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Rheological Studies Of Non-Aqueous Poly Methyl Methacrylate Dispersions Stabilised Using Graft Copolymer Steric Stabilisers.

A thesis submitted to Loughborough University for the degree of Doctor of Philosophy in the Faculty of Science.

Matthew John Savage

1998

Department of Chemistry
Abstract.

Steric stabilisers were synthesised via the copolymerisation of styrene with acrylic macromonomers. The macromonomers were prepared by end capping reactions of poly 2-ethyl hexyl acrylate (PEHA) prepolymer with vinyl containing species. Preliminary reaction routes proceeded via the use of oxalyl chloride to create an acyl chloride intermediate followed by end capping with hydroxy ethyl methacrylate. This process was found to be inefficient due to the moisture sensitivity of the acyl chloride. The second route involved the direct end capping of the PEHA pre-polymer with glycidyl methacrylate (GMA). Macromonomer conversion levels were improved for the GMA route via the use of high temperatures and tertiary amine catalysts. An optimum set of conditions was achieved using 1.4 diazabicyclo [2.2.2.] octane as the catalyst and a reaction temperature of 160 °C.

Non aqueous dispersion polymerisations of methyl methacrylate were performed. The factors affecting particle size in both single stage and twin stage polymerisation schemes were studied. Increases in the particle sizes of these dispersions were observed with increases in the total monomer concentration and also with decreases in the total stabiliser concentration. Increases in the particle size could also be achieved by increasing the proportion of the total monomer in the seed stage of the twin stage reaction and also by decreasing the proportion of the total stabiliser in the seed stage. The importance of the role of the seed upon the final particle size was firmly established.
The rheology of these non aqueous dispersions was studied over a range of concentrations and under increasing shear stresses. At low and intermediate volume fractions the dispersions were observed to be predominantly Newtonian. Non-Newtonian behaviour was only observed at the extremes of the shear stress ranges studied. At high volume fractions of the dispersions non-Newtonian behaviour was observed over the range of shear stresses studied.

Maximum volume fractions ($\phi_m$) were calculated for these dispersions using the Kreiger-Dougherty equation. When these dispersions were blended in size ratios of 2:1 it was observed that $\phi_m$ could be increased due to improved particle packing efficiency.
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Chapter 1.

Introduction
1. Introduction.

European legislation aimed at reducing the toxicity and environmental impact of many commercial polymeric products, by lowering the "maximum safe limits" of volatile organic compounds (VOC), is expected to come into force in a few years. For many polymeric products this has resulted in a move away from the use of common organic solvents, e.g. hexane, chloroform and acetone, and a resurgence in the development of aqueous based products.

There are, however, many cases where an aqueous system is not suitable or indeed simply cannot be used. An example of this is the casting of a polymer into a thin film, i.e. a layer of paint, in a cold climate. In this case the water would not evaporate at a sufficient rate (or even at all!) and, therefore, a good homogeneous film would not be achievable. In these situations it is necessary to use a non-aqueous system.

Most current formulations will exceed the impending regulations for VOC content and so reformulation will be required. The simplest way to reduce the VOC content is to lower the quantity of the solvent used. Work carried out by Chong (1), Robinson (2), Williams (3) and also by Sweeny and Geckler (4) showed that at polymer particle concentrations of approximately 60% v/v the relative viscosity of the dispersion approaches infinity. This was observed to be independent of polymer particle size for monodisperse particle size distributions. If an element of polydispersity is introduced to the dispersion, then Farris (5) observed that this limiting concentration before infinite relative
viscosity is reached can be raised to $80 \rightarrow 90\%$ v/v. This work has so far only been performed on blended multimodal particle distributions, i.e. samples of monodisperse polymer particles of differing particle size which have been mixed together and the excess solvent removed. A better solution would be to be able to produce, through the use of seeded polymerisations and feeding profiles, a method which allows the synthesis of well defined multimodal non-aqueous polymer particle dispersions. Before this can be achieved it is essential that the process of non-aqueous dispersion polymerisation and steric stabilisation is further studied and a better understanding gained.

1.1 Theory Of Steric Stabilisation.

The ability to prepare a stable dispersion of particles requires a balance between van der Waals attractive forces and repulsive forces to be achieved. If the van der Waals forces are dominant, then gross flocculation of the particles will occur; this is often observed by the existence of “raspberry-like” particles. If the repulsive forces are highly dominant, then it may prove difficult to achieve anything more than a dilute dispersion of particles as the minimum inter-particle distance is greater and thus the particle packing density is lower than in the case when the repulsive/attractive forces are more closely balanced.

The attractive van der Waals forces acting upon the particles can be classified in three ways:-

a) Mutually orientating permanent dipoles i.e. charged species.

b) Induced dipoles between dipolar and non-polar species.
c) Transient dipoles between non-polar species.

London \(^{(6,7)}\) when working with gaseous atoms suggested that if the Heisenberg uncertainty principle was applied to the electron cloud of an atom (or molecule), then it would be plausible to expect to observe short lived dipoles. These dipoles were termed transient dipoles. It then follows that these transient dipoles would be capable of causing spatial orientation between species and therefore attraction between the species.

In general, the stabilising polymers used in non-aqueous dispersion polymerisations, such as n-alkyl acrylates, do not exhibit a dipole and so the attraction must be considered to be a result of the London attractive forces or London dispersive forces. London went on to show, by deriving Equation 1.1.a, that these attractive forces only act over a short range

\[
V_A \propto r^{-6}
\]  

Equation 1.1.a

where

- \(V_A\) is the potential energy of the attraction,
- \(r\) is the separation of particles.

The rapidly decreasing potential energy, of the interaction between two particles, with separation means that the interactions can be considered to act "pair wise". This means that total attractive forces may be calculated via the summation, over all species present, of the pair wise interaction of two particles. Initial calculations by Hamaker \(^{(8)}\) were overestimated as the time required to propagate the transient dipolar interaction was neglected. Overbeek and Vervey \(^{(9)}\)
incorporated this propagation time and achieved reasonably accurate results for small particles, i.e. atoms/small molecules, in a vacuum. Lifshitz (10, 11) and more recently Ninham and Parzegian (12) have taken a more macroscopic approach to the problem of solvent-particle interactions; however, the calculations required for their methods are far too complex for general use.

It has already been mentioned that to obtain stable particles the attractive forces must be balanced out by repulsive forces. In the case of an aqueous based dispersion this repulsive force is created by covering the particles with a polar layer, e.g. by the use of ionic surfactants. This method has little application in non-aqueous systems as the solvents are seldom sufficiently polar to enable the particles to remain well dispersed. An analogous technique to electrostatic stabilisation can be used for non-aqueous systems. This technique is known as steric stabilisation. A schematic comparison between these two types of stabilisation is shown in Figure 1.1.

Steric stabilisation can be considered to be a combination of two effects:
1. An entropic factor.
2. An enthalpic factor or mixing factor.
These factors may be combined together in a simple thermodynamic equation (Equation 1.1.b)

\[ \Delta G = \Delta H - T \Delta S \]  

Equation 1.1.b

where:
\( \Delta G \) is the Gibbs free energy of the interaction,
\( \Delta H \) is the enthalpy change associated with the interaction,
Figure 1.1 A Schematic Diagram Comparing The Similarities Between Electrostatic Stabilisation (a) And Steric Stabilisation (b).
ΔS is the entropy change associated with the interaction,

T is the temperature at which the experiment is carried out.

If the free energy of the interaction is negative then flocculation of particles will occur. Thus, to achieve a stable dispersion of particles it is essential that either the enthalpy change is greater than the total entropic factor (TΔS) or that the entropy change is negative for the particle-particle interactions. As entropy is a measure of disorder, i.e. the greater the number of states of orientation an entity can possess the greater is its entropy, then it would be expected that as two particles interact then the number of orientations available to the pendant stabilising chains will be reduced and therefore the entropy will decrease. This suggests that the entropy change associated with two particles in a dispersion colliding would be negative, and thus the overall effect would lead to repulsion between the particles. However, one must also take into account how the mixing interactions can be negative and hence lead to the aggregation of the particles.

Both the mixing interactions and the entropic interactions need to be considered in greater depth to achieve a well grounded insight into the process of steric stabilisation.

1.1.1 Mixing Interactions Between Particles In Dispersion.

In 1958 Fischer (13) approached the problem of calculating the free energy of the mixing of the pendant polymer chains by assuming that the free energy of mixing of the pendant chains to be equivalent to the free energy of mixing for the same free chains in solution, i.e. the fact that the steric stabiliser is attached to the surface of a particle has little
or no effect on the free energy of mixing of steric stabilisers. From his calculations he was able to derive an equation (Equation 1.1.1. a) for free energy of mixing of stabilised particles.

\[ \Delta G_{\text{mix}} = A \cdot B \]  

Equation 1.1.1. a

where:

- \( \Delta G_{\text{mix}} \) is the free energy of the mixing of two sterically stabilised particles,
- A is a geometrical term,
- B is the second virial coefficient of the steric stabiliser.

The factor B is proportional to the polymer-solvent interaction parameter (the Flory-Huggins interaction parameter \( \chi \)) by equation 1.1.1. b.

\[ B \propto (0.5 - \chi) \]  

Equation 1.1.1. b

In a thermodynamically good solvent, the preferred interactions are solvent-polymer interactions. Hence, as the mixing of two polymer segments would lead to the displacement of solvent and thus to increased polymer-polymer interactions, then mixing would be a thermodynamically unfavourable event and hence repulsion would be expected to occur. In a thermodynamically poor solvent, the preferred interactions are polymer-polymer interactions. Thus, as the mixing of the two polymer chains would lead to an increase in the energetically preferred interactions, then mixing would be expected to occur and the particles to flocculate. In the case of a \( \Theta \) solvent where both the polymer-polymer and the solvent-polymer interactions are energetically equally favourable, then it would be expected that both attractive and repulsive forces would act on the particles upon mixing,
and therefore the free energy of mixing would be zero, i.e. the total free energy of the system would be controlled by entropic considerations. Therefore a stable dispersion would only be expected if the diluent was a thermodynamically good solvent for the stabilising segments of the steric stabiliser. Work by Napper \(^{14, 15}\) and also by Ottewill and Walker \(^{16}\) also derived similar expressions.

### 1.1.2 Entropic Interactions Between Particles In Dispersion.

As was discussed in Chapter 1.1 the repulsive forces acting upon sterically stabilised polymer particles largely arise from the reduction in the number of configurations that the stabilising chains can adopt as a pair of particles collide, i.e. a negative entropy change. In initial attempts to model this entropy change, Mackor \(^{17}\) considered the interaction between two rigid volumeless rods attached to solid particles via a freely rotating hinge. Due to the volumeless rod consideration, this model could only be applied to very low surface coverages as the interactions between neighbouring chains on the same particle were ignored. In collaboration with van der Waals, Mackor \(^{18}\) extended his initial theories to include rods of a finite volume which therefore meant his theories could be applied to particles with much greater surface coverages.

With the increasing availability of more and more powerful computers, Clayfield and Lumb \(^{19, 20}\) were able to introduce freely jointed stabilising chains, i.e. not rigid rods, in to the considerations and carry out *random flight* calculations using Monte Carlo computer simulations. In 1974 Clayfield and Lumb \(^{21, 22}\) included solvent
effects and also considered the chain configuration of random copolymers, i.e. differentiated between loops and tails (see Figure 1.2)

1.1.3 Combined Interactions Between Particles In Dispersion.

Although the mixing and entropic factors have been discussed as separate events they do occur coincidentally. Meier \(^{(23)}\) believed that the action of the two factors was additive and went on to develop a model based upon the Clayfield and Lumb random flight theories and interfacial adsorption. This work was adapted by Hesselink \textit{et al}\(^{(24)}\) to include considerations for loops resulting from the use of random copolymers. Both of these treatments of the overall free energy of two colloidal particles during collisions are inaccurate as they contain no allowances for the interdependent nature of the entropic and mixing interactions.

Many workers have produced more complex models of the interaction which effectively combine both of the thermodynamic factors in to a single configurational term. Dolan and Edwards \(^{(25)}\) approached the segmental interactions as an \textit{excluded volume effect} and thus were able to devise what was termed a \textit{self-consistent mean field theory}. Scheutjens and Fleer \(^{(26, 27, 28)}\) initially considered the scenario of a single surface which was characterised as being a lattice with each lattice site being filled by either a solvent molecule or a segment of polymer chain, (a segment of polymer chain is considered to be a portion of the polymer which is equivalent in volume to a molecule of solvent). They calculated the probability of a given configuration of polymer chain by applying what they called \textit{segmental weighting}
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Figure 1.2 A Schematic Diagram Showing How The Stabilising Chains Can Exist As Either Loops (a) Or Tails (b).
factors. It is these factors which incorporate both the entropic and enthalpic considerations of taking a polymer chain from the bulk solution and depositing it upon a surface. Using matrix calculations they were able to determine the probability of every possible configuration and thus describe the surface coverage and spatial orientation of the adsorbed polymer chains. Later \(^{29, 30}\) they introduced a second layer of coverage by polymer and recalculated the effect that this had upon the original spatial orientation of the polymers. It is this work that can be used to model the effect of two sterically stabilised polymer colloids during collision. This approach can be used to consider any polymer chain acting as a steric stabiliser in various environments, due to effects such as specific solvent-polymer interactions being incorporated into the general segmental weighting factor. De Gennes \(^{31}\) has developed a highly complex model by applying scaling theory to a dilute solution of overlapping polymer coils.

There is currently some debate as to which model is the most applicable to the behaviour of polymer particles in dispersion. The mean field theory of Scheutjens and Fleer \(^{26}\) is based around the assumption that the concentration of polymer segments at the particle surfaces is uniform. This assumption was declared to be invalid by de Gennes \(^{32}\) as the adsorbed region of the surfaces of particles is subject to large scale fluctuations, and so at low coverages there would be a large deviation from the mean field approximation of polymer segment concentration. Fleer \(^{33}\) conceded that this was true for low coverages but at the level of coverage that they were concerned with the fluctuations referred to by de Gennes would have
only a minimal effect on the density of segments at the surface. In a previous paper Fleer et al (34) claimed that the model devised by de Gennes was not a valid model for stabilised polymer particles as scaling theory can only be successfully applied to low surface coverages. The general opinion is that whilst both models have major drawbacks, when they are used in tandem they can yield good results and often successfully describe the surface of the polymer particles in dispersions and the interactions between pairs of particles.

1.2 Design And Synthesis Of Steric Stabilisers.

The previous sections have only discussed the mathematical theory behind steric stabilisation. It is necessary to consider how the requirements for steric stabilisation already described can be achieved in reality. As was observed earlier with regard to equation 1.1.b, there can be three energetically distinct methods of steric stabilisation:

a) Enthalpic $\Rightarrow \Delta H$ and $\Delta S$ are both positive and $\Delta H$ is greater than $T\Delta S$.

b) Entropic $\Rightarrow \Delta H$ and $\Delta S$ are both negative and $T\Delta S$ is greater than $\Delta H$.

c) Combined $\Rightarrow \Delta H$ is positive but $\Delta S$ is negative

In all of these cases the free energy of mixing will be positive which will therefore lead to repulsion between colliding particles. However, they all have differing sensitivities to thermal stability. Particles stabilised by enthalpic stabilisation will flocculate upon heating. This is due to the value of $T\Delta S$ becoming greater than $\Delta H$ and thus the free energy becomes negative. Entropic stabilisation leads to flocculation
upon cooling as this again leads to a negative free energy of mixing. Only combined stabilisation is stable throughout the entire temperature range possible; e.g. theoretically even at absolute zero (0 K) the free energy of mixing will be equal to the enthalpy of mixing which is positive, (of course at this temperature conventional thermodynamic considerations do not normally apply). Enthalpic and combined forms of steric stabilisation are seldom observed as the heat of solution for the stabilising chains is generally positive and therefore the enthalpy change associated with mixing of stabilising chains is negative.

Steric stabiliser polymer chains are usually composed of segments which fulfil one of two roles. The first is that of the anchor segment. It is this segment which binds the stabiliser to the dispersed particle. The second functional region of the steric stabiliser is the soluble segment. It is this segment which allows the particle to be dispersed in a diluent. The stabiliser may contain any number of each of these segments. As each of these segments operates independently of the other, then it is possible to consider the requirements of each functional segment separately.

1.2.1 Functional Requirements Of The Anchor Component Of Steric Stabilisers.

The main design priority of the anchor component is that it is not readily displaced from the surface of the polymer particle. This can be achieved in a number of ways:

1. Physical adsorption.
2. Covalent linkage.
3. Acid-base interactions.

1.2.1.1 Anchorage By Physical Adsorption.

In this type of anchorage the steric stabiliser is held to the surface of the particle by simple van der Waals attractive forces; i.e. there is no strong chemical bond between the particle and the stabilising chain although weak hydrogen bonds may exist. The formation of the anchor segment (or segments) of the stabiliser may be synthesised either concurrently during the reaction, i.e. prepared in-situ, or the complete steric stabiliser may have been synthesised previously, i.e. pre-formed.

When the anchor steric stabiliser is formed in-situ, a solvent-soluble pre-polymer is used to form the soluble segments. This pre-polymer must be capable of polymerising with the monomer of the particle and is often described as being a macromonomer. The reaction of the macromonomer with the monomer used in the dispersion polymerisation means that the anchor segments of the steric stabiliser are identical in nature to the polymer particle and thus problems of the compatibility between the particle and the anchor segment of the stabiliser are eradicated. This process of using macromonomers is comparable to the reactive surfactant work of Ottewill and Satgurunathan (35), Greene et al (36, 37) and Savage (38). The compatibility between the stabiliser and the polymer particle is, however, rarely a major problem and most of the polymers prepared by non-aqueous dispersion polymerisation can be stabilised by most lyophilic polymer containing stabilisers. Examples of this have been observed where acrylic polymer particles were prepared by stabilisers.
containing acrylic anchor groups, vinyl acetate anchor groups \(^{(14)}\) and also epoxide anchor groups \(^{(39)}\). A large proportion of the wide ranging compatibility arises from the anchor groups being short chain lengths of the non-soluble polymer and thus it would be expected that there would be fewer problems with compatibility than for higher weight analogues. It should be noted that for steric stabilisers prepared in-situ very little control can be exerted upon nature (block or graft copolymer) and architecture (number of blocks/grafts per chain) of the stabiliser and thus the more common practice is to use the pre-formed stabilisers.

As has been mentioned in passing there are two distinct types of copolymer that can lead to the stabilisation of particles in a non-polar solvent. These are described as being either block copolymers or graft copolymers. With the exception of certain block copolymers, i.e. diblocks and also triblocks with the anchor segment being the middle block, block copolymers stabilise the particles via what is termed *loopy stabilisation*. This name arises from the soluble chains extending into the solvating media as loops (see *Figure 1.3*). Graft copolymers with an anchor functional backbone (and the diblock and triblock copolymers mentioned above) stabilise the particles via a mechanism known as *hairy stabilisation*. This is due to the soluble segments extending into the solvating media as single strands somewhat akin to hairs. Graft copolymers and multi-block copolymers are much more effective stabilisers than diblock copolymers. This is a direct consequence of the increased difficulty in desorbing all of the anchor segments of a stabiliser that features *multi-point anchoring*, i.e. graft and multi-block copolymers, compared to that for stabilisers that
feature single point anchoring, i.e. diblock copolymers. Work carried out by Waters and Waite \(^{(40)}\) at Imperial Chemical Industries (I.C.I.) Paints suggests that there exists a minimum length of each anchor segment, especially for the loopy stabilisers. They believed that below a molecular mass of approximately \(500 \text{ g mol}^{-1}\) per anchor segment \((1,000 \text{ to } 2,000 \text{ for the total polymer})\) the stabilising chain tends more and more to behave as a random copolymer which are poor steric stabilisers.

1.2.1.2 Anchorage By Covalent Linking.

One of the main problems frequently observed with anchorage via physical adsorption is that upon the addition of a strong solvent the stabilising chains may become desorbed from the particle surface. This desorption will then lead to the loss of particle stability and, therefore in the worst case, to the gross flocculation of the particles. If the stabiliser can be held to the surface of the particle by forces stronger than the simple weak van der Waals forces, then this loss of stability upon the addition of a co-solvent can be greatly reduced. Covalently bonding the stabiliser to the particle means that the above desorption and also the migration of the stabiliser during film formation can be virtually eliminated. Through the use of complementary reactive groups, it is possible to achieve the required covalent bonding. An example of such a system is the post-polymerisation process involving the use of carboxylic co-monomers in association with hydroxyl bearing stabilisers in the presence of a tertiary amine to produce an ester linkage \(^{(41)}\). Another approach is the use of stabilisers bearing
Figure 1.3 A Schematic Diagram Showing The Difference Between Loopy Stabilisation (a) And Hairy Stabilisation (b).
copolymerisable functionalities. If the stabiliser possesses more than one polymerisable group then it is possible to produce a network structure covering the entire particle surface (42). The use of copolymerisable stabilisers is more effective than the use of complementary reactive groups as the spatial mobility of the anchor segment of the stabiliser is greatly reduced and therefore the ease with which the stabiliser can be desorbed is also reduced. If the network formed via the use of copolymerisable stabilisers has too fine a mesh size, then problems may occur with the coalescence of the particles during film formation. A mesh size based upon two to four polymerisable groups per stabiliser chain was considered to be the optimum.

