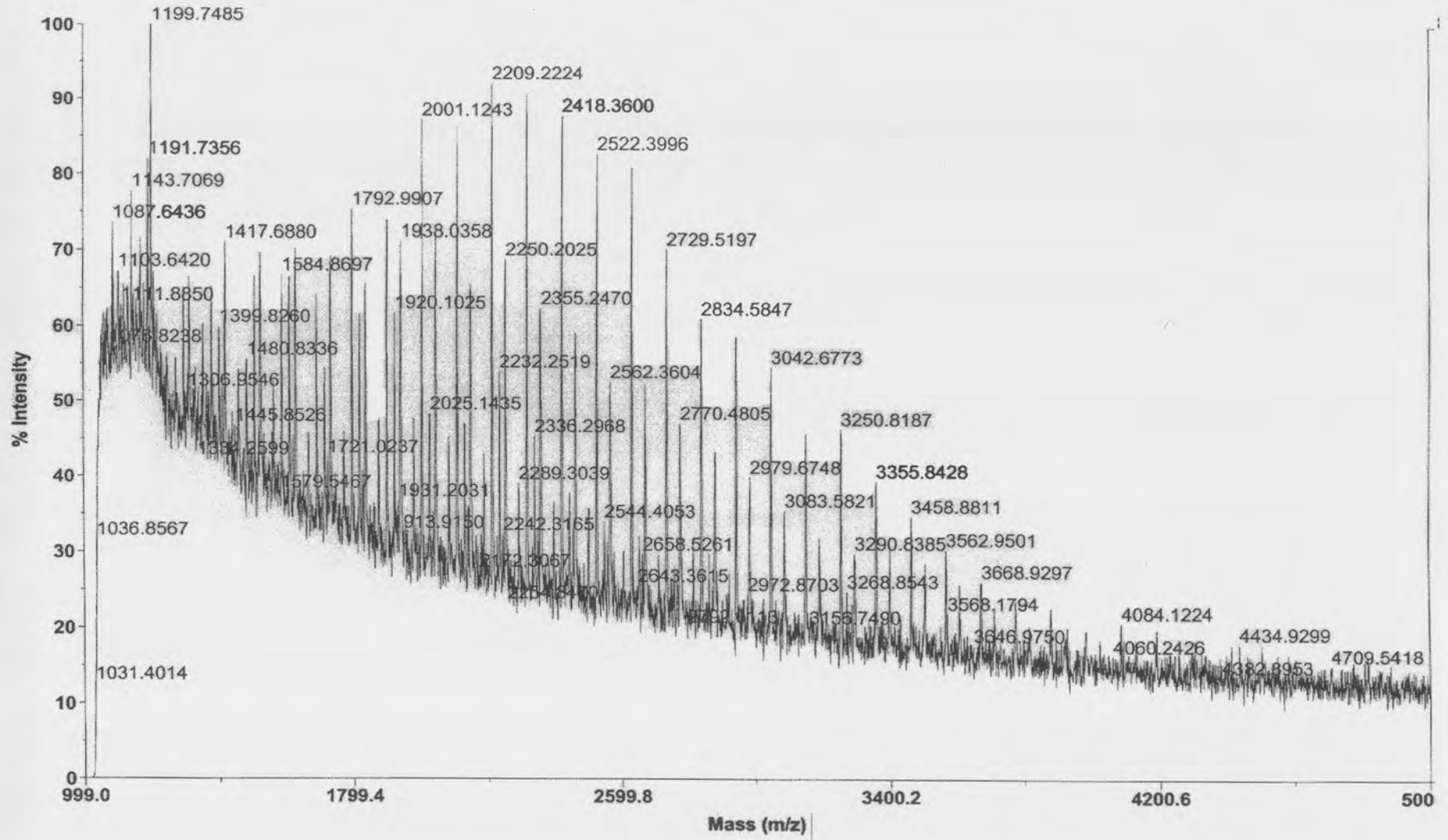
$^1\text{H-NMR}$ spectrum of poly(*t*-butyl acrylate) macroinitiator



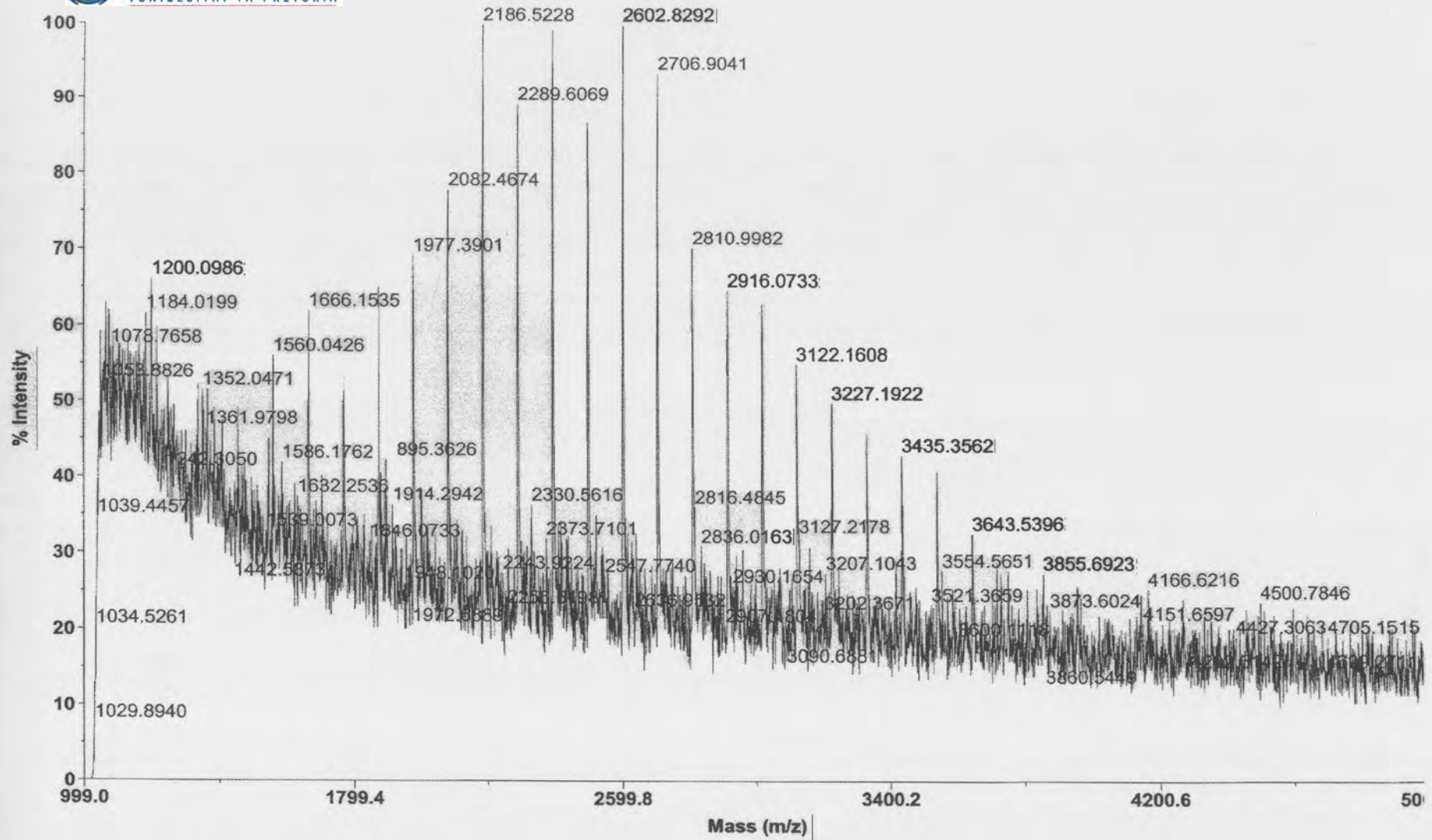
^1H -NMR spectrum of the poly(t-butyl acrylate) macroinitiator 1P(tBA)A

