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Polymerised Acrylates For Use In Adhesives

A thesis presented to The City University
in part fulfilment of the requirements for the
degree of Doctor of Philosophy

by

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H.S. Zhang

List of Abbreviations

- AA: acrylic acid
- ABQ: (2–acryloyloxyethyl)(4–benzoylbenzyl) dimethylammonium bromide
- AIBN: α,α′–azoisobutyronitrile
- AICA: 4,4′–azobis(4–cyanovaleric acid)
- BA: butyl acrylate
- BMA: butyl methacrylate
- BME: benzoin methyl ether
- BPO: benzoyl peroxide
- BTC: 4–benzoylbenzyltrimethylammonium chloride
- DSC: differential scanning calorimetry
- EA: ethyl acetate
- EGDMA: ethylene glycol dimethacrylate
- EHA: 2–ethylhexyl acrylate
- GPC: gel permeation chromatography
- IBA: Isobornyl acrylate
- MMR: monomer reactivity ratio
- MPS: mean particle size
- PSD: particle size distribution
- PVA: polyvinyl alcohol
- rpm: revolutions per minute
- SEM: scanning electron microscopy
- Tg: glass transition temperature
- TMS: tetramethylsilane
- UV: ultraviolet
- VA: vinyl acetate
- WB4698: sodium benzophenone–4–methyl sulphonate

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Abstract

Emulsion and suspension polymerisations of acrylates were carried out in the absence of emulsifiers. The reaction systems were stabilised by the combination of a small amount of protective colloid i.e. poly(vinyl alcohol) and continuous ultrasonic homogenisation. A commercially available ultrasonic homogenizer, the "whistle reactor" was used in a closed loop system comprising a pump, an ultrasonic homogenising head and a reaction vessel. Emulsion and suspension polymerisations were carried out in such equipment using thermal, redox and photo– initiators. A series of polyacrylate latexes have been produced using this whistle reactor.

Investigations have also been carried out into the possibility of using such polyacrylate latexes as an alternative for the solution–based polyacrylate pressure–sensitive adhesives. Pressure–sensitive adhesives were prepared in both a batch reactor by solution polymerisations and in the whistle reactor by emulsion and suspension polymerisations. They were characterised and compared.

Chapter 1

Introduction

1.1 Polymerisation

Reaction processes in which small molecules become chemically combined to form a large molecule are known as polymerisation. The small molecules are the monomer and the large molecule product the polymer. Often the monomers are molecules containing unsaturated carbon double bonds. Polymerisation which involves initiation by active centres, propagation, transfer and termination of the active centres, without elimination of other small molecules, is known as addition polymerisation. Free–radicals, cations and anions may serve as the active centres in such polymerisations. In a polymerisation, the active centres may be generated at elevated temperature (known as thermal polymerisation), by a redox reaction (known as redox initiated polymerisation) or by irradiation (known as radiation polymerisation).

1.2 Techniques for Effecting Polymerisation

There are several techniques for effecting free–radical addition polymerisation. These include bulk, solution, suspension and emulsion polymerisation. Traditionally, bulk polymerisation is defined as the formation of polymer from pure, undiluted monomer(s). However, the bulk polymerisation systems usually contain initiator and chain–transfer agents. Solution polymerisation refers to a polymerisation process in which the monomer(s) are dissolved in solvent(s). The term suspension polymerisation represents the heterogeneous polymerisation process in which monomer(s) are suspended as the discontinuous phase and polymerised by initiation in this discontinuous monomer phase. Emulsion polymerisation refers to a heterogeneous reaction process in which monomer(s) are dispersed in a continuous phase with the aid of an emulsifier system and polymerised with a free–radical initiator dissolved in the continuous phase. The continuous phase for suspension and emulsion polymerisation is usually water. The products of suspension and emulsion polymerisation are called synthetic polymer latexes.