1.2.2 Functional Requirements Of The Soluble Component Of Steric Stabilisers.

It is this portion of the stabilising polymer chain which is in many ways of prime importance as the soluble component keeps the particle in dispersion. The nature of the particle and indeed the nature of the anchor segment of the stabiliser are of little concern in the choice of the soluble segment of the stabiliser. This is a result of the steric barrier created by the solvent soluble polymer being effective enough to almost eradicate any attractions between the actual polymer particles themselves. This independence between the chemical nature of the particle and the chemical nature of the soluble chain has been shown by a number of workers using poly (hydroxystearic acid) as the soluble component (M_w ~ 1,500 to 1,800) in the stabilisation of particles of poly (methyl methacrylate) and polyacrylonitrile (43), nylon
and poly (ethylene terephthalate) \(^{(44)}\), titanium dioxide and copper phthalocyanine \(^{(45)}\).

For the soluble component to be fully effective it must have a \textit{limiting solubility} much greater than the concentration of the stabiliser used. The term limiting solubility is in this case used to refer to the maximum concentration of the polymer of interest that can be held in a solution under standard conditions. If the limiting solubility is close to the stabiliser concentration of interest, then the stabilising component may not be able to move freely and hence the repulsion between particles may be hindered. This effect can be clearly observed when a non-solvent, for the stabilising component, is added to the solvating media. Napper \(^{(14)}\) added various simple alcohols to dispersions of poly (methyl methacrylate) in n-heptane and noted that amongst other results that the addition of 31 wt-% of ethanol was sufficient to cause the flocculation of poly (lauryl methacrylate) stabilised particles.

1.2.3 Synthesis Of Pre-Formed Steric Stabilisers.

As has already been discussed, pre-formed steric stabilisers can be formed in two distinct architectures. These are as \textit{block copolymers} or as \textit{graft copolymers}. Some of the possible routes for the synthesis of these copolymers will be reviewed critically in the next two sections.

1.2.3.1 Synthesis Of Block Copolymers.

The free-radical polymerisation of block copolymers is well understood \(^{(46, 47)}\) but rarely employed in the synthesis of steric
stabilisers. There are two main synthetic routes which have been examined.

The first of these is by coupling condensation reactions (Figure 1.4 a). This reaction uses pre-formed blocks of anchor and stabiliser components with each block carrying distinct, and compatible, terminal functionality. Work by I.C.I. during 1968 (39) used an epoxide anchor group which featured residual glycidyl terminal groups and a polyester soluble group which featured carboxylic acid functionalities. Under base catalysed conditions it was possible to produce a steric stabiliser which could successfully stabilise non-aqueous dispersion polymerisations of vinyl and acrylic monomers. Although the character of each block can be well controlled, i.e. it is possible to produce relatively monodisperse anchor/soluble blocks, it can be difficult to control the number of blocks of each type in the steric stabiliser.

The second method for producing block copolymers is by using ionically initiated living polymerisation (Figure 1.4 b). The theory of living polymerisations is well documented in many of the standard polymer chemistry textbooks available (48, 49). By controlling the sequential addition of each monomeric component, it is possible to achieve a very high level of control not only upon the molar mass of each block but also a precise control over the nature of the copolymer. Although very well defined steric stabilisers can be synthesised via the use of living polymerisations, the process is seldom used as the reaction is highly susceptible to side reactions and termination in the presence of moisture (NB the controlled termination of a living
polymerisation is usually brought about via the addition of a low order alcohol, e.g. methanol).

1.2.3.2 Synthesis Of Graft Copolymers.

The term *graft polymer* implies that a branched chain structure exists. In a graft *copolymer* one or more of the branches will be of a different chemical structure to the main chain. There are many architectures that the branching can adopt (*Figure 1.5*). Grafting may occur through two general processes:

1. Random grafting.
2. Grafting involving specific sites.

As the differences between these types of grafting process are large they will be considered separately.

1.2.3.2.1 Random Grafting.

In random grafting or *grafting from*, the soluble component is prepared separately and subsequently reacted with the anchor monomer in a polymerisation initiated by an organic peroxide initiator such as t-butyl hydroperoxide or lauryl peroxide. The organic radical produced can react with a labile hydrogen on the main chain thus creating a main chain radical. This radical is then a site for the polymerisation of the anchor monomer and thus the location of the anchor grafts (*Figure 1.6*).

One of the major drawbacks of this type of grafting system is the
Figure 1.4 A Schematic Diagram Of The General Processes Of Coupling Condensations Reactions (a) And Living Polymerisation (b).
Figure 1.5 A Schematic Diagram Of Some Of The Architectures That A Graft Copolymer Can Adopt.
possibility of unwanted side reactions leading to the formation of ungrafted homopolymers of the anchor polymer and, perhaps more importantly, the formation of gels and networks. Cross-linking will occur if the radical on the growing anchor chain attacks another labile hydrogen on another soluble chain. If significant cross-linking occurs, then a network mixture of anchor and soluble blocks will be created (Figure 1.7) and thus the resulting polymer will not be capable of steric stabilisation. Although the formation of polymer networks can be controlled (49) via the use of chain transfer agents and lower weight main chain polymer, grafting is seldom used as a route for synthesising steric stabilisers by graft copolymerisation. This is mainly due to the lack of any real control over the number of grafts on the backbone (graft number) and the number of repeat units in each graft (graft length).

1.2.3.2.2 Grafting Involving Specific Sites.

The grafting involving the use of specific grafting sites can be split into two further categories.
1. Grafting onto.
2. Grafting through.

The *grafting onto* process can be seen in some ways as being analogous to the grafting from technique. In as much as they both involve the use of a pre-formed polymer backbone. Grafting onto, however, also involves the use of a pre-formed graft chain. An advantage of both of the components being pre-formed is that it is possible to fully characterise both the anchor and soluble segments and therefore it is possible to confidently characterise the graft.
Figure 1.6 A Schematic Representation Of The Grafting From Process.
copolymers. The backbone contains reactive groups down its length and the chains which will form the grafts possess a terminal functionality which will react with reactive backbone functionalities. These reactive sites may be ionic \(^{(50 - 52)}\) or non-ionic \(^{(53, 54)}\).

The reactive sites on the backbone may be created during the copolymerisation of a conventional monomer and a functional monomer. This was the approach used by Osmond and Waldbridge \(^{(43)}\) in the copolymerisation of lauryl methacrylate (97 wt-%) with glycidyl methacrylate (3 wt-%) which produced an acrylic backbone with epoxide reactive sites. Another approach is to create the reactive sites as a post polymerisation process. Melville et al \(^{(53)}\) partially hydrolysed poly (vinyl acetate) to give occasional vinyl alcohol functionalities on the backbone. The synthesis of monofunctional graft pre-cursors is carried out using matched initiator/chain transfer reactions. These will be discussed in a later section.

The grafting through process also uses pre-formed graft chains. The grafts in this situation possess a single terminal polymerisable group and are termed macromonomers. The macromonomers are converted into graft copolymers, capable of undertaking steric stabilisation, by solution polymerisation with the monomeric anchor component \(^{(55)}\). This then produces a comb structure (Figure 1.8).

As with the grafts produced for the grafting onto route it is imperative that the macromonomer is monofunctional to prevent the formation of a network polymer.
Figure 1.7 A Schematic Diagram Of How Network Formation Can Occur During The Grafting From Process.
Figure 1.8 Schematic Representation Of The Grafting Through Process.
1.2.3.3 Synthesis Of Monofunctional Graft Pre-Cursors.

In the synthesis of functionalised grafts, for grafting onto, and the synthesis of macromonomers, it is essential to produce a monofunctional pre-polymer with a narrow molar mass distribution. In 1955 Bamford (56) introduced the concept of matched initiator/chain transfer agent reaction systems. The functionalised initiator 4,4'-azobis(isocyano)valeric acid (ACVA) decomposes thermally to yield two identical free radical initiator fragments each with a carboxylic acid terminal functionality (Figure 1.9).

Free radical polymerisation of common monomers initiated by ACVA produces polymer with carboxylic functionality. Termination by combination leads to the production of unwanted difunctional polymer. Termination by disproportionation leads to the production of one monofunctional chain but the other chain will possess a terminal unsaturation which might undergo subsequent polymerisation and thus lead to broad molar mass distribution. Therefore neither termination mechanism yields the desired pre-polymer without also producing a range of unwanted polymers.

The use of chain functionalised chain transfer agents both controls the molar mass of the polymer chain but also virtually eliminates unwanted side reactions. The commonly used (57, 58) chain transfer agent thioglycollic acid (TGA) not only leads to the termination of the growing monofunctional chain via hydrogen abstraction but also to the initiation of another functionalised pre-cursor polymer (Figure 1.9).
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The next stage in the synthesis of macromonomers is the conversion of the functionalised pre-polymer into macromonomer. There are many possible reactions which fulfil this role. One route is the conversion of the carboxylic acid into an acyl chloride by reaction with oxalyl chloride. The acyl chloride can then be reacted with a hydroxy methacrylate to produce the desired terminal unsaturation \(^{57,58}\). A more direct route is that used by Ottewill et al.\(^{59}\). They reacted the carboxylic pre-polymer with glycidyl methacrylate, in the presence of a tertiary amine ring opening catalyst, to yield the required vinylic functionality.

1.3 Rheological Aspects Of Particle Dispersions.

The theoretical analysis of the rheology of multimodal polymer dispersions is a highly complex treatment. It is essential therefore that the rheology of monomodal polymer dispersions is understood.

1.3.1 Studies Of The Rheology Of Monomodal Polymer Dispersions.

Two of the main rheological aspects of interest are the effect that the particle concentration has upon the viscosity of the dispersion and the effect of the shear rate.

1.3.1.1 Effect Of Particle Concentration Upon Dispersion Viscosity.

Initial work by Einstein\(^{(60)}\) on rigid spheres at low volume fractions
1.)

\[
\text{CH}_3\text{C}^\cdot\text{N}^\equiv\text{N}\text{C}^\cdot\text{CH}_3 \rightarrow \text{CH}_3\text{C}^\cdot + \text{N}_2
\]

2.)

\[
\text{HO}_2\text{C-R}^\cdot + \text{nM} \rightarrow \text{HO}_2\text{C-R-M}_\text{n}^\cdot
\]

3.)

\[
\text{HO}_2\text{C-R-M}_\text{n}^\cdot \overset{\text{H-S-CH}_2\text{CO}_2\text{H}}{\rightarrow} \text{HO}_2\text{C-R-M}_\text{n}^\cdot\text{H} + \text{HO}_2\text{C-CH}_2\text{S}^\cdot
\]

*Figure 1.9 A Schematic Representation Of The Matched Initiator/Transfer Agent Reaction.*
is generally taken as the basis for nearly all theoretical treatments. Although his equations work well under the conditions he described, they cannot be applied directly to dispersions of polymers at useful volume fractions. This is because at anything other than low volume fractions interactions between particles become significant, and therefore Einstein's assumption of zero interaction between polymer particles is invalid. His consideration of polymer particles as rigid hard spheres is also questionable as the stabilising layer around the particle is viscoelastic, and in the case of small particles the soft stabilising layer can have a large contribution to the overall character of the particle.

Mooney (61) was one of the first researchers to modify Einstein's basic equation to take into account higher concentrations by the addition of an empirically determined constant (k). Mooney described this constant as a crowding factor. The equation developed (Equation 1.3 a) reduces, at low concentration, to the equation developed by Einstein.

\[
\eta_r = e^{\left(\frac{2.5\phi}{1-k\phi}\right)}
\]

Equation 1.3 a

where:

- \(\eta_r\) is the relative viscosity of the dispersion,
- \(\phi\) is the volume fraction of polymer particles,
- \(k\) is the empirical crowding factor.

The equation fitted well with what little experimental evidence existed at that time. There was very good agreement with the data reported by Vand (62) with respect to hard glass spheres and good agreement with
the results of Eilers\textsuperscript{(63)}, especially at volume fractions less than 0.5, for dispersions of bitumen. The deviation of the results of Eilers from the theoretical values was considered to be an effect of the slight polydispersity of his particles, (diameters were in the range 1.6 → 4.7 μm).

Goodwin\textsuperscript{(64)} later developed an equation (Equation 1.3 b) in which the viscosity was a function of the sum of the products of the concentration of particles and a variable related to the inter-particle interactions related to that concentration ($\alpha_i$).

$$\eta_r = 1 + \sum \alpha_i \phi_i$$  

Equation 1.3 b

At low concentrations ($\phi < 0.01$ v/v) then the viscosity is considered to be first order and with a value of $\alpha_1$ of 2.5 the equation reduces to the Einstein equation. At concentrations between 0.01 and 0.2 v/v the viscosity becomes second order and above this concentration range interactions between three particles are introduced and so $\alpha_3$ becomes important. Due to the complexity of the calculations involved in three body interactions, the value of $\alpha_3$ has only been estimated experimentally\textsuperscript{(64)}. The experimental results obtained by many workers\textsuperscript{(65→67)} on poly (methyl methacrylate) particle dispersions, at low concentrations, fitted Goodwin’s equation when the value for $\alpha_1$ was 2.9 and the value for $\alpha_2$ was 10.3. The value for higher interaction parameters was set to zero. It was noted that it was necessary to have the value for first order interactions higher than the value predicted by Einstein. It was believed that this was an effect of the viscoelastic nature of the stabilising boundary layer. In a comprehensive study by Dawkins and Taylor\textsuperscript{(66)} it was observed that as the particle size was
increased, and therefore the contribution to particle size arising from the stabilising layer decreases, that the discrepancy between the theoretical value for the first order interaction parameter and the empirical value reduced greatly.

1.3.1.2 Effect Of Shear Rate Upon Dispersion Viscosity.

In his early treatment of particle dispersions, Einstein (60) proposed that the dispersion would behave as a classical Newtonian fluid, i.e. that the viscosity is directly proportional to the shear rate. The experimental evidence (68 \rightarrow 72) does agree that that at the concentrations Einstein was considering a polymer dispersion will behave as a Newtonian fluid. At polymer contents as low as 0.03 v/v, non-Newtonian behaviour can be observed and at concentrations above 0.1 v/v the dispersion is distinctly non-Newtonian.

Milkie and Croucher (73) reported that two factors can affect the degree to which the non-Newtonian behaviour is observed. The first was that as the volume fraction of the polymer is increased then so does the non-Newtonian character of the dispersion. They also demonstrated that at higher shear rates the deviance from Newtonian behaviour is reduced. The increase in the extent of non-Newtonian behaviour with increasing volume fraction of polymer is likely to be due to the increase in the higher order particle interactions referred to by Mooney (61). The effect of the particle size of the dispersed polymer on the fluid behaviour was reported by Willey and Macosko (72). They observed that as the particle size increased then so did the Newtonian character of the fluid. The difference between the non-Newtonian
behaviour of the dispersions was again observed to decrease with increasing shear rate. This they suggested was a result of the hydrodynamic forces acting upon the particles becoming much more dominant, at high shear rates, than the Brownian motion of the particles in their contribution to the flow properties of the dispersion.

1.3.2 Studies Of The Rheology Of Multimodal Polymer Dispersions.

The theories and equations developed by both Mooney (61) and Goodwin (64) have been extended to take into account the polydispersity associated with industrially prepared particles. Most of the work reported in the literature initially considers the rheology of a bimodal dispersion and then extrapolates the considerations to address the problem of further degrees of polydispersity.

Farris (74) considered that as long as the size ratio of the two particle sizes was less than 1:10, then the rheology of a bimodal dispersion could be modelled as the addition of the large particles to a fluid which had been pre-stiffened by the small particles. From this he was able to develop an equation (Equation 1.3 c) based upon what he termed stiffening factors.

\[ \ln \eta_i = \sum \ln H_i \]  
Equation 1.3 c

where:

- \( H(\phi_i) \) is the stiffening factor for component \( i \) which is equivalent to the ratio of the viscosity of the dispersion of small particles
and particles i to the viscosity of a dispersion of small particles alone.

The equation showed good agreement with the experimental results for a bimodal dispersion with a size ratio of less than 0.1 even at high total polymer content. He then took the calculations further and developed equations to predict optimum blend ratios and thus showed that by using blend of trimodal and tetramodal polymer particles it is theoretically possible to achieve polymer volume fractions of greater than 0.9 v/v.

In a recent paper (75) Kim and Luckham extended an equation developed by Krieger and Dougherty (76) to predict the viscosity of a bimodal dispersion from the knowledge of the intrinsic viscosity of the monomodal dispersions. The extended form of the Krieger-Dougherty equation gave good agreement at high and low volume fractions of small particles ($\phi_s = 0.8$ and 0.2) but gave poor agreement at intermediate concentrations ($\phi_s = 0.4$ and 0.6). This is however, contrary to the results obtained by Padget et al (77) who found that the Krieger-Dougherty equation gave good agreement over all blend ratios studied.

It would seem therefore that the production of a reliable model for the rheology of multimodal polymer dispersions is still a long way off. This may be in many ways due to the difficulty in synthesising polymer particles with a narrow particle size distribution as was noted by Mooney (61).
1.4 Aims Of Research.

The primary aim of this research program was to study the rheology of well characterised monomodal and bimodal PMMA non-aqueous dispersions, with particular reference to the theoretical maximum packing fraction.

To achieve this overall aim each stage of the process from simple monomers to final dispersion had to be thoroughly investigated. Therefore the research can be separated into three distinct sections. These are:

1. Synthesis of steric stabilisers.
2. Control of particle size and distribution in non-aqueous PMMA dispersions.
3. Rheological studies.

The steric stabilisers were produced via a grafting through process. It was essential therefore to devise an efficient and simple synthetic route for the synthesis of the poly (2-ethylhexyl acrylate) (PEHA) macromonomers, with a narrow weight distribution. The final steric stabiliser was produced via a copolymerisation reaction of these macromonomers with styrene.

Many possible criteria were studied for particle size control in non-aqueous dispersion polymerisations. For one stage dispersions the effect of both monomer concentration and stabiliser concentration was investigated. For two stage dispersions the effect of total monomer and
total stabiliser concentrations was also studied, but the more subtle
effects of the ratio of the divide of the monomer and stabiliser between
the seed and feed stages of the polymerisations were investigated as
well. The ultimate aim of this work was to develop a range of
approaches to the synthesis of a dispersion of given particle size using
given monomer and stabiliser concentrations.

The effect of increasing shear stress upon the dispersion viscosity, at
increasing solids contents for monomodal dispersions, was studied.
From these results the maximum theoretical packing fraction was
calculated by applying the Krieger-Dougherty equation. Bimodal
blends of these monomodal dispersions were also produced and the
effect of the shear stress upon viscosity once again investigated. The
maximum packing fractions for these blended dispersions was also
calculated by applying the monomodal Krieger-Dougherty equation to
the experimental data. The bimodal Krieger-Dougherty equation was
observed to fit the data poorly whereas the monomodal equation fitted
well. The effect of the blend ratio (the ratio of volume fraction of one
particle size range to the other) upon the maximum theoretical packing
fraction was also determined.
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Experimental
2.1 List Of Chemicals Used.

- Acetone, used as supplied by Carless Solvents.
- Azobiscyanovaleric acid (ACVA), 95% purity used as supplied by Aldrich Chemicals.
- Azobisisobutyronitrile (AIBN), recrystallised from methanol.
- N-Benzyl dimethylamine (BDMA), used as supplied by Aldrich Chemicals.
- Calcium hydride, Lancaster Synthesis, used as a coarse powder.
- Chloroform (dueterated), containing tetramethyl silane.
- Cycloheptane, used as supplied by Aldrich Chemicals.
- Cyclohexane, used as supplied by Aldrich Chemicals.
- Cyclooctane, used as supplied by Fluka.
- 1.4. Diazabicyclo [2.2.2.] octane (DBCO), used as supplied by Fluka.
- Dimethylaminododecane (DMAD), 97%, used as supplied by Fluka.
- Ethyl acetate, used as supplied by Carless Solvents.
- 2-Ethylhexyl acrylate (EHA), 98% from Fluka, dried over magnesium sulphate and destabilised using an inhibitor removing column.
- Glycidyl methacrylate (GMA), 95% used as supplied by Fluka.
- Heptane, used as supplied by Fisher Scientific.
- Hexane, used as supplied by Fisher Scientific.
- Hydroxyethyl methacrylate (HEMA), 97% Aldrich chemicals, dried over magnesium sulphate.
- Magnesium sulphate, used as supplied by Fisher Scientific.
- Methanol, used as supplied by Carless Solvents.
• Methyl Methacrylate (MMA), from Fluka, destabilised using an inhibitor removing column.
• Oxaly chloride, 98%, used as supplied by Aldrich Chemicals.
• Styrene, 99%, from Fluka, destabilised using an inhibitor removing column.
• Silica gel self indicating crystals, used as supplied by Aldrich Chemicals.
• Thioglycollic acid (TGA), 97%, used as supplied by Aldrich Chemicals.
• Tetrahydrofuran, HPLC grade unstabilised, Fisher Scientific.
• Toluene, dried over calcium hydride, supplied by Carless Solvents.
• Triethyl amine (Et$_3$N), 99%, dried over sodium wire.
• Xylene, used as supplied by Fisher Scientific.
2.2 Experimental Details.