Appendix 3

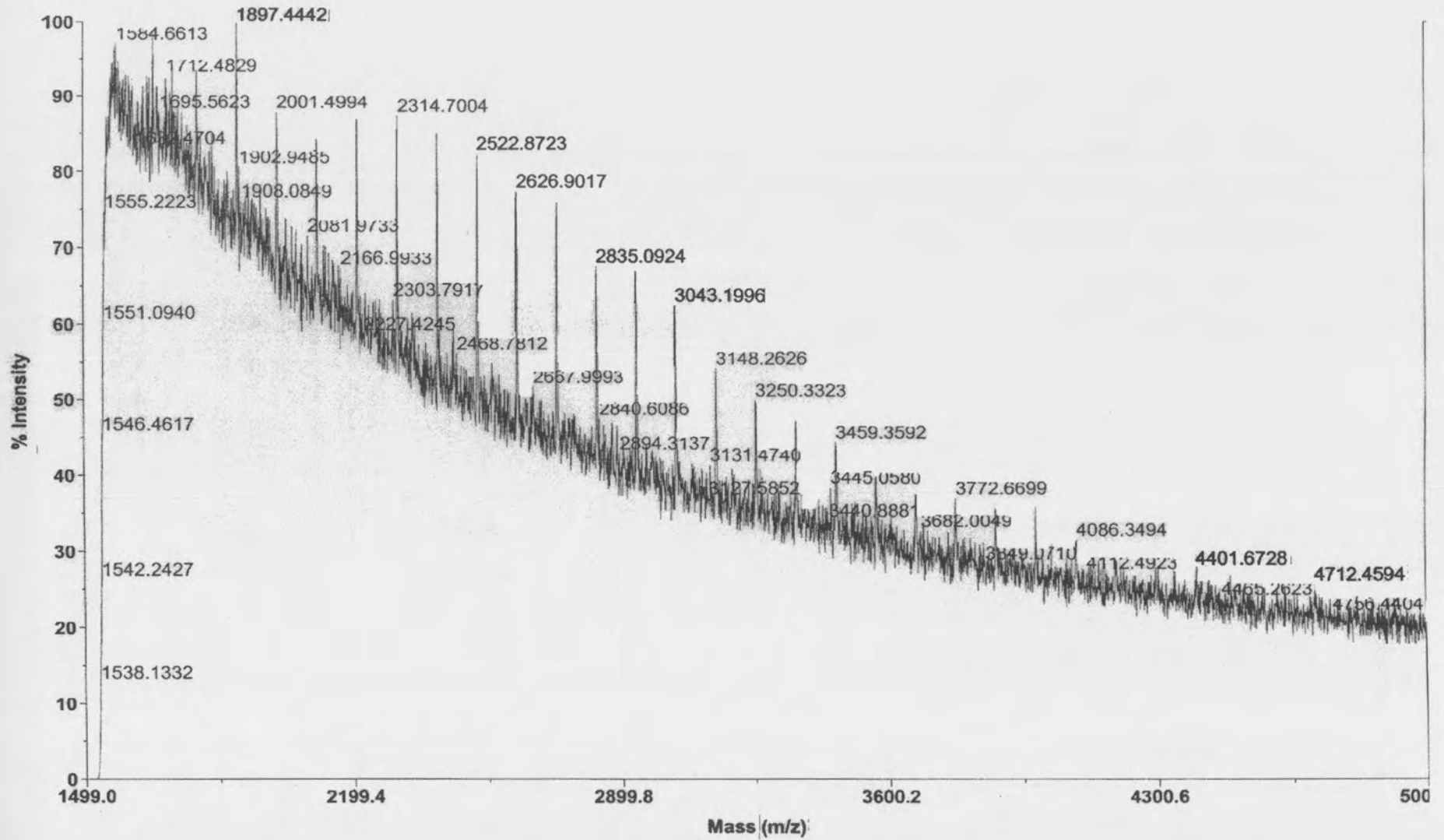
MALDI-TOF MS spectra of the polystyrene macroinitiators



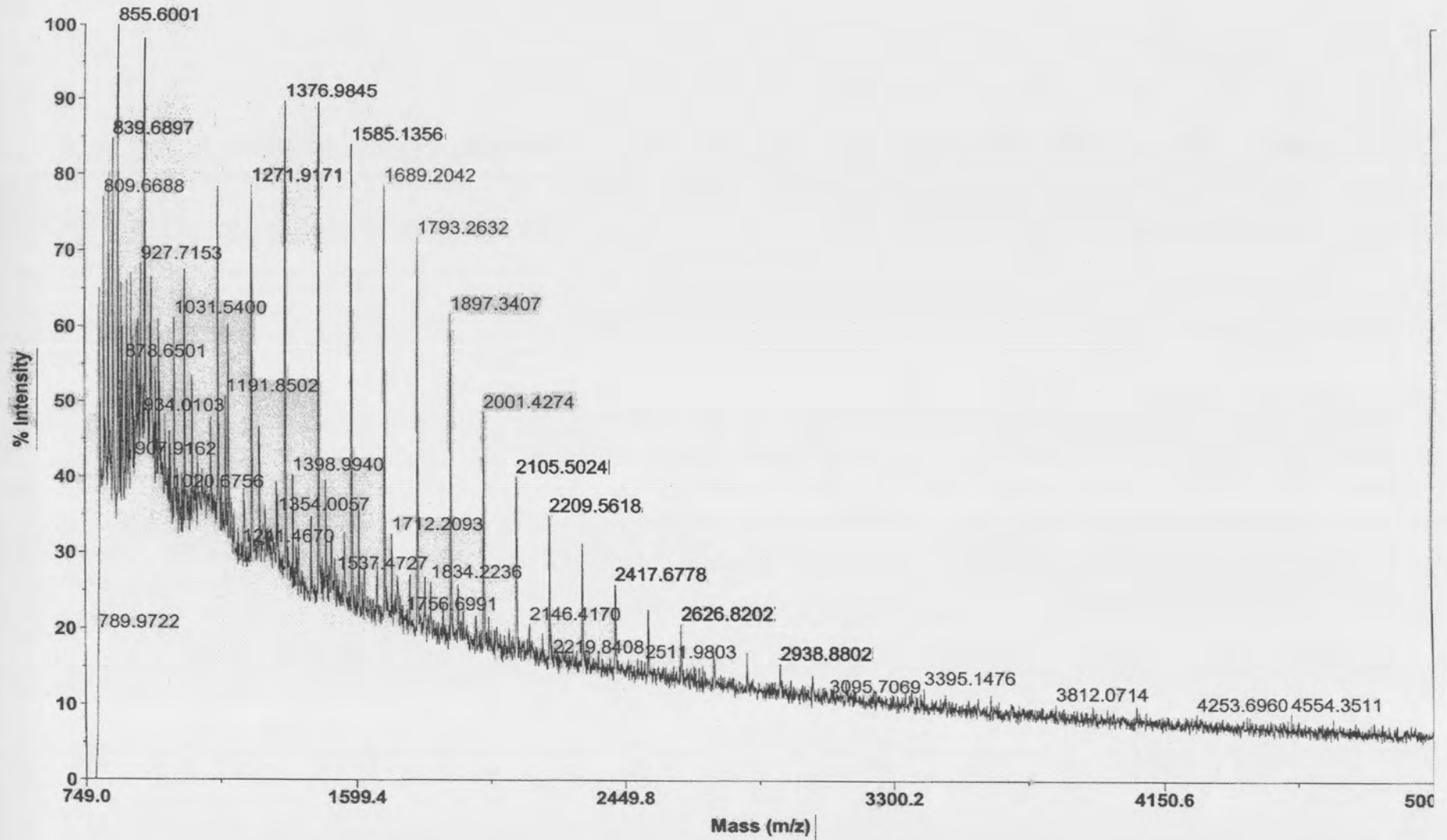
MALDI-TOF MS spectrum of the polystyrene macroinitiator 1PStA