1.3 Advantages of Emulsion Polymerisation

With the increasing awareness of environment pollution by organic solvents, emulsion polymerisation has recently undergone revitalisation with the replacement of organic solvent–based coatings, inks, and adhesives by synthetic emulsion polymer latexes. Moreover, water used in emulsion polymerisation is much less expensive than organic solvents. Another distinct advantage of emulsion polymerisation over solution polymerisation is that both high speed of polymerisation and high molecular weight can be achieved by emulsion polymerisation. Suspension polymerisation is another alternative to solution polymerisation. Because dispersing agents and protective colloids used in suspension polymerisation are less effective than emulsifiers in the stabilisation of polymer particles, the particle size of a polymer suspension is usually much bigger than that of a polymer emulsion. Due to the higher tendency of its polymer particle to coagulate, suspension polymerisation products are not usually used directly as an aqueous latex, they are coagulated and dried after polymerisation.

1.4 Disadvantages of Emulsions and Suspensions

It has long been recognised that emulsifiers (or surfactants) used in emulsion polymerisation contaminate the polymer. So do the dispersing agents (or protective colloids) for suspension polymerisation, although to a less extent. As reviewed by Blackley (1975), several approaches have been made to eliminate the detrimental effects of added surfactants in emulsion polymerisation systems. If low molecular weight emulsifiers are present in the polymer, the migration of the emulsifiers to the polymer surface can detract from the polymer surface properties. Moreover, the polymerisation products of emulsion and suspension polymerisations are generally in the form of polymer latexes in water, and if they are not to be used directly as latexes, the polymers have to be isolated and dried. The drying for removing water could be more difficult than that for removing organic solvents used in solution polymerisation.

1.5 Polymers as Adhesives

With few exceptions, all the adhesives are organic polymers of modest molecular weight and low crosslinking density. While originally a variety of naturally occurring polymers (e.g. starch, egg albumen, gelatine) were used as adhesives, these have very largely been replaced by synthetic polymers especially produced for the purpose—indeed they could be described as "tailor–made". Since the majority of adhesives are used either as solutions in organic solvents or as suspensions or emulsions in water, it is common practice to prepare the desired polymers by solution, suspension or emulsion polymerisation. Conventional emulsion polymerisation uses significant amount of emulsifiers to stabilise the emulsions. Similarly, suspension polymerisation uses dispersing agents (inorganic salts) and/or protective colloids (water–soluble polymers), and some emulsifier may also be employed. As a result, if the polymer surface property is important for the final application, the elimination of these dispersing agents and emulsifiers would be desirable. Those applications where the polymer surface property may be important are adhesives, inks and coatings.

The main objective of this research is to investigate the emulsion and suspension polymerisation of acrylates in the presence of small amount of polyvinyl alcohol without any other emulsifier using ultrasonic conditions. It is hoped that stable polymer emulsions and suspensions can be made with small amounts of mild surface active material (polyvinyl alcohol). A further and particular objective is to prepare polyacrylate emulsions and suspensions suitable for pressure–sensitive adhesive applications.

1.6 Plan of the Thesis

This present chapter gives a general introduction and background of the research. Chapters 2 and 3 are reviews of aspects of pressure–sensitive adhesives and polymerisation respectively. Chapter 4 surveys the application of ultrasound in polymer chemistry. The plan of work is described in a separate but very short Chapter 5. Chapter 6 describes the equipment and experimental work of the project. Chapter 7 follows with a description of work on the solution polymerisation in a batch reactor. In Chapter 8, the emulsification in the whistle reactor is described. Chapters 9 and 10 follow with descriptions of the work on suspension and emulsion polymerisation respectively in the whistle reactor. In Chapter 11, the PSAs prepared by suspension and emulsion polymerisation are characterised and compared with those by solution polymerisation. The conclusions and discussion are given in Chapter 12.

Chapter 2

Pressure–Sensitive Adhesives (PSAs)

2.1 What Is a Pressure–Sensitive Adhesive ?

Viscoelastic adhesives coated on flexible tapes are referred to as "pressure–sensitive", a term which derives from the early observation that the greater the pressure used in applying the tape to a substrate, the greater the force needed to remove it (Wake,W.C., 1982). A pressure–sensitive adhesive, when it is in its dry state (i.e. without solvents and residual monomer), should be tacky at room temperature and adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure.

2.2 Preparing PSAs

2.2.1 Methods Used

PSAs have been made from either natural rubber or synthetic elastomers. The process of manufacturing PSAs from natural rubber includes milling and breakdown of the rubber, the dissolution of the rubber in an organic solvent such as hexane or toluene, coating of this rubber solution on the backing and subsequent drying. For satisfactory products it is necessary that tackifying resins (such as wood rosin and its derivatives) and antioxidants are added to the rubber solution before the coating process.