In section 1.2 the general synthesis of many types of steric stabilisers was discussed. Here the precise synthetic route of the grafting through process, using poly (2-ethylhexyl acrylate) as the stabilising component, will be described followed by the preparation of polymer particle dispersions. Finally, the procedures for rheological studies of these dispersions will be discussed.

2.3 Synthesis Of Macromonomers.

There are two steps involved in the synthesis of macromonomers. The first step is the synthesis of the carboxylic acid terminated poly (2-ethylhexyl acrylate) pre-polymer chains. The second is the conversion of these pre-polymers to macromonomers via reaction of the carboxyl functionality.

2.3.1 Synthesis Of Carboxyl Terminated Pre-Polymers Of Poly (2-Ethylhexyl Acrylate).

The synthetic route that was chosen was the matched initiator/chain transfer agent route that has been well documented by a number of researchers (56, 57, 58, 78). Work carried out at Loughborough (58, 78) has shown that a molar mass for the soluble graft segment of the stabiliser of approximately 3,000 can satisfactorily stabilise particles in dispersion. The conditions therefore that have been selected are designed to produce pre-polymer of an average molar mass of 3,000 g
mol\(^{-1}\) [NB for poly (2-ethylhexyl acrylate) this molar mass corresponds to a degree of polymerisation of around 25].

Prior to polymerisation the monomer, 2-ethylhexyl acrylate (EHA), was destabilised by passing through a 30 cm column packed with hydroquinone monomethyl ether inhibitor remover. A 500 ml three necked round bottomed flask fitted with a nitrogen inlet and water cooled condenser was charged with de-inhibited EHA (95 ml) and ethyl acetate (77 ml) as the reaction solvent. This solution was then purged with nitrogen for 30 minutes, at room temperature, whilst being stirred by a magnetic follower to ensure complete mixing. The flask was then placed in a water bath held at a constant 80 °C (353 K) and the monomer solution was allowed to reach this temperature. The chain transfer agent, thioglycollic acid (TGA), (4.29 g) was added, and then finally the functionalised initiator, 4,4'-azobiscyanovaleric acid (ACVA), (4.23 g) was introduced to the reaction vessel. The polymerisation was then allowed to proceed for two hours during which time nitrogen bubbling was continued. It should be mentioned that due to the evolution of nitrogen gas during the thermal decomposition of ACVA it is essential that the ACVA is added very carefully.

The purification of the pre-polymer was brought about via the dropwise addition of the cooled reaction mixture into a three times volumetric excess of methanol which had been cooled to near its freezing point. The polymeric reaction products settled out as a very viscous opaque lower layer. The upper methanolic layer containing the residual non-polymeric reaction products and unreacted reagents was
subsequently decanted off. The polymeric fraction was then redissolved in fresh ethyl acetate and the purification repeated a further three times. The polymer was finally redissolved once more in ethyl acetate before being dried in a recrystallising dish under vacuum for 12 hours.

2.3.2 Conversion Of The Poly (2-Ethylhexyl Acrylate) Pre-Polymer Into Macromonomer.

Two synthetic routes to achieve this conversion were employed. The first route was the two step route reported by Slark (57). This involved the initial conversion of the carboxylic acid terminated pre-polymer to an acyl chloride terminated pre-polymer. This was subsequently converted to macromonomer by the reaction of the pre-polymer with 2-hydroxyethyl methacrylate (HEMA). The second synthetic route was the one step reaction of the carboxylic acid terminated pre-polymer with glycidyl methacrylate (GMA). Although this reaction has been reported by a number of workers, (58, 79, 80, 81) the reaction conditions suggested by them varies significantly.

2.3.2.1 Conversion Of Poly (2-Ethylhexyl Acrylate) Pre-Polymer Into Macromonomer Via An Acyl Chloride Intermediate.

A 500 ml three necked round bottomed flask was charged with the purified carboxyl pre-polymer (34.79 g) and dry toluene (300 ml) to make an approximately 10 wt-% solution. The toluene had been dried over finely ground calcium hydride for at least 24 hours. The flask was fitted with a nitrogen inlet and a water cooled condenser which itself
was fitted with a silica gel packed drying tube. The flask was placed in an ice bath and the polymer/solvent mixture stirred via a magnetic follower to ensure a homogeneous solution. The solution was purged with dry nitrogen for 30 minutes. The nitrogen was dried by incorporating a silica gel packed Drescher bottle into the nitrogen line. Oxalyl chloride (1.36 g) was then added to the mixture in a two molar excess. Due to high moisture sensitivity of the acid chloride, it was essential to make the drying processes as rigorous as possible. The reaction was allowed to proceed for 24 hours during which time the nitrogen bubbling and stirring were continued and the reaction was allowed to reach room temperature.

It is essential that during the purification process the acyl chloride terminated product does not come into contact with moisture, either atmospheric or direct, as this can lead to the swift reversion of the acyl chloride functionalised pre-polymer to the carboxylic acid functionalised pre-polymer \(^{(81)}\). Using a rotary evaporator any unreacted oxalyl chloride and the solvent were removed to yield the viscous pre-polymer. This was then redissolved in more dry toluene and subjected to rotary evaporation once more. Because the acyl chloride intermediate can revert to the initial pre-polymer (as already mentioned), no characterisation of the intermediate was carried out and the second stage of the reaction was undertaken as soon as possible after purification.

In the second stage the apparatus was identical to that used in the first stage. The round bottomed flask was charged with the acyl chloride intermediate (34.00 g) which was subsequently dissolved in dry
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toluene (300 ml) to make an approximately 10 wt-% solution. The reaction mixture was stirred with a magnetic follower to create a homogeneous solution which was purged with dry nitrogen, in an ice bath, for 30 minutes. Hydroxy ethyl methacrylate (1.78 g) was added to the reaction mixture and finally triethyl amine (1.00 g) was added as a reaction catalyst. The reaction was allowed to proceed for 24 hours during which time room temperature was achieved. Nitrogen bubbling and stirring were continued throughout the entire reaction.

The reaction mixture was purified by initially filtering to remove the precipitated salt of the catalyst (Et$_3$NH$^+\text{Cl}^-$). The macromonomer solution was then rotary evaporated to remove the toluene. The unpure macromonomer was redissolved in the minimum quantity of acetone and then added dropwise into a 1 L separating funnel containing 300 to 400 ml of distilled water. The polymeric fraction, containing both the desired macromonomer and unreacted pre-polymer, settled out as the lower opaque viscous layer. This layer was removed and evaporated once more to remove any residual volatile material and subsequently redissolved in fresh acetone. The purification process was repeated again before the purified polymer component was redissolved in fresh acetone and evaporated under reduced pressure. It should be recorded that the polymeric product still contains any unreacted residual pre-polymer as well as the desired macromonomer.

2.3.2.2 Conversion Of Poly (2-Ethylhexyl Acrylate) Pre-Polymer Into Macromonomer Via An Epoxide Ring Opening Route.
As has already been mentioned there are many variations of the reaction conditions for this reaction available in the published literature. As part of the work reported in this thesis, it was decided to attempt to combine some of these conditions, and thus derive what may be considered to be the optimum conditions for the reaction of a carboxylic acid with an epoxide. In this section the basic reaction, which is that described by Duddington \(^{(58)}\), will be reported. Later any variations from the basic reaction where pertinent will be described.

In the basic reaction a 500 ml three necked round bottomed flask, fitted with a water cooled condenser and a nitrogen inlet, was charged with the carboxylic acid terminated pre-polymer (22.51 g) and xylene (220 ml) to make an approximately 10 wt-% solution. This was then stirred using a magnetic stirrer to achieve a homogeneous solution. To this solution glycidyl methacrylate (1.4547 g) was added in a 50 % molar excess to the pre-polymer. The reaction mixture was then purged by nitrogen bubbling for 30 minutes after which the reaction vessel was placed in a water bath held at a constant 140 °C (413K), and the reaction allowed to proceed for 6 hours during which time the nitrogen bubbling was maintained.

The purification of the reaction that was initially carried out was to subject the reaction product mixture to rotary evaporation to remove the majority of the ethyl acetate and any other volatile compounds. Further purification was obtained by subjecting the concentrated, viscous solution of reaction products to short path distillation. The distillation was performed at 100 °C using a low revolution speed and
high vacuum for 2 hours. Care was required to ensure the products did not “boil over” into the solid CO₂ solvent trap.

2.3.2.3.1 Effect Of A Reaction Catalyst Upon The Conversion Of Poly (2-Ethylhexyl Acrylate) Pre-Polymer Into Macromonomer Via An Epoxide Ring Opening Route.

The epoxide end capping reaction was performed using the same conditions and concentrations as for the basic reaction except that a tertiary amine was present at a concentration of 1.7 wt-% on pre-polymer. The amines studied were triethyl amine (Et₃N), N-benzyl dimethyl amine (BDMA), dimethyl aminododecane (DMAD) and 1.4.diazabicyclo[2.2.2.] octane (DBCO). The chemical structures for these amines are shown in Figure 2.1.

Purification and analysis were performed as described in Section 2.3.2.2.

2.3.2.3.2 Effect Of Reaction Temperature Upon The Conversion Of Poly (2-Ethylhexyl Acrylate) Pre-Polymer Into Macromonomer Via An Epoxide Ring Opening Route.

Two variations upon the basic reaction were performed. The first was a moderate temperature reaction, which used ethyl acetate as the solvent, DMAD as a ring opening catalyst and a reaction temperature of 65 °C (338 K). The second reaction was identical to the basic reaction except for the use of the ring opening catalyst DMAD.
Figure 2.1 Chemical Structures Of The Amine Catalysts Used For The Epoxide End Capping Reaction.
Purification and analysis were performed as described in Section 2.3.2.2.

2.4 Synthesis Of Graft Copolymer.

The conversion of the macromonomer to graft copolymer was achieved by a simple solution copolymerisation of the macromonomer with styrene. The styrene was destabilised by passing the monomer through a column packed with inhibitor remover. The initiator used, \( \alpha \alpha' \) azobisisobutyronitrile (AIBN), was recrystallised from methanol.

A 500 ml three necked round bottomed flask fitted with a water cooled condenser and a nitrogen inlet was charged with the purified macromonomer (41.50 g), styrene (60.00 ml = 58.84 g) and toluene as the solvent (250 ml). The reagents were then stirred using a magnetic follower to achieve a homogeneous solution. The solution was then purged for 30 minutes with nitrogen prior to the addition of the initiator AIBN (0.7778 g). The reaction was then carried out in a thermostatically controlled water bath held at 50 °C (323 K) for 48 hours during which time the nitrogen bubbling was maintained.

The graft copolymer was purified by initially evaporating the solution of product using a rotary evaporator to remove the solvent and any unreacted styrene. The polymer fraction could be expected to contain a mixture of polymeric compounds such as graft copolymer, polystyrene homopolymer, homopolymerised macromonomer, unreacted macromonomer and residual pre-polymer. Work performed
by Slark (57) and Duddington (58) has shown that only a negligible quantity of homopolymer exists in the polymeric fraction. The further purification of the graft copolymer is achieved by dissolving the polymeric mixture in fresh toluene and adding this mixture dropwise to hot methanol. This process separates the two components as the polystyrene backbone is insoluble in methanol, at the molar masses investigated here, whereas poly (2-ethylhexyl acrylate) is soluble in hot methanol. This means that the graft copolymer will precipitate out and the unreacted macromonomer and pre-polymer will remain in solution. The purification process is repeated several times until GPC analysis indicates that all of the residual poly (2-ethylhexyl acrylate) has been removed. Characterisation was carried out using GPC, FT-IR and \(^1\)H NMR.

2.5 Discussion Of Characterisation Techniques.

This section is intended to give only a brief outline of the main techniques that will be used in the characterisation the polymers produced at the varying stages of production. It is not intended to be a detailed study of the theory behind each technique. Many of the general polymer textbooks available deal with these topics in much greater detail than can be considered here (50).

2.5.1 Gel Permeation Chromatography.

Gel permeation chromatography (GPC) is an analytical technique which is able to separate polymer molecules as they elute down a column, packed with semi-porous beads, on a size exclusion principle.
The process finds general application in the determination of molecular masses and molecular mass distribution.

The system used two 30 cm mixed-B gel column (pore size 10\(\mu\)m) attached to a Knauer refractive index detector. The eluent (tetrahydrofuran) was pumped at a rate of 1 ml min\(^{-1}\) using a Knauer pump and toluene as the marker. The data collection was handled by a personal computer running software supplied by Polymer Laboratories. The calibration of the system was carried out using polystyrene standards.

The samples injected into the system were prepared by dissolving 5 mg of the polymer in 4 ml of tetrahydrofuran which had been degassed in a sonic bath for 15 minutes. The samples were filtered using glass microfibre filter papers and 0.5 ml of the solution then injected into the system.

2.5.2 Fourier Transform Infra-Red Spectroscopy.

Infra-red (IR) spectroscopy is a frequently used technique for the structural analysis of organic compounds. With polymers this form of spectroscopy is used qualitatively to confirm the existence or disappearance of various chemical groups.

In the IR analysis of the polymers a very thin coating of the viscous material was cast on to a single sodium chloride disc. For the IR analysis of glycidyl methacrylate a single drop was sandwiched
between two polished sodium chloride discs. All of the samples were examined on a Nicolet 20 DXC infra-red spectrometer and scanned 50 times over the range 400 - 4000 cm\(^{-1}\). To reduce the appearance of any vibrations due to atmospheric moisture and adsorbed carbon dioxide, a background spectrum of air was obtained over the same wavenumber range as the samples, and subsequently subtracted from the sample spectra.

2.5.3 Proton Nuclear Magnetic Resonance Spectroscopy.

The spectra obtained from proton nuclear magnetic resonance (\(^1\)H NMR) were used both qualitatively to determine which chemical groups existed and also in a quantitative manner to determine the quantity of each group present. The calculations required to carry out a quantitative study will be discussed later where applicable.

The samples were characterised by in-house analysis using a Bruker DPX 400 MHz spectrometer. The samples were prepared by dissolving 50 mg of polymer in 1 ml of deuterated chloroform which contained tetramethyl silane.

2.6 Non-Aqueous Dispersion Polymerisations.

There are many examples of recipes for the preparation of polymer particles by non-aqueous dispersion polymerisation available in the open literature\(^{(57, 58, 79, 80, 83 \rightarrow 87)}\). The technique studied here was the
micro-dispersion process developed by Slark \(^{57}\) and later by Duddington \(^{58}\).

2.6.1. Preparation Of Poly (Methyl Methacrylate) Particles.

Two variations of the micro-dispersion process were studied. The first was single stage polymerisation whereby all of the reagents are present at the start of the polymerisation. The other variation was a two stage process whereby a seed of stable small particles is produced and then the bulk of the reagents are added subsequently.

2.6.1.1 Single Stage Non-Aqueous Dispersion Polymerisation.

Methyl methacrylate monomer was purified in the same manner as for styrene earlier, i.e. using an inhibitor remover column. Into a 100 ml round bottomed flask, equipped with a side arm water cooled condenser (Figure 2.2), hexane (15.00 g) was charged and the flask then purged with nitrogen for 30 minutes. The polymerisation vessel was then placed in an oil bath held at a constant 65 °C (338 K). In a “standard polymerisation”, a solution of methyl methacrylate monomer (4.00 g, 20 wt-%) and graft copolymer (0.5 g, 2.5 wt-%) which had been mixed previously in a separate vessel was then added and stirred with a magnetic stirrer. After a stabilised dispersion had been achieved, (approximately 5 minutes) the initiator AIBN (0.2 g, 1 wt-%) was added and the polymerisation allowed to proceed for 2 hours during which time the nitrogen blanket was maintained and the stirring of the dispersion continued. The deviations from this standard polymerisation are explained, where relevant, in Chapter 3.
Figure 2.2 Schematic Diagram Of The Apparatus Used For Non Aqueous Dispersion Polymerisations.
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The dispersion of polymer particles was purified by subjecting the dispersion to centrifugation at 15,000 rpm for 20 minutes and decanting the supernatant liquid off. The particles were then redisperssed, this time in heptane due to its lower volatility compared to hexane. The centrifugation / redispersion process was repeated three times to yield what is believed to be a clean dispersion, i.e. the dispersion medium contains polymer particles only and all the steric stabiliser is adsorbed on to the particle surface.

2.6.1.2. Two Stage (Seed-Feed) Small Scale Non-Aqueous Dispersion Polymerisation.

Essentially the polymerisation proceeds in the same manner as the single stage dispersion polymerisation. However, the reagents are divided between the seed and feed stages in the ratios described in Table 2.6.1.

The seed phase of the dispersion was formed as outlined in Section 2.5.1 with the exception that the polymerisation only proceeds for 1 hour. At this point the premix of the remaining reagents is added at a steady rate (0.2 ml/15 min) over 3 hours. During this time the nitrogen blanket was maintained, stirring continued and the polymerisation temperature held at 65 °C. Upon the complete addition of the remaining premix the polymerisation was allowed to continue for a further 1.5 hours.

Purification was achieved as described in Section 2.5.1.
Table 2.6.1. Divide Of Reagents Between The Seed And Feed Stages For The Standard Two Stage Dispersion Polymerisation.

2.6.1.3 Two Stage (Seed-Feed) Large Scale Non-Aqueous Dispersion Polymerisation.

Large scale (400g) dispersions were prepared for rheological studies. Due to the increased volume required, a flanged 1 L polymerisation vessel was used with a mechanical stirrer, controlled to 250 rpm. The reagents were used in the same proportions as for the small scale two stage dispersion polymerisation and added to the reaction over the same time period. After preliminary work was performed, it was observed that the particles synthesised were more discrete and spherical if the diluent, cyclooctane, contained 5 % hexane. This ensures that the monomer is constantly washed away from the glassware. For all of the large scale dispersions discussed in this thesis, a mixed diluent was used.

With the large volumes produced, it was not possible to purify the large scale dispersions using the same centrifugation equipment used for the small scale work. The large scale dispersions were purified using a centrifuge with a higher capacity but lower maximum spin rate.
Good separation of the particles and supernatant was attained by centrifugation at 3,000 rpm for 2 hours. Redispersion was achieved using pure cyclooctane.

2.6.2 Particle sizing methods.

There are many different techniques for the determination of both particle size and distribution. These can range from the very simple techniques such as sieving using calibrated sieves to the very complex such as the Coulter counter. In this section the theories behind several techniques are discussed and the relative advantages and disadvantages of each technique are compared. The techniques evaluated for use were:

1.) Transmission Electron Microscopy (TEM).
2.) Disc Centrifugation (DC).
3.) Photon Correlation Spectroscopy (PCS).

2.6.2.1 Transmission Electron Microscopy.

Transmission electron microscopy (TEM) is a very powerful and versatile technique for determining not only particle size and distribution but also for examining the “quality” of the particles. A good stable dispersion would be expected to produce discrete perfectly spherical particles whereas for an unstable dispersion evidence of aggregation and flocculation would be observed. This evidence may be of the form of partly coalesced particles, nonspherical particles or regions of high particle density.
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Whilst TEM can measure particle size very precisely (less than 1 nm), the reproducibility of the result may be in doubt due to the relative number of particles measured, e.g. 1 cm$^3$ of a 50 vol-% dispersion may contain $10^{12}$ particles whereas on average only $10^2$ – $10^3$ particles are normally measured. This problem can be alleviated to some extent by counting particles from different areas of the sample. Another problem encountered in TEM is the heat generated by the electron beam. The temperature inside an electron microscope can reach over 100 °C, which means that polymers with a low glass to rubber transition temperature ($T_g$) may alter their shape or even film form. This is observed to a much larger degree with larger particles which are much less efficient at dissipating the heat generated away. This problem can be relieved by using a much lower beam intensity. Unfortunately, this can result in a decrease in the observed resolution of the particles. In extreme cases, such as those for particles with very low values of $T_g$ or for sensitive biological systems such as cells, a technique known as Cryo-TEM is used. In this application the sample is placed into a liquid nitrogen cooled chamber.

2.6.2.1.1 Calculation Of Average Particle Size From Transmission Electron Microscopy.

TEM micrographs were taken of dispersions, diluted (approximately 10:1) with the relevant diluent, using a Joel Temscan 100. The particle size and distributions of the non-aqueous dispersions synthesised in this work were calculated from measurements from these TEM micrographs. The particle size of the particles on the micrograph were measured using a ruler, rounding up to the nearest millimetre where
required. These measurements were converted to actual particle size measurements by calculating a scaling factor from a micrograph of a diffraction grating, at the same magnification, which has a constant 2160 lines/mm (line to line distance of 0.463 µm). The number average particle diameter \( (D_n) \) was calculated using Equation 2.6.a.

\[
D_n = \frac{\sum n_i d_i}{\sum n_i}
\]

Equation 2.6.a.

where:

- \( n_i \) is the number of particles of particle size \( i \).
- \( d_i \) is the particle size \( i \).