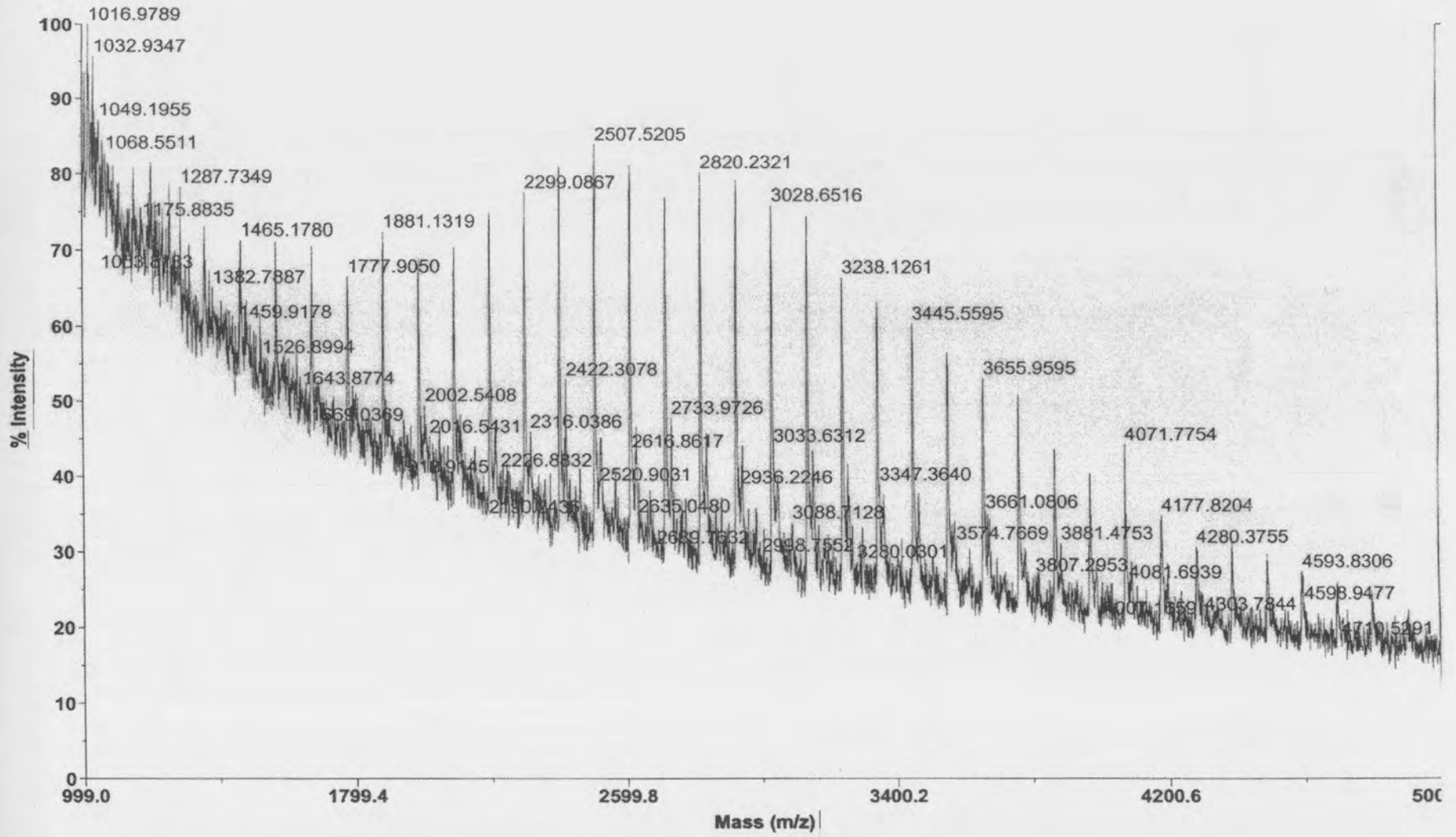
MALDI-TOF MS spectrum of the polystyrene macroinitiator 1PStB