The weight average particle diameter \( (D_w) \) can be calculated by Equation 2.6.b.

\[
D_w = \frac{\sum w_i d_i}{\sum w_i}
\]

Equation 2.6.b.

where:

- \( w_i \) is the total weight of particles of particle size \( i \).

This equation can be expressed in the same terms as Equation 2.6.a.

\[
D_w = \frac{\sum n_i \frac{1}{2} \pi \left(\frac{d_i}{2}\right)^3 \rho d_i}{\sum n_i \frac{1}{2} \pi \left(\frac{d_i}{2}\right)^3 \rho}
\]

Equation 2.6.c.
where:

\( \rho \) is the density of the particles.

This equation reduces down to simple terms as follows:

\[
D_w = \frac{\sum n_i \left( \frac{d_i}{2} \right)^3 d_i}{\sum n_i \left( \frac{d_i}{2} \right)^3}
\]

Equation 2.6.d

\[
D_w = \frac{\sum n_i \left( \frac{d_i^3}{8} \right) d_i}{\sum n_i \left( \frac{d_i^3}{8} \right)}
\]

Equation 2.6.e

\[
D_w = \frac{\sum n_i d_i^4}{\sum n_i d_i^3}
\]

Equation 2.6.f

There are many possible ways to numerically describe the polydispersity of a dispersion. For the work reported here the polydispersity index used is simply the ratio of the weight average to the number average. The value of this index will always be greater than one but will approach unity for very monodisperse systems.

2.6.2.2 Disc Centrifugation.

In disc centrifugation the particle size determination is calculated by the rate at which the particles travel through a medium, of known viscosity, under an applied force. The relationship between particle
size and rate of travel is calculated using a modification of the Stokes-Einstein equation (Equation 2.6.g).

\[ t \propto \frac{\eta R_2}{\omega^2 (\rho_p - \rho_m) R_1 d^2} \]  

\textit{Equation 2.6.g}

where:

- \( t \) is the time elapsed after sample injection.
- \( \eta \) is the viscosity of the medium.
- \( \omega \) is the rotational velocity of the centrifuge.
- \( \rho_p \) is the density of the of the particle.
- \( \rho_m \) is the density of the medium.
- \( R_2 \) is the radius at which the measurements are taken.
- \( R_1 \) is the radius at which the particles were injected.
- \( d \) is the particle diameter.

This equation can be rearranged to give \textit{Equation 2.6.h}.

\[ R_2 \propto \frac{\omega^2 (\rho_p - \rho_m) R_1 d^2 t}{\eta} \]  

\textit{Equation 2.6.h}

Removing from this proportionality the experimental constants, 
\textit{Equation 2.6.h} simplifies to \textit{Equation 2.6.i}.

\[ R_2 \propto d^2 t \]  

\textit{Equation 2.6.i}

It can be seen therefore that at a given time \( t \) the larger particles will have travelled a much greater distance and hence particle size
separation is achieved. Measurements are taken at a single point and the cumulative distribution is measured over time. As the particle separation occurs due to particle weight this technique can only accurately give a weight average and the cumulative distribution although other averages may be estimated by further data manipulation.

The instrument used was a Brookhaven BI-DCP at Zeneca Resins, Runcorn. As the instrument is usually used for analysing aqueous emulsions, it was essential to develop an effective set of operating conditions. The experimental parameters that were varied were the spin rate and the spin fluid. From Equation 2.6.4 it can be seen that increasing the spin rate would be expected to increase the separation of the particles and hence give a more accurate distribution. Altering the spin fluid will change the density and viscosity of the medium, and hence may affect the results.

2.6.2.3 Photon Correlation Spectroscopy.

Dynamic light scattering is based upon Rayleigh light scattering from small particles (88, 89). The angle through which the light is scattered is related to the size of the particle, causing the scattering pattern, and also to the wavelength of the incident light. If the ratio of the wavelength of the incident light to the particle size is much less than unity, then the scattering angle is very small, e.g. using X-ray radiation (\( \lambda \sim 10 \text{ nm} \)) to study colloidal particles (\( d \sim 100 \text{nm} \)). However, if the ratio is much greater than unity, then the light is scattered through a
much greater angle. As the particles are under constant Brownian type diffusional motion the scattering pattern will be constantly changing. This change can be observed in terms of Doppler effects and the change over time correlated (90).

Experimentally, a vertically polarised He/Ne laser beam (\( \lambda = 632 \text{ nm} \)) is scattered through a dilute dispersion of the sample. The photons of light scattered in the horizontal plane are then detected using photomultipliers at a set angle (\( \theta \)). This set up is shown schematically in Figure 2.3. The signal to noise ratio of the apparatus is significantly improved if the incident light is focused onto the sample. The fluctuations in the intensity of the photons of light reaching the detector are analysed and the diffusion coefficient calculated. From this diffusional coefficient the particle size can be calculated using Equation 2.6.j.

\[
d = \frac{kT}{3\pi \eta D}
\]

\textit{Equation 2.6.j}

where:

- \( d \) is the particle diameter.
- \( k \) is the Boltzmann constant.
- \( T \) is the absolute temperature.
- \( \eta \) is the viscosity of the dispersing media.
- \( D \) is the diffusional constant.

For the work presented here a Malvern Zeta Master S was used and the dispersions diluted using hexane.
Figure 2.3 Schematic diagram of a Photon Correlation Spectrometer
2.7 Rheology

Viscosity is the ratio of shear stress (\( \sigma \)) to shear rate (\( \gamma \)). Measurements of viscosity are performed either under controlled stress conditions or controlled rate conditions. In the first instance the sample is subjected to a constant shear stress, e.g. by an air powered motor at a set pressure, and the shear rate is measured. In the alternative, a constant shear rate is applied and the force required to maintain this rate measured.

As well as there being two different methods for determining viscosities, rheometers can also be divided into two distinct formats. These are capillary rheometers and rotational rheometers and can either controlled stress or controlled rate versions. Capillary rheometers simply force the material through a narrow (capillary) die (Figure 2.4) and the mass flow rate or volume flow rate is calculated. Although from the flow rate and pressure data the viscosity can be calculated, it is often sufficient to simply determine the flow rate as generally it is the flow behaviour that is of most interest. This approach is a successful method for modelling the extrudability of polymer melts or the pumpability of plastisols. For rotational rheometers the sample is placed between a stationary surface and a rotating surface. This can occur via a number of geometries (Figure 2.5) such as cone and plate types or concentric cylinders. This type of rheometer is more suitable to studies of changes in rheological behaviour over time or changing conditions. Utilising the different geometries available, it is possible to study a very wide range of
Figure 2.4 Schematic Diagram Of Capillary Rheometers.
Figure 2.5 Schematic Diagram Of Some Of The Common Rotational Measuring Geometries.
viscosities. At very low viscosities the double gap configuration is used as this provides the greatest surface area and hence will have the greater resistance to motion. At very high viscosities the parallel plate system is used for the opposite reason, i.e. the surface area is minimised.

2.7.1 Experimental Conditions For Rheological Studies.

The rheometer used was the Bohlin CS-50 controlled shear stress rotational viscometer at Zeneca Resins. As temperature can critically affect the viscosity observed, the rheometer was maintained at a constant 25 °C using a water controlled system. Samples of the synthesised non-aqueous dispersions were studied using both a double gap geometry and a concentric cylinders system. The viscosity of cyclooctane was also measured using the double gap apparatus.

Measurements were taken over a sweep of shear stresses with the system allowed to reach equilibrium before each reading. These experiments were designed to study the effect that increasing the shear stress upon the system had upon the viscosity. In a Newtonian system, increasing the shear stress has no effect upon the viscosity. Other common effects are shear thickening, an increase in viscosity with increasing stress, and shear thinning, a decrease in viscosity with increasing shear stress. An important effect is dilatancy which is a reduction in the viscosity over time at a constant shear stress. To avoid this effect the stress sweep was as rapid as possible.
These experiments were repeated at a number of concentrations. To achieve concentrations lower than the initial state dispersion the samples were diluted using pure cyclooctane. The more concentrated samples were prepared by blowing a strong nitrogen stream over the surface of the dispersion. The solids content was calculated by drying an accurately weighed sample (approximately 0.5 g) of the dispersion in a 120 °C oven until a constant weight was achieved. The weight fraction of the dispersion is then simply the dry weight divided by the wet weight. This value was then converted into volume fraction using Equation 2.7.a.

\[
\phi_v = \frac{F_s \rho_{co}}{\left[F_s (\rho_{co} - \rho_p)\right] + \rho_p} \quad \text{Equation 2.7.a}
\]

where:
- \(\phi_v\) is the volume fraction of the dispersion
- \(F_s\) is the solids fraction of the dispersion
- \(\rho_{co}\) is the density of cyclooctane at 25 °C
- \(\rho_p\) is the density of the polymer at 25 °C

The maximum packing fraction for these dispersions was calculated using the procedures outlined in Section 3.7.2.
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Results and Discussion

The synthetic route employed was effectively a three stage process as outlined in Section 2.3.2.1.

3.1.1. Synthesis Of Carboxylic Acid Terminated Poly (2-Ethylhexyl Acrylate) Pre-Polymer.

After purification via dropwise addition of the concentrated poly (2-ethylhexyl acrylate) (PEHA) solution into cold methanol, the resulting clear colourless viscous polymer (MSEH 1) was carefully analysed using GPC, FT-IR and $^1$H NMR. Monomer conversion was calculated at a value of 65.02% on monomer.

GPC analysis of the polymer (Figure 3.1) yielded a number average molar mass ($M_n$) of 3,400 g mol$^{-1}$ and a polydispersity of 1.3. Values calculated from $^1$H NMR (Figure 3.2), however, gave a number average degree of polymerisation ($D_P_n$) of 24 which corresponds to a $M_n$ value of 3,900 g mol$^{-1}$. This discrepancy of around 500 g mol$^{-1}$ is equivalent to a difference of 3 repeat units. It should be remembered that the value calculated by GPC refers to a “polystyrene equivalent molar mass”. This is because the GPC columns are calibrated with polystyrene standards and not acrylic polymer standards. Hence, the molar mass is calculated as the molar mass of the polystyrene molecule required to exhibit the same hydrodynamic radius as the polymer being analysed. If a carboxylic acid terminated PEHA
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Figure 3.1 GPC Chromatogram Of The Carboxylic Acid Terminated PEHA Pre-Polymer.

Mn = 3352
Mw = 4471
Polydispersity = 1.334
Figure 3.2 $^1$H NMR Spectrum Of The Carboxylic Acid Terminated PEHA Pre-Polymer.
pre-polymer had a smaller hydrodynamic radius than the equivalent styrene polymer at the same molar mass, then GPC would be expected to underestimate the actual molecular mass. For the purposes of the work presented in this thesis, we have taken the GPC data to be reasonably accurate and used the values calculated by $^1$H NMR analysis for confirmation purposes only. This decision was taken on the basis that peaks observed in main chain polymer $^1$H NMR tend to be somewhat broad and hence peak integration may not always be as precise as is desirable. It should be mentioned that for the majority of cases in this thesis the difference between the results calculated by the two techniques is generally in the region of 1 - 2 repeat units.

Infrared Spectroscopy of the pre-polymer (*Figure 3.3*) showed three significant groups of absorptions. These occurred at:

i.) $1,734 \text{ cm}^{-1}$, a sharp intense peak relating to the carbonyl C=O stretch,

ii.) $2,859 - 2,960 \text{ cm}^{-1}$, a group of four sharp intense peaks relating to main chain C-H stretches,

iii.) $3,255 \text{ cm}^{-1}$, a broad and very weak peak relating to the terminal O-H stretch.

The observation of the terminal carboxylic acid, by FT-IR, is important, as this functionality was not observed by $^1$H NMR.

3.1.2. Conversion of pre-polymer to acyl chloride terminated PEHA intermediate.
Due to the extremely high moisture sensitivity of the acyl chloride and resulting oxidation to the carboxylic acid (Figure 3.4) there was no rigorous analysis performed.

\[ \text{Figure 3.4 Reaction Of Acyl Chloride With Water.} \]

### 3.1.3. Conversion of an acyl chloride terminated PEHA intermediate to macromonomer.

GPC analysis of the resulting opaque viscous oil (MSEM 1) gave a chromatogram (Figure 3.5) with no significant shoulders and a polydispersity of 1.3. This is the same polydispersity as calculated for the carboxylic acid terminated pre-polymer in Section 3.3.1. This indicates that there has been negligible homopolymerisation of the macromonomer during the end-capping reaction. The value for the $M_n$ of the macromonomer, from GPC, was 3,500 g mol$^{-1}$ which is in agreement with a pre-polymer $M_n$ of 3,400 g mol$^{-1}$. A large proportion of this increase in molar mass can be attributed to the end-capping entity.
Figure 3.5 GPC Chromatogram Of The Methacrylate Terminated PEHA Macromonomer.
From the $^1$H NMR analysis (Figure 3.6) of the polymer two previously unobserved peaks were clearly apparent. These resonances at 5.6 ppm and 6.1 ppm were assigned to the terminal vinylic unsaturation. The split in the chemical shift ($\delta$) is believed to be due to the stereochemical differences between the two protons on the vinyl methylene group (Figure 3.7).

\[
\begin{align*}
\text{Figure 3.7 Stereochemical Nature Of The Vinyl Bond.}
\end{align*}
\]

As can be seen from the above diagram the methylene protons exist as both cis and trans forms relative to the polymer main chain. This means that they are in different chemical environments and so will possess differing chemical shifts.

Macromonomer functionality ($F_{C=C}$) is defined as the proportion of the total polymer present possessing terminal unsaturation. This can be calculated simply from $^1$H NMR using Equation 3.1.3.a.

\[
F_{C=C} = \frac{\left( \frac{H_{k/l}}{4} \right)}{\left( \frac{H_b}{2} \right)}
\]

Equation 3.1.3.a

where:

$H_{k/l}$ is the integral of the peaks related to the protons labelled $k$ and $l$ in Figure 3.6
Figure 3.6 $^1$H NMR Spectrum Of The Methacrylate Terminated PEHA Macromonomer.
H_b is the integral of the peaks related to the protons labelled b in Figure 3.6

The macromonomer conversion calculated for MSEM 1 was only 33.69%. This means that only approximately one third of the polymer chains are macromonomers. It is believed that the low value may be due to moisture converting the acyl chloride intermediate back into the initial carboxylic acid terminated pre-polymer and thus preventing many of the pre-polymer chains being converted into macromonomer.

Some evidence for the reverse reaction can be observed in the IR spectrum (Figure 3.8) for the macromonomer MSEM 1. The carboxylic stretch (3,255 cm\(^{-1}\)) referred to in section 3.1.1 is greatly reduced which suggests that conversion of pre-polymer to macromonomer has occurred. The fact that it still exists infers that there is still carboxylic acid present in the final purified product. Although a peak can be observed which corresponds to the vinyl group stretch (1,685 cm\(^{-1}\)) it is a weak narrow vibration and can often only be observed as a shoulder on the strong C=O vibration (1,749 cm\(^{-1}\)).

From this evidence it was concluded that it is possible to prepare macromonomer via an acyl chloride intermediate. However, extreme care must been taken at all stages to ensure that there is minimal contact between the acid chloride terminated pre-polymer and any moisture either atmospheric or residual in the reagents used.
Figure 3.8 IR Spectrum Of The Methacrylate Terminated PEHA Macromonomer.
3.2. Evaluation Of The “Epoxide” Route For The Synthesis Of Macromonomer.

3.2.1 Effect Of Different Ring Opening Catalysts.

To allow for more accurate characterisation and analysis, this series of experiments was conducted using a low weight PEHA pre-polymer (MSEH 6). The polymer was produced in the same manner as previously described but using a higher thioglycollic acid to ethlyhexyl acrylate mole ratio. In this case the ratio used was 0.21:1 compared to the ratio of 0.1:1 used to produce MSEH 1. After the usual purification procedure of dropwise addition into cold methanol the resulting viscous polymer was characterised using GPC, FT-IR and $^1$H NMR.

After the subtraction of a spectrum for background moisture and CO$_2$ the FT-IR spectrum for MSEH 6 (Figure 3.9) showed the usual hydroxyl vibration at 3,246 cm$^{-1}$ and carbonyl vibration at 1,739 cm$^{-1}$. This indicates the existence of a carboxylic acid functionality. Again this IR evidence is important as $^1$H NMR (Figure 3.10) was unable to reveal the existence of a carboxylic acid proton expected between 10 ppm and 12 ppm. This is due to the low concentration relative to the main chain protons. The methylene protons adjacent to the carboxylic acid functionality and the sulphur atom were assigned to the peak occurring at 3.25ppm. From this NMR spectrum it was calculated that the pre-polymer had a DP$_n$ of 8 which corresponds to a M$_n$ of 1,600 g mol$^{-1}$. This value is in very good agreement with the GPC results, which also gave a M$_n$ of 1,600 g mol$^{-1}$. 
Figure 3.9 IR Spectrum Of A Low Molecular Weigh Carboxylic Acid Terminated PEHA Pre-Polymer.
Figure 3.10 $^1$H NMR Spectrum Of A Low Molecular Weight Carboxylic Acid Terminated PEHA Pre-Polymer.
Macromonomer conversions were carried out at 140 °C in xylene using a 1.5 molar excess of GMA. The tertiary amine catalysts were used at 1.7 wt-% on pre-polymer. Purification was achieved by subjecting the reaction mixture to evaporation under reduced pressure, using a Buchi rotary evaporator, to remove the reaction solvent. The resulting viscous, vivid orange oil was then further purified using Buchi short-path distillation equipment, set to 100 °C for 2 hours, to remove the high boiling residual GMA.

In all cases, IR spectroscopy (Figure 3.11) showed a marked reduction of the hydroxyl vibration at 3,250 cm⁻¹ whilst there was no significant loss of the carbonyl vibration at 1,740 cm⁻¹.

GPC analysis (Figure 3.12) shows a $M_n$ increase of approximately 300 g mol⁻¹ relative to the value for MSEH 6. Whilst this is much larger than the 91 g mol⁻¹ that could be attributed to the GMA adduct, it was considered that the size of the increase was not a matter of major concern. This is because the change in the nature of the end group, from carboxylic acid to vinylic unsaturation, could have a significant effect upon the interactions between the polymer and the column packing. It is probable that there will be stronger interactions between the acidic pre-polymer and the packing material than for the macromonomer. This would therefore lead to an increase in the retention time for the pre-polymer and therefore an underestimation of the $M_n$ calculated by size exclusion methods. The effect of the end group on the separation is much more pronounced for small polymer molecules than for larger ones. This is because, in shorter polymer chains, the overall adsorption contribution from the chain ends, is
Figure 3.11. (a) Comparison Between The IR Spectra Of Pre-Polymer And Macromonomer Produced Using No Catalyst.
Figure 3.11.(b) Comparison Between The IR Spectra Of Pre-Polymer And Macromonomer Produced Using Et$_2$N Catalyst.
Figure 3.11. (c) Comparison Between The IR Spectra Of Pre-Polymer And Macromonomer Produced Using BDMA Catalyst.
Figure 3.11.(d) Comparison Between The IR Spectra Of Pre-Polymer And Macromonomer Produced Using DBCO Catalyst.
Figure 3.11 (e) Comparison between the IR spectra of pre-polymer and macromonomer produced using DMDA catalyst.

Wavenumbers (cm⁻¹)

3249.4 cm⁻¹
3243.7 cm⁻¹
2865.6 cm⁻¹
2964.0 cm⁻¹
1741.6 cm⁻¹
1739.2 cm⁻¹

% T
Figure 3.12 GPC Chromatogram Of A Macromonomer Produced Using A Ring Opening Catalyst.
significantly increased. None of the GPC chromatograms displayed any observable main peak shoulders or secondary peaks, which would be characteristic of the existence of unwanted side reactions involving the vinyl functionality of the macromonomer.

Analysis by $^1$H NMR (Figure 3.13) showed the presence of two groups of peaks at 5.6 ppm and 6.1 ppm which were not observable in the NMR of the pre-polymer MSEH 6 (Figure 3.10), but had been assigned to the unsaturated chain end in the $^1$H NMR spectrum of GMA (Figure 3.14). Macromonomer conversion can be calculated as before using the formula described in section 3.1.3. The results for the four tertiary amine and catalysed reactions and for an uncatalysed reaction are presented in Table 3.2.1.

<table>
<thead>
<tr>
<th>Macromonomer</th>
<th>Catalyst</th>
<th>$M_n$ *</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSEG 2 **</td>
<td>None</td>
<td>3,500 g mol$^{-1}$</td>
<td>13.69 %</td>
</tr>
<tr>
<td>MSEG 8</td>
<td>Et$_3$N</td>
<td>1,700 g mol$^{-1}$</td>
<td>64.91 %</td>
</tr>
<tr>
<td>MSEG 9</td>
<td>BDMA</td>
<td>1,900 g mol$^{-1}$</td>
<td>52.24 %</td>
</tr>
<tr>
<td>MSEG 10</td>
<td>BDCO</td>
<td>1,900 g mol$^{-1}$</td>
<td>84.64 %</td>
</tr>
<tr>
<td>MSEG 11</td>
<td>DMAD</td>
<td>2,000 g mol$^{-1}$</td>
<td>51.42 %</td>
</tr>
</tbody>
</table>

* As calculated by GPC

** Based upon a 3,500 g mol$^{-1}$ pre-polymer

Table 3.2.1 Macromonomer Conversion Results For Different Ring Opening Catalysts.

Although the uncatalysed conversion reaction was performed using a 3,500 g mol$^{-1}$ pre-polymer, it is unlikely that this has had any
Figure 3.13 $^1$H NMR Spectrum Of A Macromonomer Produced Using A Ring Opening Catalyst.
Figure 3.14 $^1$H NMR Spectrum of GMA.
significant contribution to the comparatively poor macromonomer conversion.

The uncatalysed end capping reaction occurs by a different mechanism to the catalysed reaction and indeed produces a slightly different end product. Describing the reaction that produced MSEG 2 as uncatalysed is a misnomer, it is in fact a self catalysing, acid catalysed ring opening reaction and occurs via the mechanism shown in Figure 3.15. The important point to observe is that the nucleophile, the carboxylic acid, attacks at the most substituted ring carbon. This initially seems unusual as attack at the less substituted would sterically be more favourable. The more substituted carbon is, however, able to bear a greater positive charge because of its strong resemblance to the, comparatively, stable tertiary carbocation. This reaction is inefficient for three main reasons:

i.) The predominant driving force for the reaction is the relief of ring strain. Whilst epoxides are highly strained molecules, they are very stable compared to similar 3 membered ring systems.

ii.) The level of free acid falls with increasing macromonomer conversion.

iii.) Nucleophilic attack occurs at the more substituted ring carbon and therefore reaction is restricted by steric factors.

With all of the catalysts investigated there was a distinct improvement to the macromonomer conversion compared to the uncatalysed reaction. The tertiary amine catalysed reactions occur by a very different mechanism (Figure 3.16) to the acid catalysed reactions. In
Figure 3.15 Schematic Representation Of The Mechanism For The Acid Catalysed Reaction Between Glycidyl Methacrylate And A Carboxylic Acid Terminated Pre-Polymer.
Figure 3.16 Schematic Representation Of The Mechanism For The Tertiary Amine Catalysed Reaction Between Glycidyl Methacrylate And A Carboxylic Acid Terminated Pre-Polymer.
this reaction the nucleophile is the tertiary amine which attacks the less substituted epoxide ring carbon as is conventional for a nucleophilic substitution (Sn2) reaction. This reaction centre is preferred due to its reduced steric crowding factors, and hence the increase in the macromonomer conversion between the catalysed and uncatalysed reactions.

The two large catalysts DMAD and BDMA showed the least improvement of all of the catalysts (an increase of less the 40%). This may be caused by the large bulky side groups (C10 and phenyl respectively) physically reducing the access for the pre-polymer to the activated GMA. The simple molecule Et3N with its much smaller side groups consequently shows a further increase of 10% on the values for DMAD and BDMA. The diamine DBCO showed the greatest improvement (over 70%) compared to the uncatalysed reaction. This improvement over the previous catalysts may be due to DBCO possessing two amine functionalities, and hence two possible active centres per molecule. This in turn suggests that it is plausible to expect DBCO to be able to catalyse many more end capping reactions over the same period of time relative to a catalyst containing a single amine functionality.

3.2.2. Effect Of Reaction Temperature On Macromonomer Conversion.

Reactions for these experiments were carried out on a 2,600 g mol⁻¹ carboxylic acid terminated PEHA pre-polymer (MSEH 3). This prepolymer had been synthesised, purified and characterised by the
methods previously described in Section 2.3.2.3.2. Due to the temperatures involved, the macromonomer conversions were performed in two different solvents. The high temperature reaction (MSEG 6) was carried out in xylene at 140 °C and the lower temperature reaction (MSEG 5) carried out in ethyl acetate at 65 °C. The macromonomer conversion reactions used the tertiary amine dimethylamino dodecane (DMAD) as a ring opening catalyst. Purification was achieved in the same manner as described in the previous section, i.e. the use of short path distillation equipment.

Analysis of the resulting viscous orange oils by GPC (Figure 3.17) showed no evidence characteristic of secondary polymerisation for either macromonomer. This evidence would include features such as peak broadening, increased polydispersity or secondary peaks of significant proportions. None of these effects were observed, and indeed the GPC chromatograms show a reduction in the polydispersity of the macromonomers compared to the pre-polymer. Number average molar masses were increased by 250 g mol\(^{-1}\) and 400 g mol\(^{-1}\) for MSEG 5 and MSEG 6 respectively. As had been observed in the catalysis work a large proportion of this molar mass increase can be attributed to the extra end capping moiety and its effect upon the retention time.

Comparing the IR spectra for both reactions with the spectrum for the pre-polymer (Figure 3.18) it is evident that a number of peaks have appeared that did not exist in the pre-polymer and some pre-polymer peaks no longer exist, or are greatly reduced. The two regions of importance here are at:


Figure 3.17 GPC Chromatogram Of A Macromonomer Produced At High Reaction Temperatures.
Figure 3.18 (a) Comparison Between The IR Spectrum Of The Macromonomer Produced At High Temperature And The Spectrum Of The Related Pre-Polymer.
Figure 3.18 (b) Comparison Between The IR Spectrum Of The Macromonomer Produced At Moderate Temperature And The Spectrum Of The Related Pre-Polymer.
i.) 1,700 cm\(^{-1}\), a sharp but weak peak, observed as a shoulder on the intense carbonyl at 1,750 cm\(^{-1}\), relating to a vinylic unsaturation vibration.

ii.) 3,100 cm\(^{-1}\) - 3,400 cm\(^{-1}\), a broad, weak peak relating to the carboxylic acid hydroxyl stretch.

In the two macromonomer spectra, the carboxylic acid stretch is greatly reduced suggesting that reaction has occurred at the chain ends for both reactions. In the case of MSEG 6, for the 140 °C reaction, this peak is almost unobservable whereas in the spectrum for MSEG 5 the hydroxyl stretch is clearly evident. This suggests that the level of pre-polymer to macromonomer conversion (F\(_{C-C}\)) is much greater for the reaction at the higher temperature than the lower temperature. The vinyl peak, which is much stronger in the spectrum for MSEG 6, confirms the suggestion of higher macromonomer conversion with increasing temperature.

Applying Equation 3.1.3.a to the NMR spectrum of MSEG 5 and MSEG 6 (Figure 3.19) the difference in the level of macromonomer conversion between the two reactions may be compared quantitatively. The reaction at the lower temperature had a macromonomer conversion of 15.36 % compared to the high temperature reaction, which had a macromonomer conversion of 71.38 %. This five-fold increase in conversion clearly demonstrates the importance of using an elevated temperature when conducting an epoxide ring opening reaction of this kind. Considering the proposed reaction mechanism (Figure 3.16), for this end capping reaction, it is
Reaction Temperature

Figure 3.19: H NMR of the Macromonomer Produced at High

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likely that the rate determining step (RDS) will be the initial opening of the epoxide ring. An increase in the thermal energy of the system would be expected to lead to a reduction in the stability of this ring and hence improve the speed of this RDS.

It is interesting to observe that a catalysed reaction at 65 °C gives a slightly higher macromonomer conversion than the uncatalysed reaction at 140 °C. This highlights how important both factors are in achieving a high level of pre-polymer to macromonomer conversion.

3.3 Graft Copolymer Synthesis.

Copolymers were synthesised using macromonomers prepared by both the acyl chloride route and the epoxide route. Purification was achieved via the dropwise addition of the concentrated polymer solution into hot methanol. The methanolic supernatant, containing the residual PEHA macromonomer, was decanted off and the precipitated polymer dried in a vacuum oven to remove trapped solvent.

The purification process was followed throughout using GPC. In the GPC chromatogram for an unpurified copolymer, (Figure 3.20), two overlapping peaks are evident. The peak occurring at the shorter retention time (A) corresponds to the copolymeric material and the second peak (B) to unreacted macromonomer. After each purification cycle the macromonomer peak is reduced until it can only be observed as a slight shoulder on the main copolymer peak (Figure 3.21). Reduction of the residual macromonomer content below this level is
Figure 3.20 GPC Chromatogram Of The Unpurified Graft Copolymer.
Mn = 27211
Mw = 50663
Polydispersity = 1.862

Figure 3.21 GPC Chromatogram Of The Graft Copolymer After Several Purification Cycles.
difficult and occurs at the great expense of the loss of the copolymer. One possible explanation for this is that the copolymer may form micelles in the methanolic medium (Figure 3.22.a) and that much of the residual unreacted macromonomer becomes entrapped in these macromolecular aggregates (Figure 3.22.b). Theoretically this problem should be simple to overcome by using a sufficiently high quantity of methanol, such that the copolymer concentration is well below its Critical Micelle Concentration (CMC) at all times.

However, CMCs are often only fractions of a percent, e.g. the CMC of the Synperonic surfactant Fl27 at 25 °C is approximately 0.1 wt-% (91, 92). Whilst it would be expected for a non-aqueous steric stabiliser to have a higher CMC this would still require the use of the order of a hundred times volumetric excess of methanol. This would be difficult to achieve in a laboratory environment on the size scale in this study. It was found that the precipitation of the copolymer was rapid and so the total copolymer concentration in the methanolic solution would be low at any one instance and a ten-fold excess was considered to be a satisfactory compromise.

It is essential, however, that the rate of addition of the polymeric solution to the hot methanol is very slow. This is because in the microscopic area where the copolymer solution comes into contact with the methanol, the copolymer concentration is well above the CMC and hence may form a localised micellar region. If the rate of addition of copolymer is sufficiently slow then these micelles have a much greater probability of breaking up in the medium, therefore leading to a micelle free macroscopic picture. If, however, the
Figure 3.22. (a) Schematic Diagram Of Micelle Formation.
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Figure 3.22. (b) Schematic Diagram Of The Entrapment Of Macromonomer Into Micelle.
copolymer addition rate is too rapid, then the copolymer will form large heterogeneous particles, containing macromonomer, which will swiftly precipitate out thus leading to an inefficient purification process.

The existence of a small quantity of macromonomer contaminant in the purified copolymer will not adversely affect its performance as a steric stabiliser. Indeed it may help to increase to the stability of the dispersion particles as polymerisation can occur between the monomer and macromonomer which will consequently lead to the production of a polymeric particle core with a chemically bound surface stabilising moiety. Hence, desorption of the stabiliser becomes physically impossible.

From the GPC analysis of the unpurified copolymer (*Figure 3.20*) it is possible to calculate the level of conversion of macromonomer to copolymer. This is based upon the method developed by Niwa et al.\(^{93}\) for the calculation of macromonomer conversion in the homopolymerisation of macromonomers. The equation they developed was:

\[
X_a = 1 - \frac{RL}{K_{am}(RI).c}
\]

Equation 3.3.a

where:

- \(X_a\) is the macromonomer conversion
- \(RL\) is the peak area of the low weight (macromonomer) peak B
- \(K_{am}(RI)\) is an empirical instrument constant
This equation had to be modified for it to be applicable to the situation reported here. The peaks observed in Figure 3.20 overlap significantly and so the peak area (RL) cannot be used. Although the GPC Caliber software does allow for the deconvolution of overlapping peaks it is a function that was not considered to be suitable for quantitative analysis. The solution employed here was to use the peak height of the unreacted macromonomer (Pu). It was essential that the concentration term \( c \) was modified to take into account the presence of styrene in the initial monomer mixture. The new concentration was calculated using the following equation:

\[
C = c F_M \tag{Equation 3.3.b}
\]

where:

- \( C \) is the maximum macromonomer concentration
- \( c \) is the sample concentration
- \( F_M \) is the fraction of macromonomer in the initial monomer mixture

A further correction could be introduced into this concentration term to take into account the macromonomer functionality (\( F_{C-c} \)). However for the majority of the macromonomers copolymerised during this work \( F_{C-c} \) is high and so this additional correction was subsequently ignored.
Since the peak height was used for the calculations of macromonomer conversion then it is also important that the empirical constant is derived from peak heights. This new empirical constant \((K)\) is obtained by measuring the peak heights of a number of chromatograms over a range of macromonomer concentrations. The gradient of a plot of these peak heights against their macromonomer concentration (Figure 3.23) is the empirical constant \(K\). So equation 3.3.a now becomes:

\[
X_a = 1 - \frac{P_u}{KC}
\]

Equation 3.3.c

The incorporation of the macromonomer into the backbone is confirmed by the IR spectrum of the purified polymer. Comparing the copolymer spectrum to the spectrum for the related macromonomer (Figure 3.24), a number of significant factors can be observed.

i.) 1,494 cm\(^{-1}\), 1,581 cm\(^{-1}\) and 1,601 cm\(^{-1}\). Sharp strong peaks relating to the styrene ring carbon resonances on the copolymer spectrum.

ii.) 1,682 cm\(^{-1}\). Loss of weak vinyl unsaturation vibration from macromonomer spectrum.

iii.) 1,735 cm\(^{-1}\). Strong sharp peak relating to the macromonomer main chain carbonyl remaining in the copolymer spectrum.

iv.) 2,855 cm\(^{-1}\) → 2,961 cm\(^{-1}\). Group of four intense peaks relating to the macromonomer main chain remaining in the copolymer spectrum.

v.) 3,004 cm\(^{-1}\) → 3,101 cm\(^{-1}\). Five sharp intense peaks relating to the copolymer styrene ring C–H stretches.
Figure 3.23 Calibration Curve For The Determination Of The Response Constant $K$. 

$MSEG 17/18$

$y = 2.90x$
Figure 3.24 Comparison Of The IR Spectra For The Graft Copolymer And The Macromonomer.
The two groups of multiple peaks, i.) and v.), indicated that styrene had been incorporated into the final copolymer. The peaks at 1,494 cm\(^{-1}\) and 1,601 cm\(^{-1}\) result from the vibrations involving the meta–para carbon bonds and the ortho–meta carbon bonds. The much smaller peak, at 1,581 cm\(^{-1}\), is from the vibration of the bonds between the ortho carbons and the pendant ring carbon. This vibration is much weaker than the other carbon ring vibrations due to the much bulkier side group, the polymer chain, of the pendant carbon and thus will require a greater energy contribution to initiate bond motion. The groups of peaks between 3,004 cm\(^{-1}\) and 3,101 cm\(^{-1}\) are probably, in fact, a group of six peaks rather than the observable five peaks, with the sixth peak being masked by the group of peaks iv.). The six peaks are two slightly offset groups of three peaks with the stronger in-plane bend being followed by its related out-of-plane bend. The weakest pairing at 3,101 cm\(^{-1}\) is from the stretch of the C–H bond at the para position. This stretch is the weakest simply because there is only one such bond per styrene ring. The strongest pair (3,025 cm\(^{-1}\)) are those relating to the meta positioned C–H bonds. These meta resonances are marginally stronger than those occurring at the ortho position as there is less possibility of steric interaction between the meta ring protons and other atoms.

The groups of peaks observed at 1,735 cm\(^{-1}\) and between 2,855 cm\(^{-1}\) – 2,961 cm\(^{-1}\), iii.) and iv.) are the PEHA resonances observed in Section 3.1.1. The loss of the vinyl peak ii.), at 1,680 cm\(^{-1}\), suggests that there is negligible unreacted macromonomer left in the purified polymer and therefore the PEHA resonances observed in the copolymer spectrum must be from polymerised macromonomer. From
the IR spectrum of the copolymerised material it cannot be determined if there are two homopolymers, a copolymer or some combination of all three. It can be seen from the earlier GPC analysis (*Figure 3.21*) that the purification technique employed here works very well at removing a large proportion of PEHA. This together with the observation by Duddington (*58*) that PEHA macromonomers do not homopolymerise readily suggests that negligible quantities of homopolymacromonomer have been produced. Slark (*57*) demonstrated, using thin layer chromatography, that during the copolymerisation of styrene with acrylic macromonomers there was no appreciable amount of homopolystyrene produced. Therefore, it can be stated that graft copolymers of styrene with PEHA macromonomers can be readily produced from simple monomers by the method described here.

For a copolymer to work well as a steric stabiliser a balance must be achieved between the ratios of the anchor content and the stabilising content. If the proportion of the anchor component is too high, then although the graft copolymer will be well anchored to the polymer particle surface the barrier layer will be insufficient and therefore the particles will be unstable. This high anchor content could arise from the following conditions:

1. Macromonomer to monomer ratio too far in the favour of the monomeric anchor.
2. Stabilising chain length too short.
In the first case the graft frequency will be too low for effective stabilisation. This means that whilst good surface coverage can be achieved by the graft copolymer the steric barrier will be weak, in terms of stabilising functionalities per unit surface area, and hence particles may easily aggregate. In the second case too short a macromonomer chain length will offer an insufficiently thick barrier layer. Thus, there will be less repulsive force acting between particles than is required for the formation of stable particles.

However, if the anchor to stabiliser balance (ASB) is too low then stable particles will not form because the graft copolymer will not be adhered to the particle surface with sufficient strength and may be easily desorbed. In this situation the graft copolymer may be considered to be in equilibrium between the diluent and the particle surface. As such the equilibrium is sensitive to alterations to the local environment. Changes to the overall concentration of the stabiliser, during the purification cycles of centrifugation and redispersion, will upset this delicate balance allowing the stabiliser to leach off from the particle surface and into the diluent. A low ASB may occur for the following reasons:

1. No strong physical/chemical attraction between the polymer particle surface and the intended anchor section of the graft copolymer.
2. Macromonomer to monomer ratio too far in favour of the stabilising macromonomer.
In the first instance if there is no specific attraction between the anchor group of the graft copolymer and the polymer particle, then there will be no driving force for the adsorption of the graft copolymer onto the particle surface. In certain circumstances, such as the stabilisers reported here, there may be no apparent attraction between the anchor group and particle surface and yet they function well as steric stabilisers. These types of stabilisers work because the anchor section is very insoluble in the diluent and so the graft copolymer and growing polymer chains will aggregate together to form areas of low diluent concentration which will become the polymer particles. The growing polymer chains may, as they grow, overlap the steric stabiliser physically binding that chain to the polymer particle and thus prevent desorption. In the second case a low monomer to macromonomer ratio may cause unstable particles, as the stabiliser will not form the required micellar structure. This is because the high graft frequency will keep the graft copolymer fully diluent soluble.

It is therefore necessary to calculate both the graft frequency and ASB. These are calculated using the following equations:

$$S: E = \frac{\left(\frac{P_{\text{STY}}}{5}\right)}{\left(\frac{P_{\text{EHA}}}{2.\text{DP}_n}\right)}$$  

Equation 3.3.d

where:

$S : E$ is the mole ratio of styrene to macromonomer
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$P_{\text{STY}}$ is the peak area of the styrene ring peaks ($\delta = 6.5$ and 7.2) from the $^1$H NMR of the purified copolymer (Figure 3.25)

$P_{\text{EHA}}$ is the peak area of the EHA $\text{S-CH}_2$ peak ($\delta = 4.0$) from the $^1$H NMR of the purified copolymer

$\text{DP}_n$ is the number average degree of polymerisation of the macromonomer determined from $^1$H NMR of the purified macromonomer (Figure 3.13)

$$W_g = \frac{M_n\text{GRAFT}}{M_n\text{GRAFT} + (S\cdot E\cdot M_{\text{STY}})}$$

Equation 3.3.e

where:

$W_g$ is the weight fraction of grafts per chain

$M_n\text{GRAFT}$ is the number average molar mass of the macromonomer as determined by GPC (Figure 3.17)

$M_{\text{STY}}$ is the molar mass of styrene.

$$N_g = \frac{M_n\text{COPOLY} \cdot W_g}{M_n\text{GRAFT}}$$

Equation 3.3.f

where:

$N_g$ is the number average of grafts per chain

$M_n\text{COPOLY}$ is the number average molar mass of the purified copolymer as determined by GPC (Figure 3.21)

$$\text{ASB} = \left( \frac{M_n\text{COPOLY}}{M_n\text{GRAFT} \cdot N_g} \right) - 1$$

Equation 3.3.g
Figure 3.25 H NMR of the Purified Copolymer
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where:

ASB is the anchor to stabiliser balance

The values of $N_g$ and ASB for all of the copolymers used in the synthesis of polymer particles in this thesis are presented in Table 3.3.1. From this table it can be seen that the stabilisers prepared fall into three broad classes.

1. Low graft frequency ($\sim 1.6$) and high ASB ($\sim 4:1$), i.e. MSES 1
2. Intermediate graft frequency ($\sim 3.25$) and lower ASB ($\sim 2.15:1$), i.e. MSES 6 and MSES 7
3. Higher graft frequency ($\sim 5$) and low ASB ($\sim 1.5:1$), i.e. MSES 2, MSES 3, MSES 4 and MSES 5.