MALDI-TOF MS spectrum of the polystyrene macroinitiator 1PStD



MALDI-TOF MS spectrum of the polystyrene macroinitiator 1PStE

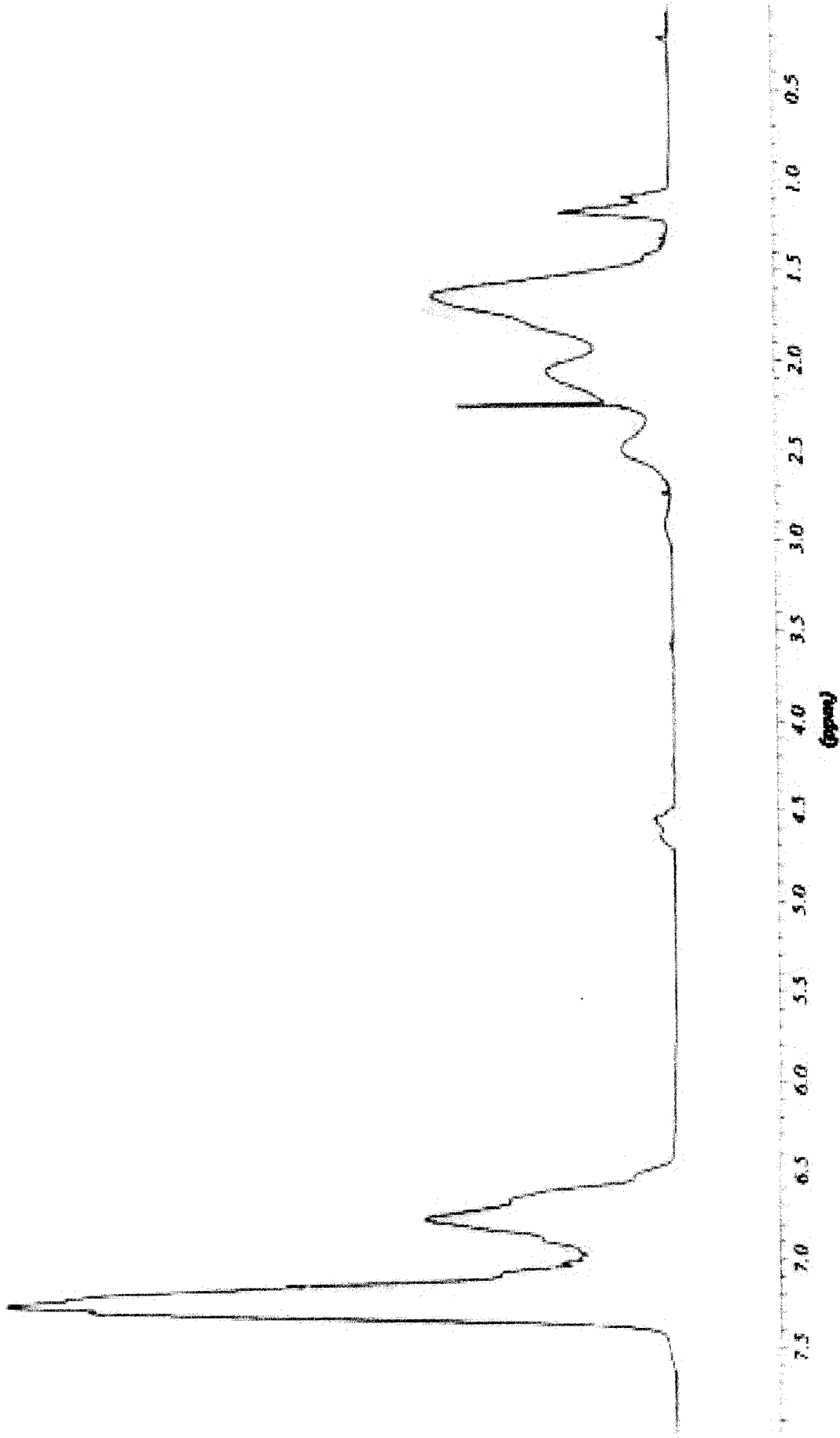


MALDI-TOF MS spectrum of the polystyrene macroinitiator 1PStF

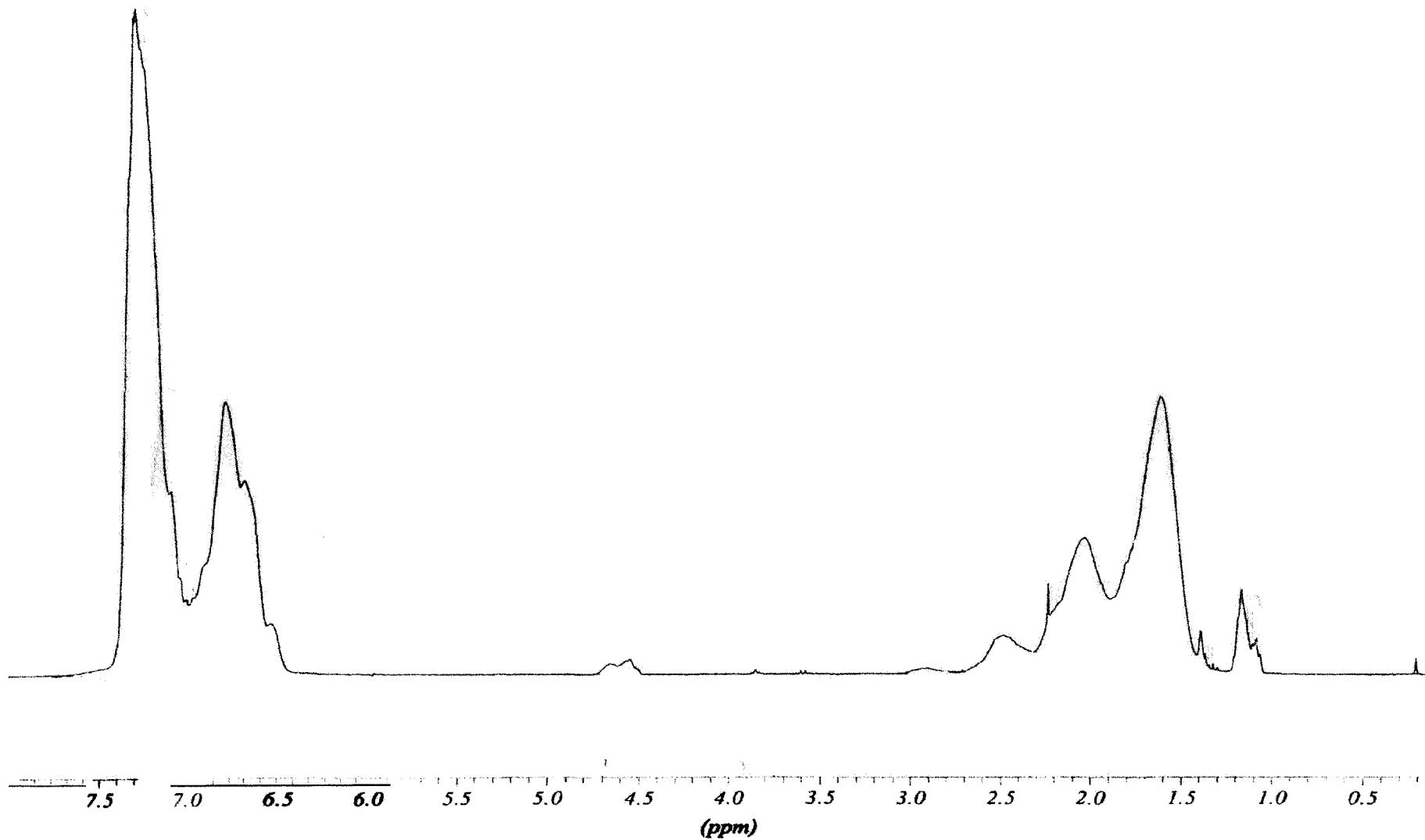


Appendix 4

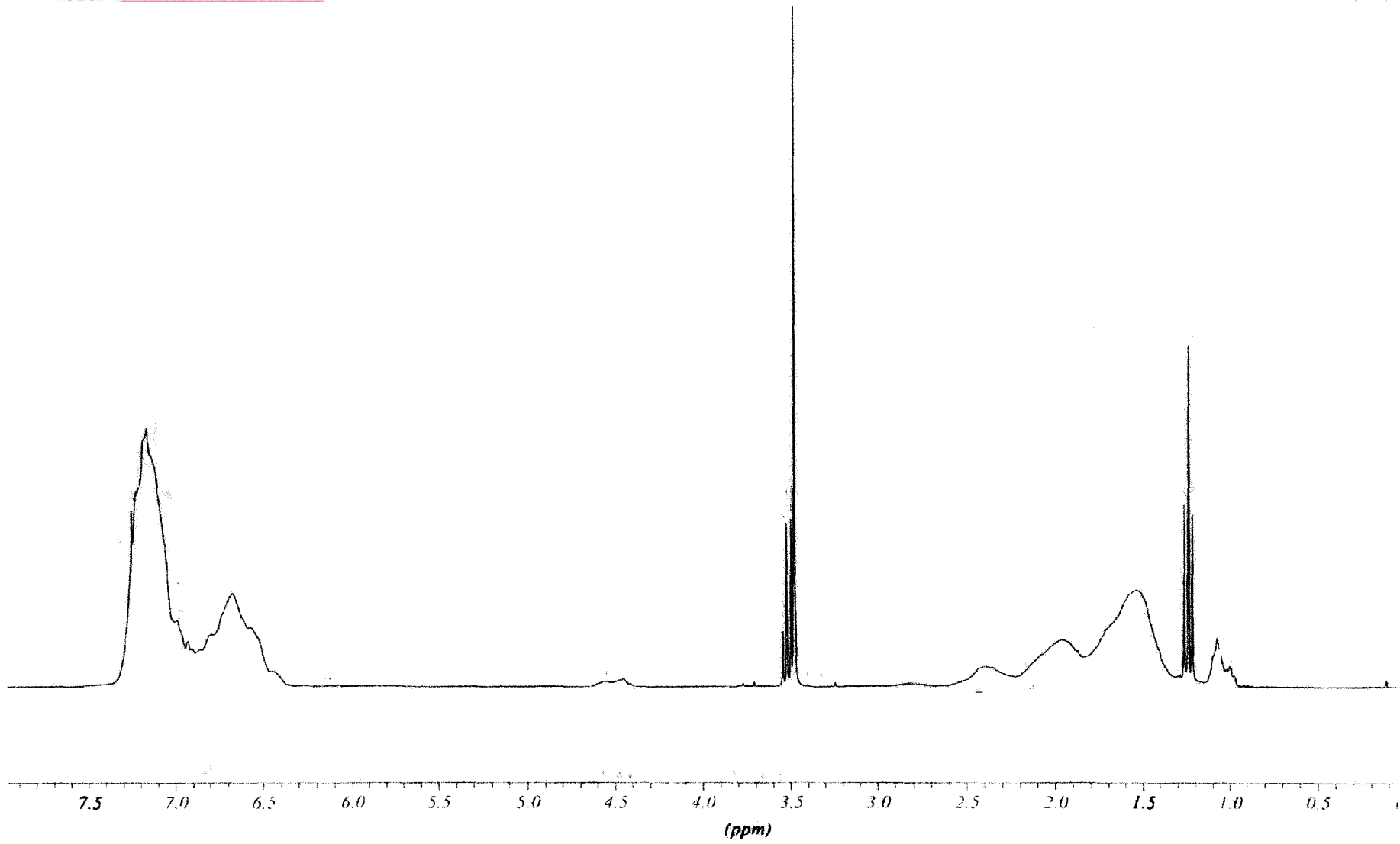
^1H -NMR spectra of polystyrene macroinitiators