That there were three ranges of stabiliser produced was initially surprising as all of the copolymerisations were based around the same mole ratios. There was one difference between the polymerisation for MSES 1 and the polymerisations for the other copolymers. This difference was that for MSEM 1, the macromonomer functionality ($F_{C-C}$) had not been taken into account when calculating the quantities required and thus significantly less active macromonomer was present in the reaction mixture than was intended. This clearly accounts for the low graft frequency and high ASB values that have been calculated for MSES 1. The variations between the other copolymers are somewhat harder to explain as all of the polymerisations had the macromonomer functionality taken into account. However, this once more may be the root cause of the variation in graft frequency. If the macromonomer functionality had been overestimated then there would be less active
macromonomer in the polymerisation than was believed and hence there would be fewer grafts per chain than expected. This overestimation is possible as $F_{C=C}$ is calculated from the peak heights of small peaks in the $^1H$ NMR spectrum and hence a small error in the peak integration may have a large effect on the calculation of the macromonomer functionality.

<table>
<thead>
<tr>
<th>Stabiliser</th>
<th>Graft Mn (gmol$^{-1}$)</th>
<th>$F_{C=C}$ (%)</th>
<th>$M_{n, COPOLY}$ (gmol$^{-1}$)</th>
<th>$N_5$</th>
<th>ASB</th>
<th>$X_a$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSES 1</td>
<td>MSEM 1 3,500</td>
<td>33.69</td>
<td>27,200</td>
<td>1.57</td>
<td>3.9</td>
<td>7.8</td>
</tr>
<tr>
<td>MSES 2</td>
<td>MSEG 6 3,000</td>
<td>71.38</td>
<td>31,300</td>
<td>4.33</td>
<td>1.4</td>
<td>57.68</td>
</tr>
<tr>
<td>MSES 3</td>
<td>MSEG 12 3,000</td>
<td>99.5</td>
<td>36,600</td>
<td>5.06</td>
<td>1.5</td>
<td>61.85</td>
</tr>
<tr>
<td>MSES 4</td>
<td>MSEG 15 2,300</td>
<td>85.52</td>
<td>34,400</td>
<td>5.45</td>
<td>1.8</td>
<td>57.01</td>
</tr>
<tr>
<td>MSES 5</td>
<td>MSEG 15 2,300</td>
<td>85.52</td>
<td>21,900</td>
<td>5.12</td>
<td>0.9</td>
<td>56.07</td>
</tr>
<tr>
<td>MSES 6</td>
<td>MSEG 16 2,600</td>
<td>77.15</td>
<td>27,300</td>
<td>3.37</td>
<td>2.1</td>
<td>33.88</td>
</tr>
<tr>
<td>MSES 7</td>
<td>MSEG 17/18 2,600</td>
<td>80.45</td>
<td>25,900</td>
<td>3.12</td>
<td>2.2</td>
<td>68.01</td>
</tr>
</tbody>
</table>

*Table 3.3.1 Characterisation Of The Steric Stabilisers Used In The Non-Aqueous Dispersion Polymerisation Of Poly (Methyl Methacrylate).*
3.4 Synthesis Of Poly (Methyl Methacrylate) Particles Via Non-Aqueous Dispersion Polymerisation.

3.4.1 Comparison Of Particle Sizing Techniques.

For the remainder of the work reported here, it was important that the particles synthesised, via non-aqueous dispersion polymerisation, were characterised thoroughly and accurately. To determine which of the many possible techniques to employ, three of the simplest and most common methods available were critically studied with three non-aqueous polymer dispersions. These techniques were:

i.) Disc Centrifugation (DC)
ii.) Photon Correlation Spectroscopy (PCS)
iii.) Transmission Electron Microscopy (TEM)

The dispersions were formed using hexane as the diluent and were one stage polymerisations. The dispersions were subsequently purified by the centrifugation/redispersion process described in Section 2.6.1.1., using heptane as the redispersing medium. Heptane was preferred to hexane for this role since its lower volatility means that the diluent is less likely to evaporate during the purification cycles, whilst still retaining chemical characteristics similar to those of hexane. Four purification cycles were considered to be sufficient for the complete removal of unadsorbed steric stabiliser and unreacted monomer.

Characterisation by DC was performed at Zeneca Resins, Runcorn with guidance from Dr. Andy Overend. The instrument at Zeneca is usually set up for running aqueous dispersions and so it was essential
that a new set of operating conditions was developed. For DC to work effectively, the rate of travel of the dispersion sample through the operating medium must not be too great. In the case of aqueous dispersions this is not usually a problem as the densities of both the polymer particles (~1.2 g ml⁻¹) and water are close. For non-aqueous dispersions however, the difference may be great, e.g. density of hexane is approximately 0.8 g ml⁻¹. There are three possible ways to reduce the rate at which the polymer travels through the fluid under centrifugation.

The first option is to create a liquid barrier, in the operating fluid, which will move slowly through the spin fluid. This is achieved using a small quantity of a viscous material of similar density to the spin fluid which means that polymer will flow at a slower, more controlled, rate through the instrument (Figure 3.26). This, however, requires very careful interpretation and can only be used on a well understood and well documented system, such as aqueous dispersions where the required corrections are known.

The second system is to use a spin fluid denser than the dispersing medium. Whilst this does involve mixing diluents, the effect of the dispersing medium is minimal due to the small sample size required.

A third option involves the careful selection of the spin rate. If the spin rate is too high, then the polymer particles will travel through the spin fluid at too high a rate and thus overestimate the particle size whilst underestimating the particle size distribution. If the spin rate is too slow, then the centrifugal force upon the particles will not be the
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*Without secondary liquid barrier*

Rapid particle travel

*With secondary liquid barrier*

Restricted particle travel

Rotor direction

Barrier fluid

Figure 3.26. Schematic Diagram Of The Viscous Barrier System Used In Disc Centrifugation.
dominant force causing motion and thus feathering of the front of the particle band will occur.

In this study the first option was rejected due to the lengthy procedure required in calculating the viscosity and refractive index of the spin fluid at specific points through the region under measurement. The second and third options were studied in combination and the results for the dispersion MSMD 4 are presented in Table 3.4.1. Using cyclooctane (CO) as the spin fluid required a higher spin rate, compared with isopropyl alcohol (IPA), due to the higher viscosity of cyclooctane.

<table>
<thead>
<tr>
<th>Spin Fluid</th>
<th>Spin Rate</th>
<th>$D_n$</th>
<th>$D_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPA</td>
<td>1,500 rpm</td>
<td>455 nm</td>
<td>574 nm</td>
</tr>
<tr>
<td>IPA</td>
<td>2,000 rpm</td>
<td>382 nm</td>
<td>457 nm</td>
</tr>
<tr>
<td>IPA</td>
<td>2,500 rpm</td>
<td>426 nm</td>
<td>532 nm</td>
</tr>
<tr>
<td>CO</td>
<td>5,000 rpm</td>
<td>250 nm</td>
<td>374 nm</td>
</tr>
<tr>
<td>CO</td>
<td>6,000 rpm</td>
<td>295 nm</td>
<td>371 nm</td>
</tr>
</tbody>
</table>

Table 3.4.1. Number ($D_n$) And Weight ($D_w$) Average Particle Size Determined For MSMD 4 By Disc Centrifugation Using Different Spin Fluids And Spin Rates.

These values vary greatly and there does not appear to be the expected relationship between higher spin rates and an overestimation of particle size. One of the reasons for this is that the refractive index (RI) difference between the polymer particles and the spin fluid is small and the RI detector is unable to record a strong response at the
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desired concentrations and hence the signal to noise ratio is poor. Increasing the polymer concentration improves the detector response but leads to a broadening of the distribution recorded. The data obtained using CO and 6,000 rpm gave the best raw data curve and hence a more reliable result. This may be because the higher spin rate reduced the diffusive peak broadening associated with higher polymer particle concentrations and so it was possible to obtain a better detector response with a larger sample size.

Characterisation by TEM was performed at the Institute of Polymer Technology and Materials Engineering (IPTME) at Loughborough University. The TEM micrographs were taken by Mr. John Bates in the electron microscopy suite and the negatives subsequently developed by Youngs Cameras of Leicester. The PCS work was performed in the particle sizing laboratories in the Department of Chemical Engineering using a Malvern Zeta-sizer. The results acquired for the three dispersions, by the three techniques, are presented in Table 3.4.2. The DC data was achieved using CO as the spin fluid and a spin rate of 6,000 rpm.

As can be seen from the above table there is poor agreement between the three particle sizing techniques with respect to the average particle sizes calculated. However, associated with each technique there are a number of possible causes in the inaccuracy of each reported result. For PCS it is likely that rapid settling of the particles observed during the lifetime of experiment would have caused errors in the measurement. For PCS to perform effectively the most dominant motion must come from the Brownian motion of the particles and not...
from settling forces. In the case of DC the errors are likely to be due to a combination of problems. To achieve a good signal to noise ratio, a high sample concentration is required; however, to reduce feathering of the polymer particle band as it travels through the spin fluid a high spin rate is required. If this spin is too high though, then turbulent effects may occur in the fluid retarding the travel of the particle band and hence underestimating the particle size. The most significant problem with TEM analysis is the comparatively low number of particles measured and also the subjectivity of the operator in both selecting which particles to photograph and also in the measurement of the particles.

<table>
<thead>
<tr>
<th></th>
<th>PCS</th>
<th></th>
<th>DC</th>
<th></th>
<th>TEM</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D_n</td>
<td>D_w</td>
<td>D_n</td>
<td>D_w</td>
<td>D_n</td>
<td>D_w</td>
</tr>
<tr>
<td>MSMD 4</td>
<td>767.4</td>
<td>969.3</td>
<td>295</td>
<td>371</td>
<td>297.6</td>
<td>666.0</td>
</tr>
<tr>
<td></td>
<td>464.1</td>
<td>486.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSMD 5</td>
<td>442.0</td>
<td>453.2</td>
<td>174.0</td>
<td>192.0</td>
<td>224.7</td>
<td>350.4</td>
</tr>
<tr>
<td>MSMD 6</td>
<td>461.6</td>
<td>468.6</td>
<td>153.0</td>
<td>159.0</td>
<td>254.0</td>
<td>305.1</td>
</tr>
</tbody>
</table>

*Table 3.4.2. Comparison Of Particle Sizes (nm) For Three Polymer Dispersions Measured By Three Different Sizing Techniques. NB a double entry indicates a bimodal dispersion.*

It was concluded that TEM analysis offered less scope for the introduction of errors and as such was selected as the favoured particle sizing technique for the remaining work presented here.
3.4.2 Effect Of Stabiliser Concentration Upon Particle Size In One Stage Feeding Profiles.

Three dispersions were prepared based upon the standard one stage procedure reported by Duddington \(^{(58)}\) and Slark \(^{(57)}\) and described in Section 2.6.1.1. The polymerisations of destabilised MMA (20 wt-%) were initiated using AIBN (1 wt-%) and hexane as the diluent. The graft copolymer MSES 2 was used as the steric stabiliser at different concentrations. The calculated particle size results are shown in Table 3.4.3 and plotted in Figure 3.27.

From these results it can be seen that an increase in the stabiliser concentration leads to a reduction in the particle size achieved. This trend was expected, as it has been observed in many non-aqueous dispersion systems \(^{(84, 94 \rightarrow 97)}\) as well as heterogeneous aqueous systems such as emulsion and suspension polymerisations \(^{(85)}\).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>MSES 2</th>
<th>(D_n)</th>
<th>(D_w)</th>
<th>(D_w/D_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 4</td>
<td>2.55 %</td>
<td>298 nm</td>
<td>666 nm</td>
<td>2.23</td>
</tr>
<tr>
<td>MSMD 5</td>
<td>4.04 %</td>
<td>225 nm</td>
<td>324 nm</td>
<td>1.44</td>
</tr>
<tr>
<td>MSMD 6</td>
<td>6.05 %</td>
<td>278 nm</td>
<td>321 nm</td>
<td>1.15</td>
</tr>
</tbody>
</table>

*Table 3.4.3. Effect Of Stabiliser Concentration Upon Particle Size And Distribution.*

Initially, there can be considered to be two plausible explanations for this phenomenon. The first is that higher stabiliser concentration allows for a greater surface area to be covered by the graft copolymer.
Figure 3.27 Effect Of Stabiliser Concentration, In One Stage Non-Aqueous Dispersion Polymerisations, On Particle Size.
This means that as the particles grow they will remain sufficiently stabilised for a longer period and thus particle growth will be predominantly by monomer absorption and not by particle coalescence. Some evidence for this increased particle stability can be drawn from the polydispersity, as calculated by $D_w/D_n$. As the stabiliser concentration increases then the polydispersity decreases which infers that a narrower particle size distributions exists at the higher concentrations.

The second possibility is that a higher stabiliser concentration will lead to the formation of a greater number of seed particles and thus each particle would contain less monomer, leading to smaller particles. For this explanation to be correct two assumptions must be correct,

1. Stabiliser concentration must have a strong effect on particle nucleation.
2. Monomer is adsorbed into the particles and that the locus of polymerisation is the core of the polymer particle.

To assess the first criteria it is essential to determine the particle nucleation process. Non-aqueous dispersion polymerisations during the early stages of reaction, are effectively homogeneous solution polymerisations of the monomer, forming oligomeric radicals. It is these oligomers that condense to form the heterogeneous nuclei. Barrett\(^{99}\) considered that these oligomers would form particle nuclei by a number of possible mechanisms. These included,

1. Self nucleation.
2. Aggregative nucleation.
3. Nucleation from within monomer swollen micelles.

The self nucleation mechanism was initially suggested by Fitch and Tsai \(^{(99)}\). They proposed that the oligomeric chains grow in an extended chain conformation, such as would be observed for a dissolved polymer in a better than \(\Theta\) solvent. As the chains grow the solubility of the polymer decreases and when a critical molar mass is reached the chain collapses into a condensed random coil conformation (Figure 3.28). It was this condensed form that was considered to be the particle nucleus. This theory assumes that each oligomer is unaffected by the presence of other radicals, a reasonable assumption at low radical concentrations, and that therefore each oligomer that achieves this critical molar mass forms a new particle. In practice the number of particles observed is significantly less than the number that would be expected from the polymerisation kinetics. This is possibly due to aggregation of particles during the polymerisation.

In the case of aggregative nucleation it was suggested that as the oligomeric radicals grow then the tendency for them to aggregate together would also increase. Below a certain critical particle nuclei diameter these infant nuclei are in equilibrium with the free oligomeric radicals in the diluent. However, above this critical size the infant nuclei are stable and will become the established particle nuclei (Figure 3.29). This theory is in accordance with the classical homogeneous nucleation theory developed and proposed by Becker and Döring \(^{(100)}\) and Volmer \(^{(101)}\). In this theory the rate of nucleation can be calculated from the activation energy required to form the critical aggregate size, which in turn can be determined from the
Figure 3.28. Schematic Diagram Of The Self Nucleating Particle Nucleation Mechanism In Dispersion Polymerisations.
Figure 3.29. Schematic Diagram Of The Aggregative Particle Nucleation Mechanism In Dispersion Polymerisations.
interfacial tension between the two phases and the supersaturation point of the oligomers. Thus the predicted rate of nucleation rapidly increases with increasing oligomer molar mass and oligomer concentration. In this model, however, particle nucleation is suppressed by the absorption of the oligomeric radicals into particles that have already nucleated.

The third model of nucleation, micellar nucleation, is equivalent to the model proposed by Harkins \(^\text{102}\) for nucleation in emulsion polymerisations. It was suggested that particles nucleate from monomer swollen micelles via the initiation of the polymerisation inside the micelle (Figure 3.30). In the case of non-aqueous dispersion polymerisations this model can be rejected as the monomer readily forms a homogeneous solution with the diluent and therefore the monomer concentration inside the micelles present would be expected to be low. Indeed, for aqueous emulsion systems this theory is disputed in favour of the theory offered by Robb \(^\text{103}\) and Dunn \(^\text{104}\) of nucleation via the absorption of growing oligomeric radicals into swollen micelle.

Barrett \(^\text{98}\) concluded that both self nucleation and aggregative nucleation may occur in dispersion polymerisations depending upon the solubility of the polymer in the monomer/diluent mixture. When the polymer is highly insoluble in the reaction mixture, then self nucleation would be the predominant nucleation mechanism. At the other end of the polymer/diluent solubility spectrum the nuclei would tend to be formed by aggregative nucleation with each nuclei containing many large oligomers. From the acceptable nucleation
Figure 3.30. Schematic Diagram Of The Micellar Particle Nucleation Mechanism In Dispersion Polymerisations.
models proposed here, it would appear that the stabiliser plays only a minor role in the nucleation mechanism. Rather its role in the polymerisation is to prevent particle aggregation during the particle growth phase. Therefore, it can be concluded that the reduction in particle size with increasing stabiliser concentration is due to the increased stability of the particles and not due to the production of a greater number of initial particles.

3.4.3 Effect Of Monomer Concentration Upon Particle Size In One Stage Feeding Profiles.

Five non-aqueous dispersion polymerisations were performed with a stabiliser (MSES 3) concentration of 2.5wt-% and an AIBN concentration of 1 wt-%. This stabiliser concentration was chosen because although it offered adequate surface coverage, the polydispersity of the final dispersion was broad and therefore any subsequent improvements would be easily detected. The particle size data for this series of polymerisations are shown in Table 3.4.4 and graphically in Figure 3.31.

As can be seen from the above table an increase in the initial monomer concentration leads to an increase in the particle size produced. It can also be observed that the particle size distribution becomes broader and that the dispersion produced become bimodal above a MMA concentration of 20 wt-% and that both modes are of relatively narrow polydispersity.
Figure 3.31. Effect Of Monomer Concentration, In One Stage Non-Aqueous Dispersion Polymerisations, On Particle Size.
This relationship between increasing particle size with increasing monomer concentration has been reported by a number of previous researchers. The results obtained by Lok and Ober (105) (Figure 3.32) showed an almost linear dependence, for size of the polystyrene particles, on styrene concentration over the range of concentrations studied (6 - 35%).

<table>
<thead>
<tr>
<th>MMA Concentration</th>
<th>D_n</th>
<th>D_w</th>
<th>D_w/D_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 12</td>
<td>5.00 %</td>
<td>67 nm</td>
<td>71 nm</td>
</tr>
<tr>
<td>MSMD 17</td>
<td>10.17 %</td>
<td>110 nm</td>
<td>120 nm</td>
</tr>
<tr>
<td>MSMD 10</td>
<td>20.29 %</td>
<td>201 nm</td>
<td>226 nm</td>
</tr>
<tr>
<td>MSMD 13</td>
<td>30.09 %</td>
<td>380 nm</td>
<td>397 nm</td>
</tr>
<tr>
<td>MSMD 14</td>
<td>40.08 %</td>
<td>380 nm</td>
<td>397 nm</td>
</tr>
<tr>
<td>MSMD 15</td>
<td>49.93 %</td>
<td>537 nm</td>
<td>578 nm</td>
</tr>
</tbody>
</table>

Table 3.4.4. Effect Of Monomer Concentration Upon Particle Size
And Distribution.

Two reasons were proposed for this increase. The first was simply that increasing the available monomer would lead to greater polymerisation occurring and hence larger particles. The second explanation is that with the polymer being soluble in its own monomer, an increase in the monomer concentration increases the solubility of the polymer in the

Page 157
Monomer - Styrene
Diluent - EtOH/H₂O
Stabiliser - Cellulose ester

Figure 3.32. Particle Size Results Reported By Lok And Ober (105).
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diluent/monomer mixture. This results in the formation of larger particle nuclei and hence larger final particles.

The increasing polydispersity is also a result of the solvency of the reaction media. Initially, the particle nucleation will predominantly be by aggregative nucleation; however, as the polymerisation proceeds the monomer is used up and thus the solvency of the polymerisation media decreases rapidly. This can lead to a point where the reaction environment is such that self nucleation becomes favourable and a second crop of particle nuclei is produced. If there is sufficient stabiliser present then these particles will be stable and grow to mature particles; if not, then the new nuclei may be absorbed into other particles.

Work reported by Antl et al (59) for the polymerisation of MMA in hexane covered a much greater range of monomer concentrations. For MMA concentrations below 8.5 %, they observed the linear relationship between particle size and monomer concentration (Figure 3.33). However, for MMA concentrations between 8.5 % and 35 % they reported no data. They observed that in this region the dispersions were unstable and would readily flocculate or agglomerate. They suggested that in this unstable region the two nucleation mechanisms exist and the particles produced are competing against each other and therefore creating unstable dispersion particles. In a study of the time for flocculation/agglomeration to occur in these dispersions, they observed that the shortest time (15 minutes) occurred at 24 ± 2 %, i.e. in the middle of the region of instability.
Figure 3.33. Particle Size Results Reported By Anth Et Al\(^{(59)}\).
Above 35 % MMA they observed the same increasingly rapid rise in particle size with MMA concentration as reported here. They reasoned that the rapid rise in particle size was not simply due to the increased solvency of the polymerisation medium leading to larger particle nuclei, but that the higher solvency will also reduce the effect the stabiliser present has on the system. Therefore, the polymerisation will behave as if there was a lower stabiliser concentration present.

The theory that the solvency of the polymerisation is the predominant factor in the increasing particle size trend was demonstrated by Winnik et al (95) who performed a series of polymerisations of MMA in hydrocarbon but varied the concentration of carbon tetrachloride (CCl₄) present (Figure 3.34). CCl₄ is a “solvent” for PMMA and so increasing its concentration leads to an increase in the solvency of the reaction media. It was observed that the particle size increases rapidly with the CCl₄ concentration in a manner similar to the behaviour with increasing monomer. They noted however that for polymerisations above 75 % CCl₄ no particles were observed and the reaction behaved as a solution polymerisation.

However, Shen et al (84) observed a slightly different trend. Their work showed (Figure 3.35) that below 10% monomer the particle size actually decreases with increasing monomer concentration. This result initially seems unlikely; however, all the systems discussed so far have used preformed stabilisers whereas Shen used a poly (vinyl pyrrolidone) precursor stabiliser. The use of precursor stabilisers is industrially favourable as it removes at least one stage from the stabiliser production process as the stabiliser backbone is produced.
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Figure 3.34 Particle Size Results Reported By Winnik Et Al (95).

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Figure 3.35 Particle Size Results Reported By Shen et al \(^{(84)}\).
during the dispersion polymerisation by the reaction between the monomer and the precursor. Increasing the monomer concentration in the polymerisation would therefore lead to an increased polymer content in the stabiliser and hence push the ASB more towards the anchor component therefore increasing the rate at which the stabiliser precipitates out to form new nuclei. This has the effect that increasing the monomer concentration increases the efficiency of the in-situ formed stabiliser. This increased stabiliser efficiency is in balance with the effect of the increased solvency of the media, which leads to the later increase in particle size. As was observed in the work by Winnik et al. (95) (Figure 3.34) the solvency effect is less significant at the lower monomer concentrations, hence the dip in the particle size reported by Shen at the lower end of the concentration range studied.

There can be little doubt, therefore, that the major factor in the increasing particle size, and distribution, with increasing monomer concentration is the solvency of the media with some contribution from other factors such as the increased bulk material available for reaction and the increase nucleating efficiency of in-situ formed stabilisers.

3.4.4 Effect Of Stabiliser Concentration Upon Particle Size In Two Stage (Seed-Feed) Feeding Profiles.

For these polymerisations the monomer, initiator and stabiliser were divided between the seed and feed stages in a 30:70 ratio. The total stabiliser concentration was varied between 1 and 4 wt-%. The dispersions were performed in cyclooctane due to its higher viscosity.
and density, which reduced the rate of settling of the particles. The results for these polymerisations are shown in Table 3.4.5. and in Figure 3.36.

These results follow the same general trend of decreasing particle size with increasing stabiliser concentration that was observed for one stage dispersion polymerisations. However, in one stage dispersions the particle size initially decreases rapidly and then levels off to a point where increasing the stabiliser concentration no longer has a significant effect.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>MSES 3</th>
<th>(D_n)</th>
<th>(D_w)</th>
<th>(D_n/D_w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 23</td>
<td>1.01 %</td>
<td>522 nm</td>
<td>533 nm</td>
<td>1.02</td>
</tr>
<tr>
<td>MSMD 24</td>
<td>1.49 %</td>
<td>473 nm</td>
<td>518 nm</td>
<td>1.10</td>
</tr>
<tr>
<td>MSMD 25</td>
<td>2.01 %</td>
<td>451 nm</td>
<td>509 nm</td>
<td>1.13</td>
</tr>
<tr>
<td>MSMD 22</td>
<td>2.49 %</td>
<td>361 nm</td>
<td>380 nm</td>
<td>1.05</td>
</tr>
<tr>
<td>MSMD 26</td>
<td>3.00 %</td>
<td>375 nm</td>
<td>394 nm</td>
<td>1.05</td>
</tr>
<tr>
<td>MSMD 21</td>
<td>3.98 %</td>
<td>152 nm</td>
<td>172 nm</td>
<td>1.13</td>
</tr>
</tbody>
</table>

*Table 3.4.5. Effect Of Stabiliser Concentration Upon Particle Size And Distribution In Two Stage Feeding Profiles.*

For seed-feed dispersions the particle size decrease is more pronounced at the higher stabiliser concentrations. This initially contradicts the observations by Dawkins *et al.* (97) who observed a trend analogous to the one stage results, for their two stage dispersion polymerisations of PMMA and of poly (vinyl acetate). It should be
Figure 3.36. Effect Of Stabiliser Concentration, In Two Stage Non-Aqueous Dispersion Polymerisations, Upon Particle Size.
noted, however, that the stabiliser used by Dawkins and coworkers\(^{(97)}\) was the diblock copolymer poly (styrene-b-[ethylene-co-propylene]) and therefore could be expected to exhibit slightly different particle size relationships.

The difference in the particle size curves obtained for one stage and two stage protocols was initially surprising. Closer examination, however, shows that the two stage procedures extended further into the low concentration region than the one stage work and that the region where the stabiliser concentration has least effect, in the two stage results, was not studied for the one stage process. It is interesting to observe that there appears to be a critical stabiliser concentration, below which altering the stabiliser concentration has only a slight effect upon the particle size, i.e. a change of approximately 25 nm between 1 and 2 wt-% compared with 116 nm between 2 and 3 wt-%. To explain this trend it is essential to consider the behaviour at very low stabiliser concentrations. In the extreme case, 0 % stabiliser, the reaction is essentially a precipitation polymerisation and as such there are two possibilities for the particle size produced. The first option is that the polymerisation will produce a single large particle, of the volume of the monomer present. The second is that the growing polymer chains will precipitate out of the diluent when they reach a critical molar mass, and therefore the particle size of the dispersed material will be zero.

Since one of the main criteria for dispersion polymerisation to occur is that the polymer is insoluble in the diluent, the second suggestion, of very small dispersed particles at very low stabiliser concentration, is more probable although the existence of large precipitated material
would also be expected. Hence, the full relationship between particle size and stabiliser concentration may be similar to Figure 3.37, with the region of low dependence, observed in the two stage work, corresponding to the apex of the curve.

Comparing the results between the one stage and two stage work shows that the polydispersity achieved is much narrower for the two stage process. There are two probable explanations for this:

1. Less secondary nucleation.
2. Lower degree of particle settlement.

In the first case, during the feed stage, both the monomer and stabiliser are fed at a rate such that their respective free concentrations are low and relatively constant. This pseudo steady state situation means that large fluctuations in the solvency of the reaction medium are unlikely and that therefore secondary nucleation would be limited.

In the second situation the higher density and viscosity of CO compared to hexane mean that the particles are less likely to settle out when CO is used as the diluent (two stage) compared to hexane (one stage). It is plausible that the particles that collect at the bottom of the reaction vessel will undergo some degree of coalescence during the polymerisation. This coalescence is unlikely to occur during the centrifugation/redispersion purification process, as in this situation the particles are well below their glass transition temperature (Tg) and as such would be expected to behave like hard spheres. Although the polymerisation may take place below the Tg of the polymer, it is likely that the monomer may act in some way as a plasticiser.
Figure 3.37. Schematic Representation Of The Effect Of Stabiliser Concentration On Particle Size In Two Stage Dispersion Polymerisations.
3.4.5 Effect Of Stabiliser Divide Upon Particle Size In Two Stage (Seed-Feed) Feeding Profiles.

Dispersions were prepared using the standard two stage dispersion conditions of 2.5wt-% stabiliser, 20 wt-% MMA, 1 Wt-% AIBN and using CO as the diluent. However, the stabiliser component was divided in varying proportions between the seed and feed stages. The results for these dispersions are presented in Table 3.4.6. and Figure 3.38.

<table>
<thead>
<tr>
<th></th>
<th>% MSES 3 in Seed</th>
<th>$D_n$</th>
<th>$D_w$</th>
<th>$D_w/D_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 28</td>
<td>10.05 %</td>
<td>799 nm</td>
<td>806 nm</td>
<td>1.01</td>
</tr>
<tr>
<td>MSMD 34</td>
<td>20.03 %</td>
<td>337 nm</td>
<td>457 nm</td>
<td>1.36</td>
</tr>
<tr>
<td>MSMD 22</td>
<td>30.00 %</td>
<td>361 nm</td>
<td>380 nm</td>
<td>1.05</td>
</tr>
<tr>
<td>MSMD 35</td>
<td>39.59 %</td>
<td>285 nm</td>
<td>332 nm</td>
<td>1.16</td>
</tr>
<tr>
<td>MSMD 27</td>
<td>50.03 %</td>
<td>277 nm</td>
<td>320 nm</td>
<td>1.16</td>
</tr>
<tr>
<td>MSMD 36</td>
<td>69.92 %</td>
<td>153 nm</td>
<td>179 nm</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Table 3.4.6 Effect Of Stabiliser Divide Upon Particle Size And Distribution In Two Stage Feeding Profiles.

Increasing the relative seed concentration of stabiliser has the effect of decreasing the particle size. This is similar to the effect observed for increasing the total stabiliser concentration in one stage polymerisations (Section 3.4.2) and two stage profiles (Section 3.4.4). In these cases it was argued that the increasing stabiliser concentration lead to greater stabilisation of the particles during the particle growth.
Figure 3.38. Effect Of Stabiliser Divide, In Two Stage Non-Aqueous Dispersion Polymerisations, Upon Particle Size.
period. In this case, however, there is only one total stabiliser concentration and so the nucleation must occur by some other mechanism.

There are two possible processes that may affect the particle size variance. If the feed stage is the period where the particle size control occurs, then it would be logical to expect the lower feed stabiliser concentration of the higher divide ratio dispersions to lead to particles with poor stabilisation and thus larger coarser particles would form. This clearly is not the case observed here. However, if the seed stage is considered to be a one stage polymerisation in its own right, then it would be expected that the higher relative stabiliser concentration will lead to smaller particles for the higher divide ratio dispersions. If these seed particles were sufficiently stable, then it would not be unreasonable to expect the final dispersion particles to also follow this trend. These results are industrially interesting as they show how good particle size control can be achieved by simply modifying the stabiliser divide in a standard formulation.

3.4.6 Effect Of Monomer Concentration Upon Particle Size In Two Stage (Seed-Feed) Feeding Profiles.

Non-aqueous dispersions were prepared using the standard reagent parameters of 2.5 wt-% steric stabiliser (MSES 3), 1 wt-% AIBN and performed using CO as the diluent. The total MMA concentration was varied from 10 wt-% to 50 wt-% and all functional materials were divided between the seed and feed stages in a ratio of 30:70. The
results from these dispersions are displayed in Table 3.4.7 and in Figure 3.39.

Comparing these results with those obtained for the single stage dispersions (Section 3.4.3) two observations are immediately apparent. The first is that the general trend of increasing particle size with increasing total monomer concentration, observed earlier, also holds here. The second observation is the apparent barrier to stable dispersions observed at high total monomer concentrations.

<table>
<thead>
<tr>
<th></th>
<th>MMA Concentration</th>
<th>D_n</th>
<th>D_w</th>
<th>D_w/D_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 29</td>
<td>10.13 %</td>
<td>172 nm</td>
<td>227 nm</td>
<td>1.32</td>
</tr>
<tr>
<td>MSMD 22</td>
<td>20.05 %</td>
<td>361 nm</td>
<td>380 nm</td>
<td>1.05</td>
</tr>
<tr>
<td>MSMD 30</td>
<td>30.15 %</td>
<td>689 nm</td>
<td>710 nm</td>
<td>1.03</td>
</tr>
<tr>
<td>MSMD 31</td>
<td>50.14 %</td>
<td>Flocculated</td>
<td>Flocculated</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 3.4.7. Effect Of Total Monomer Concentration Upon Particle Size And Distribution In Two Stage Feeding Profiles.

It is likely that the reasons for an increase in the particle size with increasing total monomer concentration observed in the two stage polymerisations are similar to the reasons discussed for the same behaviour for one stage polymerisations (Section 3.4.3). These were twofold. The first was due to a greater monomer concentration, but with only sufficient graft copolymer to stabilise the same surface area then larger particles will need to be produced. This, however, was only a small factor in the particle size observed. A much larger
Figure 3.39. Effect Of Total Monomer Concentration, In Two Stage Non-Aqueous Dispersion Polymerisations, Upon Particle Size.
contribution to the particle size would have come from the increased solvency of the medium with increasing monomer concentration and hence a lower stabiliser efficiency.

The feeding profile leads to an observed smaller particle size, at the higher total monomer concentrations, than was observed for one stage procedures because in the two stage procedures the actual monomer concentration in the system at any one point is lower than the total monomer concentration.

The flocculation of the high monomer concentration dispersion was initially surprising as a two stage system is considered to be able to produce dispersions of better particle definition and also produce stable particle dispersion under extreme conditions, i.e. high monomer concentrations or low stabiliser concentrations. In this case, however, it is possible that the monomer concentration in each feed addition was too large and caused an unstable system. To overcome this problem the feed would need to be added in smaller, more frequent additions, or a continuous drip feed process applied. Due to the small scale of the initial dispersions reported here, neither of these polymerisation options was feasible.

3.4.7 Effect Of Monomer Divide Upon Particle Size In Two Stage (Seed-Feed) Feeding Profiles.

Dispersions were performed using a standard formulation of 2.5 wt-% steric stabiliser (MSES 3), 1 wt-% AIBN, 20 wt-% MMA and CO was used as the diluent. The monomer was divided between the seed and feed stages in varying ratios and the stabiliser and AIBN in a
seed:feed ratio of 30:70. The particle size results for these polymerisations are shown in Figure 3.40 and in Table 3.4.8.

<table>
<thead>
<tr>
<th></th>
<th>% of MMA in Seed</th>
<th>$D_n$</th>
<th>$D_w$</th>
<th>$D_w/D_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 37</td>
<td>10.05 %</td>
<td>215 nm</td>
<td>282 nm</td>
<td>1.31</td>
</tr>
<tr>
<td>MSMD 22</td>
<td>30.35 %</td>
<td>361 nm</td>
<td>380 nm</td>
<td>1.05</td>
</tr>
<tr>
<td>MSMD 32</td>
<td>49.75 %</td>
<td>459 nm</td>
<td>465 nm</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Table 3.4.8 Effect Of Monomer Divide Upon Particle Size And Distribution In Two Stage Feeding Profiles.

The observed increase in particle size with increasing seed monomer content follows the trends previously observed for one stage profiles (Section 3.4.3) and also for the total monomer studies in two stage profiles (Section 3.4.6). Again the increase in particle size is predominantly due to the increased relative monomer concentration in the seed stage yielding a larger seed particle. This larger seed particle is created as a result of the increased solvency of the reaction medium, which reduces the particle nucleation rate, and also the efficiency of the steric stabiliser.

It is plausible that the higher polydispersity ($D_w/D_n$) observed for the low seed concentration is due to the relatively high monomer concentrations added during the feed stage causing instability in the dispersion and therefore causing secondary nucleation to occur.
Figure 3.40. Effect Of Monomer Divide, In Two Stage Non-Aqueous Dispersion Polymerisations, Upon Particle Size.
3.5 Rheological Studies Of Monomodal Non-Aqueous PMMA Dispersions.

The rheological behaviour of nine large scale monomodal PMMA dispersions was studied. Of initial interest was the effect that increasing the shear stress, applied to the system, had upon the resulting viscosity and how this behaviour varied at increasing particle concentrations.

3.5.1 Effect Of The Applied Shear Stress Upon The Resulting Viscosity Over A Range Of Volume Fractions.

The results for five of these dispersions are shown in *Figure 3.41*. The classes of viscosity behaviour observed fall into three distinct volume ranges. These ranges are:

1. Low volume fractions, less than 12%.
2. Intermediate volume fractions, 12 – 35%.
3. High volume fractions, 35 – 50%.

NB. The actual limits of each range vary between dispersions.

In the *low volume fraction range* there is a long Newtonian plateau until a shear stress of approximately 1 Pa is reached. At this point the rheology of the dispersion becomes shear thickening, that is as the shear stress, or shear rate, increases so does the resulting viscosity.
Figure 3.41. (a) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For MSMD 38.
Figure 3.41. (b) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For MSMD 45.
Figure 3.41. (c) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For MSMD 48.

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Figure 3.41. (d) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For MSMD 57.
Figure 3.41. (e) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For MSMD 58.
The Newtonian behaviour can be explained by the low particle interactions that exist at low volume fractions. In the dilute state the interparticle distances are relatively large (Figure 3.42) and so the forces acting between the particles are weak. Therefore, when the dispersion is under shearing stresses and the particles are forced closer together there is only a minimal increase in the repulsive forces between adjacent particles. Although the force with which the particles are forced together increases with increasing shear stress, the interparticle distance is sufficiently large as to make the resulting increased repulsion negligible.

The shear thickening behaviour observed at the higher stresses is due the creation of turbulence in the dispersion. The point of the onset of shear thickening is abrupt as it marks the point where the "order" in the system breaks down (Figure 3.43). This trend is characteristic of low viscosity fluids and can be observed in the pure diluent (Figure 3.44). The critical stress where breakdown occurs increases with increasing volume fraction as can be seen by comparing the plots for 7.3 % and 9.7 % in Figure 3.41 (b). This is due to there being a higher degree of "structure" in the higher volume fraction dispersions and so a greater force is required to destroy the order in the system.

At the intermediate volume fractions the behaviour is once again predominantly Newtonian although shear thickening behaviour is evident for the dispersions MSMD 38 (Figure 3.41(a)) and MSMD 45 (Figure 3.41(b)). The long Newtonian region is a result of the comparatively strong interparticle "structure" resisting the disruptive turbulent forces. This is in effect an extension of the theory for the
Figure 3.42 Schematic Diagram Of A Low Volume Fraction Dispersion.
Figure 3.43 Schematic Diagram Of A Low Volume Fraction Dispersion Under Shear Stress.
Figure 3.44 Effect Of Shear Stress Upon The Viscosity Of Pure Cyclooctane.
delay of the onset of shear thickening observed for the low volume fraction dispersions.

For the smaller particulate systems (MSMD 38 and MSMD 45) it is plausible that they will have a weaker overall structure as the particles have a less dense steric barrier and hence lower long range interparticle repulsion. This means that the turbulent forces will dominate at a lower stress than observed for the larger particles.

At high volume fractions the dispersions initially exhibited shear thickening behaviour before going through a Newtonian plateau and finally shear thickening once more (Figure 3.41 (a) and (b)). This behaviour was only observed for the dispersions that showed shear thickening behaviour at intermediate volume fractions. The Newtonian region is believed to be due to the formation of layers of particles in the dispersion which then undergo laminar flow. This theory is supported by the diffraction studies reported by Hoffman (71). For 1 μm PVC spheres below a critical shear stress a diffuse diffraction pattern was observed. This was interpreted as resulting from a disordered system; i.e. the particles are moving in a random way. Above the critical point, however, a well defined pattern was achieved relating to the particles forming layers. It is expected that the initial shear thickening region relates to the transition between a completely random structure and the lamellar structure. As the shear stress on the system increases further, these sheets will eventually distort causing the rapid shear thickening behaviour observed after the Newtonian region (Figure 3.45).
Figure 3.45 Schematic Diagram Of The Lamellar Structure In Concentrated Dispersions.
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A number of theories have been proposed for the shear thinning behaviour observed for the dispersions MSMD 48 (Figure 3.41 (c)), MSMD 57 (Figure 3.41 (d)) and MSMD 58 (Figure 3.41 (e)) at high volume fractions. Wagstaff and Chaffey (59) suggested that the steric barrier stabiliser on the particles is compressed during the shearing procedure. This they suggested meant that the actual volume fraction of particles present in the sample studied would decrease with increasing shear stress and as such would be expected to have a lower viscosity. In their review paper Croucher and Milkie (73) claimed that the stress acting upon each particle would be of the order 1.2 pN whereas the force required to collapse the steric barrier by 50% would be approximately 75 pN. Therefore, they concluded this was unlikely to be a major contributor to the shear thinning observed. It is also unlikely that the volume change would be sufficient to account for the level of thinning observed without total collapse of the steric barrier.

Willey and Macosko (72) and Croucher and Milkie (73) explained the effect in terms of interparticle interactions with specific emphasis on the polymer-solvent interaction parameter $\chi$. Croucher and Hair (105) considered that this parameter is a combination of two considerations. The first is a contact energy factor ($\chi_{ce}$) which describes the energetic interactions between the steric stabiliser molecules and the diluent. The second term is a free volume factor ($\chi_{fv}$) which describes the volume occupied by the stabiliser chains in terms of the occluded diluent (Figure 3.46). As the volume fraction of the dispersion increases, the effect $\chi_{ce}$ will become more important as the
Figure 3.46 Schematic Diagram Of The Free Volume Occupied By A Polymer Chain.
interparticle interactions become more frequent, but at the very high concentrations it is the $\chi_{fv}$ term that is most important. At these volume fractions it was suggested by Croucher and Milkie (73) that the stabiliser chains will become entangled leading to an increase in the occluded volume. However, it was proposed that upon increased shearing this entanglement of the stabilising chains would be reduced and hence the viscosity would also be reduced.