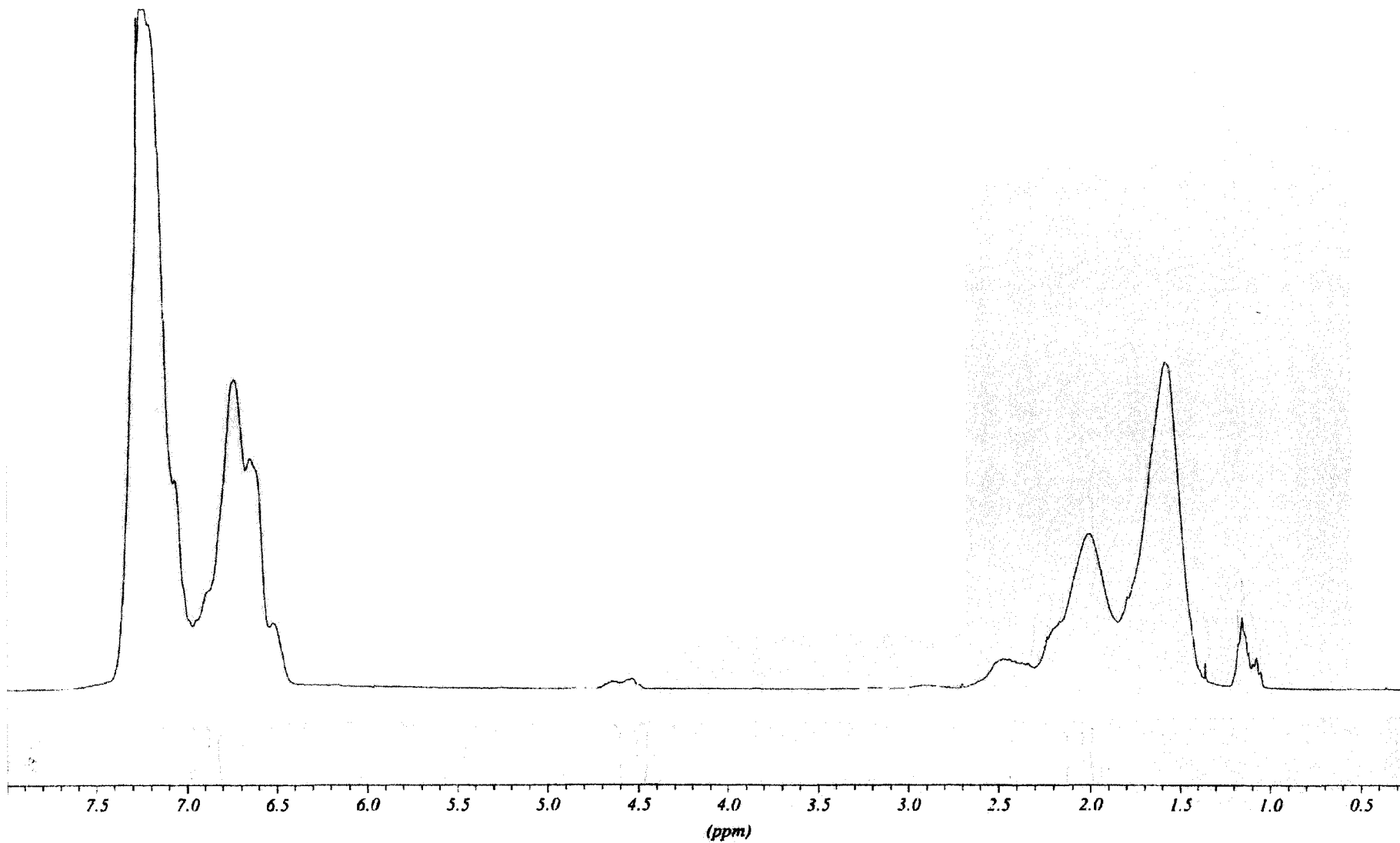
¹H-NMR spectrum of the poly(styrene) macroinitiator 1PSC



^1H -NMR spectrum of the poly(styrene) macroinitiator 1PSD



$^1\text{H-NMR}$ spectrum of the poly(styrene) macroinitiator 1PSE

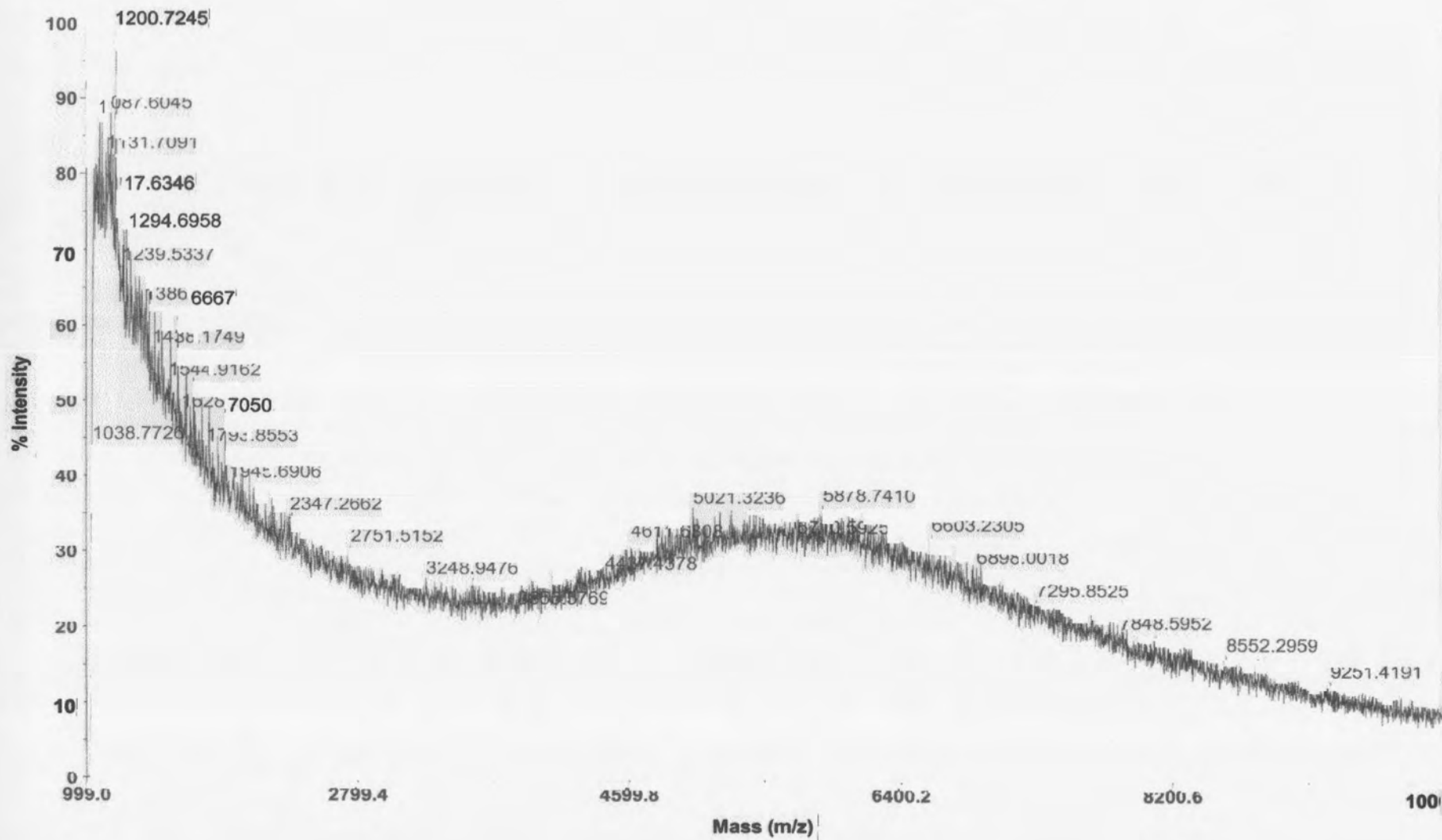


¹H-NMR spectrum of the poly(styrene) macroinitiator 1PSF

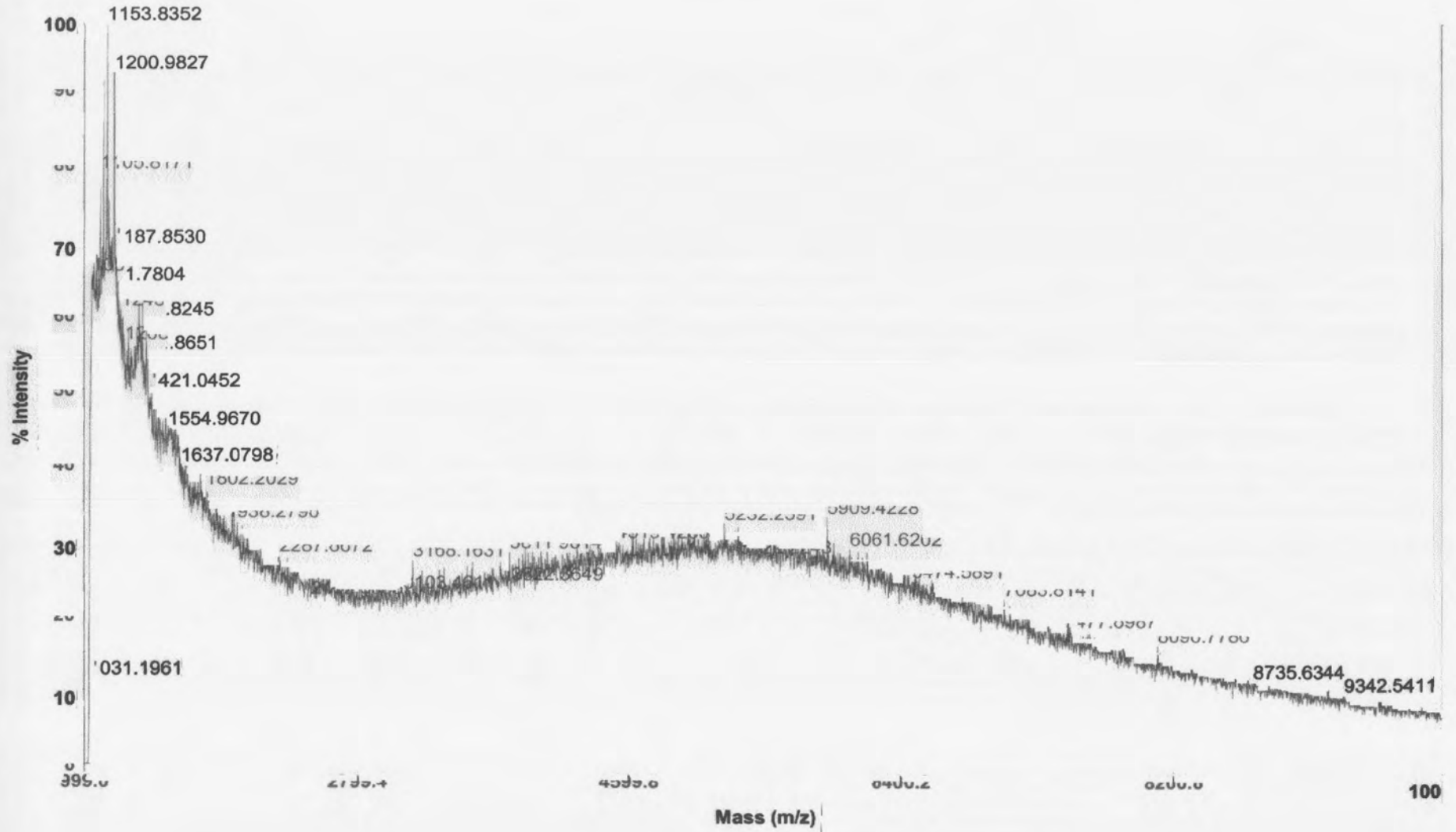