3.5.2 Determination Of The Maximum Volume Fraction For Monomodal Non-Aqueous PMMA Dispersions.

The maximum theoretical volume fraction for each dispersion studied was calculated by applying the Krieger-Dougherty equation (Equation 3.5.a) to the viscosity-volume fraction data from the previous section using curve fitting data handling software.

\[ \eta_r = \frac{\eta}{\eta_s} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \]  

Equation 3.5.a

where:

- $\eta_r$ is the relative viscosity of the dispersion
- $\eta$ is the measured viscosity of the dispersion
- $\eta_s$ is the viscosity of the diluent
- $\phi$ is the volume fraction
- $\phi_m$ is the maximum volume fraction
- $[\eta]$ is the intrinsic viscosity of the dispersion.
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The intrinsic viscosity was estimated using Equation 3.5.b.

\[
[\eta] = \left( \frac{\eta_r - 1}{\phi} \right)_{\phi \to 0}
\]

Equation 3.5.b

In the previous section it was observed that the measured viscosity of a dispersion is a function of the applied shear rate. Therefore, for the curve fitting work it was essential to make a decision upon which particular measured viscosity represented a "true viscosity". To ensure that the comparison between sets of data was meaningful, only viscosities in a Newtonian flow region were used. Where two Newtonian plateaus were observed, the lower plateau value was used as this allows for a higher maximum volume fraction to be calculated. The plots derived from this are shown in Figure 3.47 and also the data results in Table 3.5.1.

<table>
<thead>
<tr>
<th></th>
<th>(\phi_m)</th>
<th>[(\eta)]</th>
<th>(D_w)</th>
<th>(D_n)</th>
<th>(D_w/D_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSMD 38</td>
<td>57.24 %</td>
<td>4.48</td>
<td>399 nm</td>
<td>374 nm</td>
<td>1.07</td>
</tr>
<tr>
<td>MSMD 45</td>
<td>71.25 %</td>
<td>6.52</td>
<td>415 nm</td>
<td>347 nm</td>
<td>1.20</td>
</tr>
<tr>
<td>MSMD 48</td>
<td>62.58 %</td>
<td>6.30</td>
<td>591 nm</td>
<td>493 nm</td>
<td>1.20</td>
</tr>
<tr>
<td>MSMD 57</td>
<td>69.86 %</td>
<td>8.15</td>
<td>488 nm</td>
<td>434 nm</td>
<td>1.12</td>
</tr>
<tr>
<td>MSMD 58</td>
<td>53.78 %</td>
<td>7.53</td>
<td>531 nm</td>
<td>475 nm</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Table 3.5.1 Krieger-Dougherty Data Fit Results For Monomodal Non-Aqueous Dispersions.
Figure 3.47. (a) Effect Of Volume Fraction Upon The Viscosity Of MSMD 38.
Figure 3.47. (b) Effect Of Volume Fraction Upon The Viscosity Of MSMD 45.
Figure 3.47. (c) Effect Of Volume Fraction Upon The Viscosity Of MSMD 48.
Figure 3.47. (d) Effect Of Volume Fraction Upon The Viscosity Of MSMD 57.
Figure 3.47. (e) Effect Of Volume Fraction Upon The Viscosity Of MSMD 58.
From these plots it can be seen that the Krieger-Dougherty equation describes the rheological properties of these dispersions very well.

According to packing theories (107, 110) there are four possible arrangements for packing uniform monomodal spheres efficiently. The packing arrangement for each of these structures is shown in Figure 3.48. The maximum theoretical volume fractions for these structures are:

1. Cubic. 52.36 %
2. Body centred cubic. 60.45 %
3. Face centred cubic. 74.05 %
4. Hexagonal close packing. 74.05 %

Many workers (109–112) have studied the achievable maximum volume packing fraction for various hard spheres such as glass spheres (109), steel balls (110, 111) and lead shot (112). All findings indicated that under dense packing conditions the maximum packing fraction was approximately 64 % independent of material and sphere size. For loose packing conditions the maximum packing fraction dropped to 59 %. The difference between these values and those expected from packing theory can be attributed to defects, such as vacancies and disruptions, in the layers leading to a reduction in the packing efficiency. In similar studies of polystyrene microgels in bromoform (113) and sterically stabilised silica in cyclohexane (114) higher maximum packing fractions of approximately 62 % and 72 % were found at low and high shear rates respectively. These values are higher than for true hard spheres because the compressible stabilising layers allow for
Figure 3.48 Schematic Diagram Of The Possible Packing Arrangements Of Hard Spheres.
closer interparticle distances than is allowed for in the hard sphere model. Therefore, non-aqueous dispersions should be considered as quasi-hard spheres as opposed to true hard spheres.

The results calculated for the monomodal non-aqueous dispersions presented here refer to low shear conditions. From the data in Table 3.5.1 it can be seen that the maximum packing fractions for the dispersions reported here correlate well with the theoretical maximum packing fractions for several packing geometries. For the dispersion with the narrowest particle size distribution (MSMD38) the calculated maximum packing fraction is in the range that would be expected for a body centred cubic arrangement. For MSMD 58, however, a maximum packing fraction comparable to simple cubic packing was calculated. The TEM micrograph for MSMD 58 (Figure 3.49.\(a\)) shows that the distribution of particle sizes in MSMD 58 is not well defined and that therefore efficient close particle packing would not be expected. For MSMD 38, however, the TEM micrograph (Figure 3.49.\(b\)) shows a much more well defined particle size distribution and the efficient packing nature of the dispersion can be seen.

MSMD 48 exhibits a maximum packing fraction relating to a body centred cubic packing scheme despite possessing a broad particle size distribution. Examination of the TEM micrograph (Figure 3.50), however, indicates the existence of a second crop of small particles. It is proposed that these smaller particles improve the efficiency of the particle packing by readily forming a thinner body centred layer than would exist for a truly monomodal dispersion.
Figure 3.49 TEM Micrographs For MSMD 38 And MSMD 58.
Figure 3.50 TEM Micrograph For MSMD 48.
The remaining dispersions, MSMD 45 and MSMD 57, show a packing fraction approaching that predicted for face centred cubic or hexagonal close packing. The TEM micrographs for these dispersions (Figure 3.51) once again show the existence of a secondary particle size range. In the case of these dispersions, however, it is probable that the larger particles are packing in a conventional body centred cubic manner but the smaller particles are occupying the interstices of the structure. This phenomena of the increased maximum packing fraction of a bimodal system over a monomodal system has been well documented \(^{(61, 74, 77, 108, 115)}\) for heterogeneous aqueous systems and therefore would also be expected to occur in non aqueous systems.

3.6 Rheological Studies Of Bimodal PMMA Non-Aqueous Dispersions.

Following from the observation of a higher maximum packing fraction in the dispersions possessing a secondary group of particles, further investigations were undertaken to examine the extent to which this packing fraction could be increased. For the initial studies bimodal dispersions were prepared by blending well characterised monomodal dispersions.

3.6.1 Effect Of The Applied Shear Stress Upon The Resulting Viscosity Over A Range Of Volume Fractions For Blended Bimodal Dispersions.

Four blends of MSMD 38 and MSMD 48 were prepared at different blend ratios. These dispersions were chosen as the small particles
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Figure 3.51 TEM Micrographs For MSMD 45 And MSMD 57.
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(MSMD 38) were approximately half the size of the large particles (MSMD 48) and this was the size ratio observed for the superior packing “monomodal” dispersions in Section 3.5.2. The shear stress-viscosity curves for the blended dispersions (Figure 3.52) exhibit similar trends to those observed for the parent monomodal dispersions (Figures 3.41. (a) and 3.41.(e)) at low and intermediate volume fractions. This observation was expected because at the low and intermediate volume fractions the particles are not closely packed together and so particle geometry has little influence upon the viscosity and shear behaviour. Under non-concentrated conditions, the major influences affecting viscosity are the interparticle interactions and the solvent-particle interactions.

At high volume fractions (greater than 38%), however, particle packing becomes crucial. For all of the blends of MSMD 38 and MSMD 48 studied here the secondary shear thickening period observed for MSMD 38 is not evident. After the initial non-Newtonian period the viscosity of the blends decreases to a Newtonian plateau. The shear thickening behaviour can be attributed to the formation of the close packing structures. Under the low shear conditions the packing of the particles is random with a tendency towards simple cubic packing at the higher volume fractions. For the packing arrangements to change from these inefficient packing arrangements to a more efficient one such as face or body centred cubic, the disorder in the system must initially be increased to allow the particles to form well ordered planes of particles.

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Figure 3.52. (a) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For A 25:75 Blend of MSMD 38 And MSMD 48.
Figure 3.52. (b) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For A 34:66 Blend of MSMD 38 And MSMD 48.
Figure 3.52. (c) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For A 64:36 Blend of MSMD 38 And MSMD 48.
Figure 3.52. (d) Effect Of Shear Stress Upon Viscosity At Increasing Volume Fractions For A 79:21 Blend of MSMD 38 And MSMD 48.
The absence of shear thickening behaviour can be attributed to the existence of the second group of particles. During the shearing of a dispersion, particle layers will become distorted. In monomodal dispersions this would lead to the eventual disruption of subsequent layers as shown in Figure 3.45. In a bimodal dispersion, however, the small particles occupy the vacancies in the packing structure and as such would lead only to a disruption of the small particle layer which would have only a small effect upon the viscosity of the dispersion (Figure 3.53).

3.6.2 Determination Of The Maximum Volume Fraction For Bimodal Non-Aqueous PMMA Dispersions.

Maximum packing fractions were calculated via the same process as for the monomodal dispersions. As with the monomodal dispersions there is good agreement between the experimental data (Figure 3.54) and the Krieger-Dougherty equation. Kim and Luckham \(^{(75)}\) compared the results they obtained experimentally for an aqueous polystyrene suspension with the viscosities predicted by the extended Krieger-Dougherty equation for bimodal mixtures, Equation 3.6.a.

\[
\eta_r = \left(1 - \frac{\phi_s}{\phi_{m(s)}}\right)^{-[\eta]_s \phi_{m(s)}} \times \left(1 - \frac{\phi_1}{\phi_{m(1)}}\right)^{-[\eta]_1 \phi_{m(1)}}
\]

\text{Equation 3.6.a.}

where:

\(\phi_s\) is the volume fraction of small particles

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Figure 3.53 Schematic Representation Of The Cushioning Effect Of The Small Particle Layers In A Concentrated Dispersion.
Figure 3.54. (a) Effect Of Volume Fraction Upon Viscosity At Increasing Volume Fractions For A 25:75 Blend of MSMD 38 And MSMD 48.
Figure 3.54. (b) Effect Of Volume Fraction Upon Viscosity At Increasing Volume Fractions For A 34:66 Blend of MSMD 38 And MSMD 48.
Figure 3.54. (c) Effect Of Volume Fraction Upon Viscosity At Increasing Volume Fractions For A 64:36 Blend of MSMD 38 And MSMD 48.
Figure 3.54. (d) Effect Of Volume Fraction Upon Viscosity At Increasing Volume Fractions For A 79:21 Blend of MSMD 38 And MSMD 48.
\( \phi_{m(s)} \) is the maximum packing fraction for a monomodal dispersion of small particles

\([\eta]_s\) is the intrinsic viscosity of a monomodal dispersion of small particles

\( \phi_l \) is the volume fraction of large particles

\( \phi_{m(l)} \) is the maximum packing fraction for a monomodal dispersion of large particles

\([\eta]_l\) is the intrinsic viscosity of a monomodal dispersion of large particles

This equation however, was not found to describe the viscosity of a bimodal dispersion well. At 40% and 60% large particles, Kim and Luckham \(^{75}\) observed very poor agreement between the extended equation and experimental results. There is also poor agreement between the experimental results presented here and the extended form of the Krieger-Dougherty as can be seen in Figure 3.55 (Figure 3.54 (c) with a fit for the extended equation) for the blend containing 21% of the large particles MSMD 48. It is believed that a simple blend ratio equation such as the extended Krieger-Dougherty equation is insufficient to describe the complex behaviour of concentrated dispersions and cannot reliably predict optimum blend ratios. Therefore, optimum blend ratios must be predicted via experimental methods.

From Figure 3.56 the effect of blend ratio upon maximum packing fraction, as determined in Figure 3.54, can easily be observed. At 21
Figure 3.55 Comparison Between The Viscosities Calculated Via The Krieger-Dougherty Equation And The Extended Krieger-Dougherty Equation For A Dispersion Containing 21% Large Particles.
Figure 3.56 Effect Of Particle Size Blend Ratio Upon Maximum Packing Fraction.
% large particles, there is only a slight increase in the maximum packing fraction compared to the parent monomodal dispersion (MSMD 38) with 0 % large particles. This probably results because at this blend ratio the packing procedure is one of fitting a small quantity of large particles into the packing arrangement of the smaller particles. Therefore, highly efficient packing methods are unlikely, resulting in a body centred arrangement with the large particles occupying the centred positions.

At 36 % large particles in Figure 3.56, the maximum packing fraction is significantly greater than for either 0 % large (MSMD 38) or 100 % large (MSMD 48). It is probable that at this blend ratio the large particles are packing as a body centred cubic but with the small particles filling the voids. At this blend ratio a more efficient packing method than body centred cubic would not be expected because the number of small particles would be too high to pack efficiently.

At 66 % large particles and 75 % large particles in Figure 3.56, packing fractions higher than those predicted for the most efficient monomodal packing methods are achieved. At these blend ratios it is believed that hexagonal close packing or face centred cubic packing exists for the large particles and that the small particles are filling the interstices. These blend ratios agree well with results of 80 % for aqueous latices of acrylic resins reported by Padget et al (77), between 60 % and 80 % for polystyrene aqueous latices by Kim and Luckham (75) and of 75 % for suspensions of polystyrene in bromoform by Rodriguez and Kaler (113).
Chapter 4.

Conclusions

From the work presented here the major conclusions are considered to be:

The use of tertiary amine catalysts significantly improved the conversion level compared to those reactions where no added catalyst was used. For the simple amine, triethyl amine, the conversion is increased to 65%. This increase is significantly higher than was observed for the tertiary amines with bulkier side groups, N-benzyl dimethyl amine (52%) and dimethylaminododecane (52%). This is believed to be a result of the lower steric barrier exhibited by triethyl amine than the larger molecules. For the catalyst featuring two tertiary amine functionalities, 1.4. diazabicyclo [2.2.2.] octane, the conversion level was 85%. This increase was believed to be a result of the increased relative amine concentration. The direct end capping reaction at 140 °C using glycidyl methacrylate, when uncatalysed, offers a conversion level of only 14%. This is due to the reaction being self acid-catalysing. However, as the reaction proceeds the free acid level will drop as the carboxylic acid functions react and hence the reaction is reduced.

Many aspects of particle size control in non-aqueous dispersions were studied. From these investigations a series of curves demonstrating methods for particle size control were produced. The primary control factors studied were the total and relative monomer and stabiliser concentrations for both one stage and two stage dispersion polymerisations. These curves were used effectively to derive the
experimental conditions required to synthesise dispersions with a particular particle size with the required solids content and using the minimum stabiliser concentration.

During the rheological studies it was observed that the maximum packing fractions for all of the blend ratios were significantly higher than those observed for the parent dispersions with the exception of the blend with 20 % large particles. This is because at 20 % large particles it is the large particles that must fit into the packing structure of the small particle dispersions which would lead to a less efficient packing structure such as body centred cubic. The optimum blend ratio was between 60 % and 80 % large particles which will have a packing fraction greater than 85 %.

The following observations and conclusions were also drawn.

The conversion of carboxylic acid terminated PEHA pre-polymer to vinylic macromonomer can be achieved via simple reactions. The end capping reaction, using hydroxy ethyl methacrylate, proceeding via an acyl chloride intermediate yielded a conversion level of 34 %. This conversion is limited due to the high moisture sensitivity of the intermediate causing rapid reversion of the acyl chloride back to the carboxylic acid.

Decreasing the reaction temperature, for the dimethylaminododecane reaction, from 140 °C to 65 °C lead to a conversion level of 15 %. This is due to the relatively high stability of the epoxy ring which
therefore requires a high temperature or aggressive catalyst to initiate the ring opening sequence.

It was observed that the macromonomers produced using the glycidyl methacrylate end capping route could be copolymerised with styrene to produce well defined graft copolymers. These copolymers were designed such that they would perform as steric stabilisers in non-aqueous dispersion polymerisations.

In one-stage polymerisations an increase in the stabiliser concentration lead to a decrease in the particle size and also a decrease in the polydispersity. The decrease in particle size is caused by the greater quantity of stabiliser present creating nuclei with a higher stability which therefore leads to lower particle aggregation. This decrease in particle aggregation also leads to the decrease in polydispersity.

Increasing the monomer concentration, for one stage polymerisations, lead to an increase in both particle size and polydispersity. The particle size increase arises from the increased solvency, of the dispersion medium, for the stabiliser which leads to less stable nuclei and hence a lower rate of nucleation. The increase in polydispersity is a result of the change in the solvency, of the medium, during the course of the polymerisation as the monomer is polymerised. This has the result that secondary particle renucleation can occur creating a bimodal dispersion.

For a two stage non-aqueous dispersion, an increase in the total stabiliser concentration lead to a decrease in the particle size. This is
also a result of the increased nuclei stability that the higher stabiliser concentration offers. Increasing the proportion of the stabiliser fed during the seed stage also lead to a decrease in particle size. This was seen as further evidence for the stable nuclei theory.

Increasing the total monomer concentration, in two stage non-aqueous dispersion polymerisations, lead to an increase in particle size. This is due to the higher solvency of the medium, for the stabiliser, and therefore a lower nucleation rate. There is little change in the polydispersity as the monomer is fed throughout the polymerisation and so there is a comparatively steady monomer concentration present during the particle growth period. Increasing the proportion of the total monomer in the seed stage lead to an increase in particle size and a decrease in the polydispersity. The particle size increases because the particles formed during the seed stage would be expected to be larger and hence the final particle will be larger. The decrease in polydispersity was due to the formation of smaller seed particles which are then more sensitive to the relatively high feed monomer concentration, which lead to instability during the particle growth stage.

Rheological studies of these dispersions at increasing volume fractions indicated that at low and intermediate volume fractions the dispersions were effectively Newtonian. This was due to the interparticle distance being such that particle packing was not significant. For the more concentrated samples in the intermediate range the particles were believed to form “loose rings” which were “lubricated” by the diluent. For high volume fractions both shear thickening and shear thinning
were observed. For the monodisperse samples the shear thickening behaviour was predominant. This was due to the formation of close packing structures which then must be disrupted under the shearing process. Where a secondary group of particles could be observed the shear thinning behaviour was dominant. This was a result of the small particles occupying the interstices in the packing structure and also acting as a cushion between the layers of the larger particles.

For these dispersions the maximum theoretical packing fractions were calculated using the Krieger-Dougherty equation. Maximum packing fractions for the monodisperse dispersions were comparable to the theoretical packing fractions calculated by a model of hard spheres (54 % - 60 %). For the dispersions with a small secondary group of particles the packing fractions measured were significantly higher (70 %). These values are comparable to the packing fractions calculated by the model for hard spheres for close packing arrangements.

The effects of increasing shear stress at increasing volume fractions were also studied for blended bimodal dispersions. As was observed for the monomodal dispersions at the low and intermediate volume fractions, the viscosity was predominantly Newtonian. This is because at these concentrations the particle size distribution has only a minor effect upon the rheology of the system. At the high concentrations the viscosity is shear thinning. This is a result of the improved packing efficiency of the bimodal dispersions.
Chapter 5.
Recommendations For Further Work.
5. Recommendations For Further Work.

During the course of this work the only particle size ratio blended was 2:1. It is recommended that further particle size blend ratios are also investigated; suggested ratios are 5:1, 7.5:1 and 10:1. Blend ratios greater than 10:1 are not expected to yield a significant increase in the maximum packing fraction achievable \(^{(108)}\).

Following on from the rheological results for the blended bimodal dispersions, attempts were made to prepare bimodal dispersions, in a controllable manner, \textit{in-situ}. The approaches made were to use a triple stage polymerisation whereby the feed phase was divided into two further phases. During the final feed stage it was believed that secondary renucleation could be induced by using either a very high relative monomer concentration or very high relative stabiliser concentration. Neither of these approaches were successful in yielding a stable dispersion. It is believed that this was due to the extreme shifts in the relative concentrations leading to an unstable dispersion. A second approach, however, was more successful. In this approach the diluent was formed using a diluted well characterised monomodal dispersion. The polymerisation conditions were then chosen such that the polymerisation would yield a crop of small particles as well as the preformed large particles. The rheology of these dispersions was, however, disappointing due to the rapid aggregation of the particles under shear. It is recommended therefore that further investigations are undertaken to develop this approach for the controlled synthesis of \textit{in-situ} bimodal dispersions and that detailed rheological studies of these dispersions are also performed.
The experimental work should also be extended to study other properties of coating dispersions such as the effects of the bimodality upon the film forming time/temperature and film strength. It is also suggested that the work be performed on a "real" acrylic coating formulation rather than a model system as presented here.
Chapter 6.

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