Appendix 5

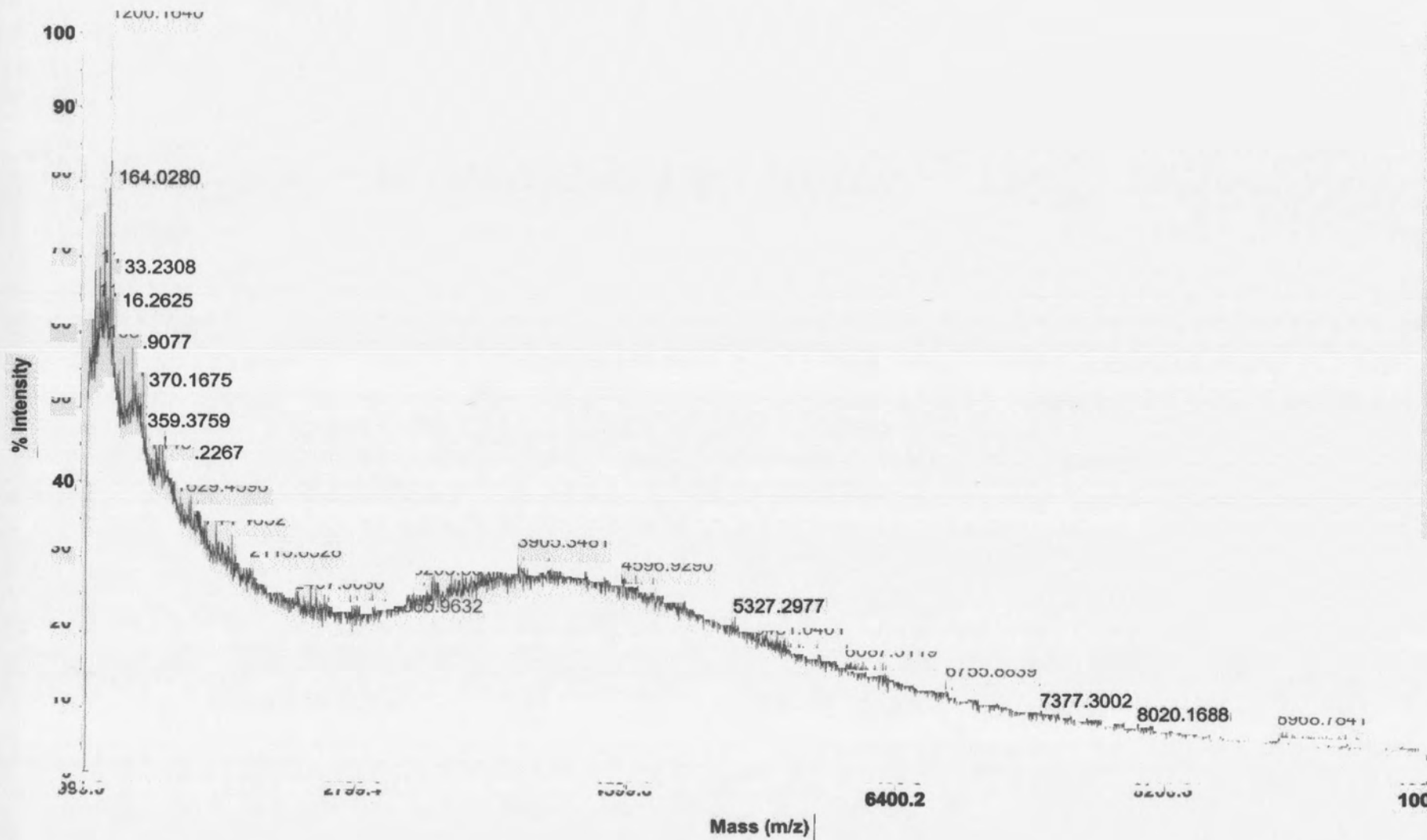
MALDI-TOF MS spectra of poly(styrene-co-t-butyl acrylate) block copolymers



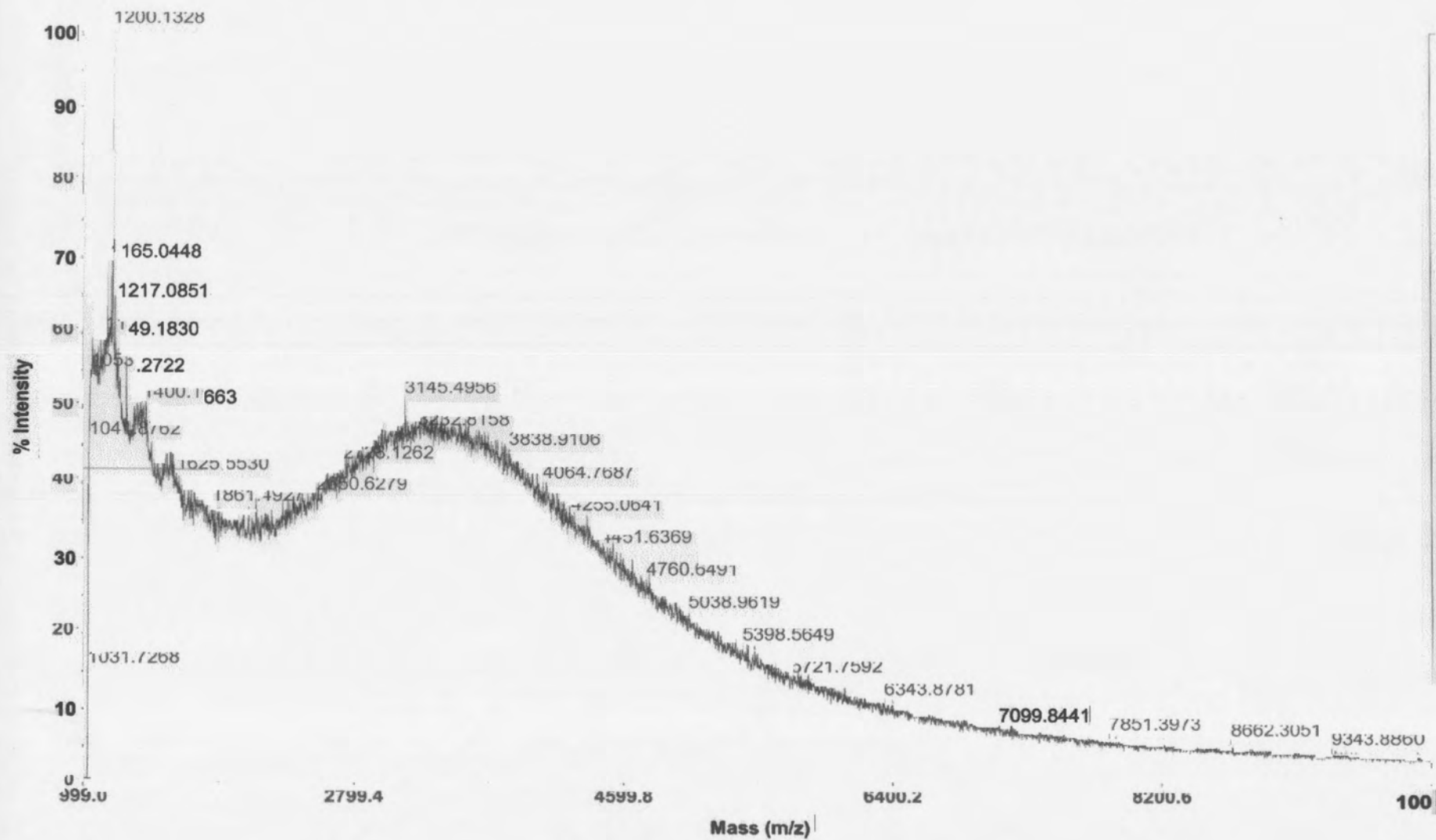
MALDI-TOF MS spectrum of the poly(styrene-co-t-butyl acrylate) block copolymer 1PS-P(tBA)A



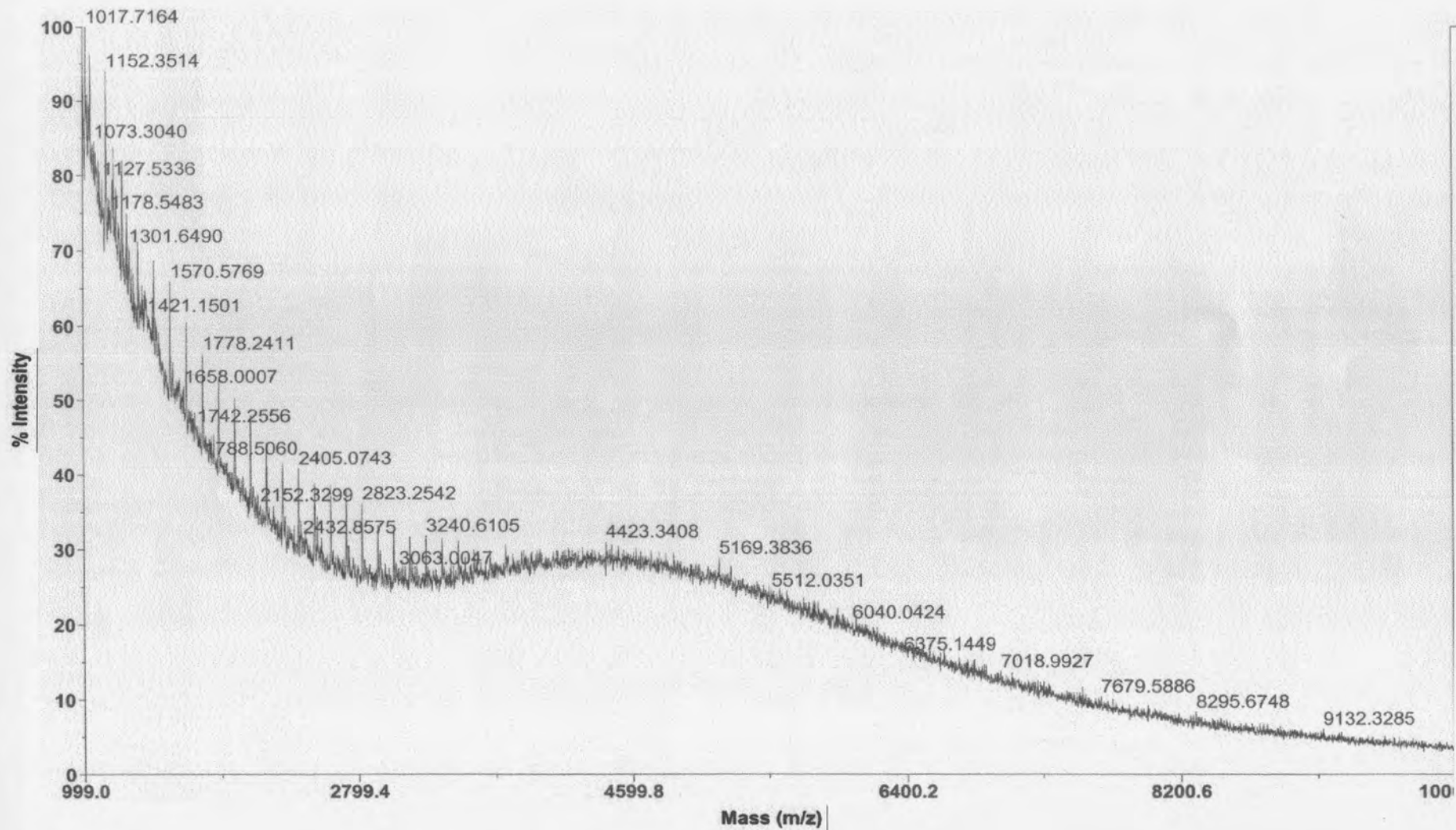
MALDI-TOF MS spectrum of the poly(styrene-co-t-butyl acrylate) block copolymer 1PS-P(tBA)B



MALDI-TOF MS spectrum of the poly(styrene-co-t-butyl acrylate) block copolymer 1PS-P(tBA)D



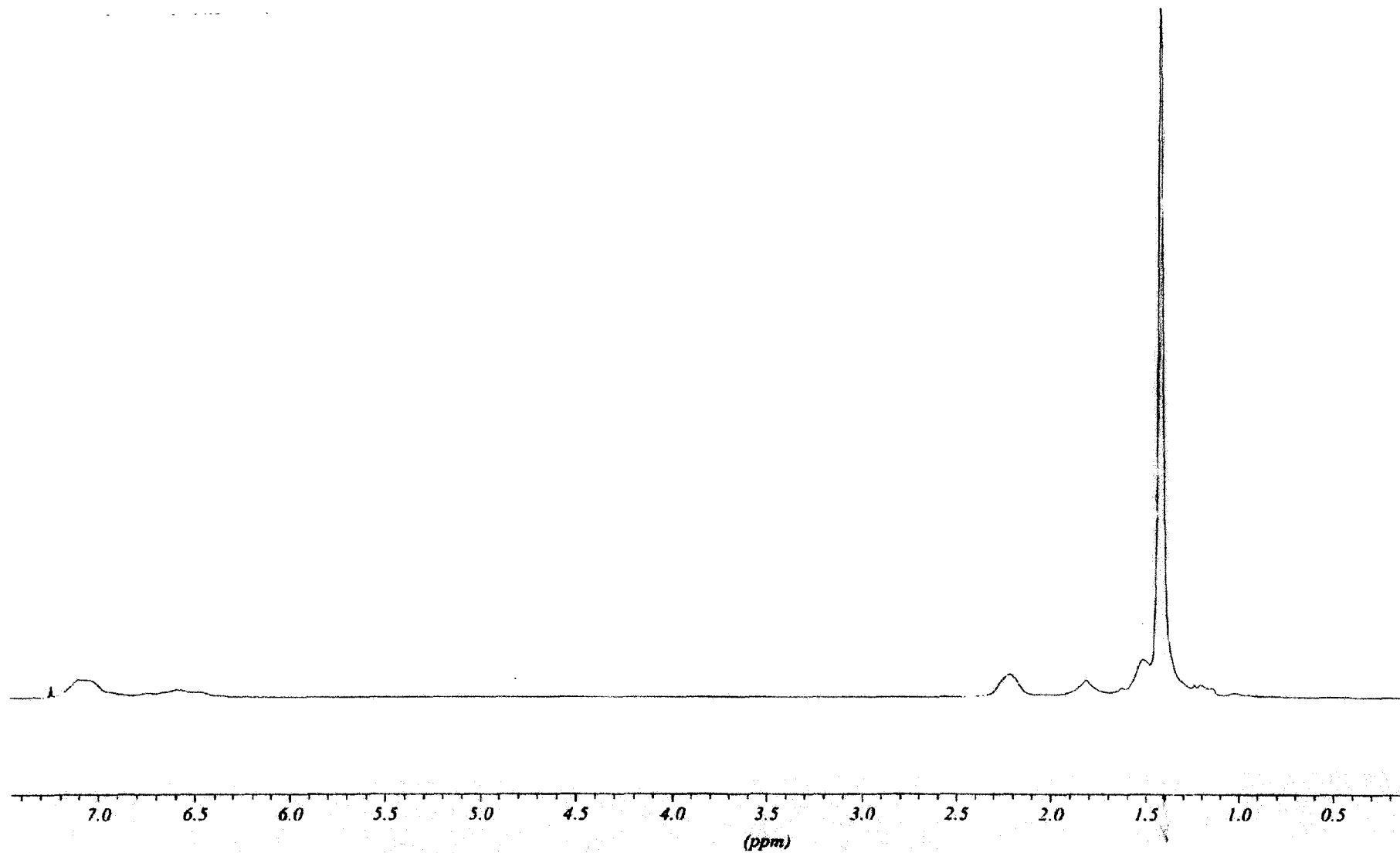
MALDI-TOF MS spectrum of the poly(styrene-co-t-butyl acrylate) block copolymer 1PS-P(tBA)E



MALDI-TOF MS spectrum of the poly(styrene-co-t-butyl acrylate) block copolymer 1PS-P(tBA)F

Appendix 6

¹H-NMR spectra of poly(styrene-co-t-butyl acrylate) block copolymers



$^1\text{H-NMR}$ spectrum of the poly(styrene-co-t-butyl acrylate) block copolymer 1PS-P(tBA)C