In the last few decades, synthetic elastomers has been increasingly used to replace natural rubber in the manufacturing of these adhesives. The adhesive formulations are usually sophisticated mixtures, examples of which may be made by one of the following methods:

2.2.1.1 Solution Polymerisation

Polymerisation of a mixture of monomers dissolved in a solvent or solvent mixture is initiated by a free radical initiator such as benzoyl peroxide (BPO) or azoisobutyronitrile (AIBN). This results in a polymer solution which is coated onto a backing with or without prior dilution. A pressure–sensitive film is formed upon the evaporation of the solvent(s). A typical formulation of a solvent–based acrylic PSA (Schneberger,G.L. 1983) is given in Table 2.1.

Table 2.1 Formulation of a Solvent-based PSA

Copolymer based on	Methyl acrylate	100
	n-Butyl acrylate	290
	2-Ethylhexyl acrylate	590
	Glycidyl methacrylate	20
Acetone		300
Benzene		130
p-Toluene sulphonic acid		5
Dried, cured 3 min at 100°C		

2.2.1.2 Emulsion Polymerisation

Under the emulsification effect of a surfactant, the monomer is suspended in water to form an emulsion. Polymerisation is induced by a water–soluble initiator. The polymerisation product (i.e. a polymer latex) is coated on a backing with or without additional thickening. The coated product is dried to form a pressure-sensitive film. A typical formulation of an emulsion-based acrylic PSA (Schneberger,G.L. 1983) is given in Table 2.2.

Table 2.2 Formulation of an Emulsion-based PSA

Nonylphenol ethylene oxide condensate (97%by weight oxyethylene units)	22.4
Vinyl acetate	83.6
2-Ethylhexyl acrylate	352.0
Acrylic acid	4.4
Sodium acetate	1.0
Water	465.0
Sodium metabisulphite (in 10 parts water)	
Ammonium persulphate (in 10 parts water)	
The mixture is maintained at 60-75°C for 3 hours after which 0.45 parts ammonium persulphate (in 10 parts water) is added and heating for 1 hour more.	

2.2.1.3 Radiation Polymerisation

Pressure-sensitive adhesives can be prepared directly on a substrate by irradiating a film of a mixture of monomers or a solution of polymer in monomers, with UV light or EB (electron beam). Radiation curing has great potential advantages although the technologies of such systems have not yet been fully developed (Schneberger,G.L. 1983).

2.2.1.4 Suspension Polymerisation

Suspension polymerisation has not been used in PSA technology due to its high tendency for polymer particle agglomeration. Attempts were made in this present work (see Chapter 9) to produce aqueous-based acrylic PSA by suspension polymerisation in the whistle reactor.

2.2.2 Comparison

Each of the methods for preparing PSAs has its own advantages and disadvantages. A comparison of these methods is given in Table 2.3.

Table 2.3 Comparison of Different Methods for Preparing PSAs

Method	Advantages	Disadvantages
Solution Polymerisation	technology well developed; high peel strength; good coating quality; good humidity resistance.	organic solvents are expensive, flammable, toxic, air polluting; low cohesive strength.
Emulsion Polymerisation	water-- the cheapest solvent, odourless, nontoxic, nonpolluting, nonflammable; high cohesive strength.	presence of surfactants and thus low water/humidity resistance, low peel strength; poor coating quality.
UV and EB Curings	do not need solvent, and thus eliminate any solvent evaporation and problems associated with the use of solvent; grafting and crosslinking give better adhesive performance; fast line speed possible.	for UV curing, a photoinitiator is necessary; need nitrogen blanketing; more residual monomers especially for UV curing

2.3 Properties of Pressure–Sensitive Adhesives

Pressure–sensitive adhesives are generally characterised by two properties: tack and peel strength.

2.3.1 Tack

Tack is the adhesive property which enables the adhesive to form a bond with the surface of the substrate upon brief contact under light pressure. Pressure–sensitive tack is measured by one of several methods: rolling ball tack test; probe tack tests for the strength of the bond formed between the probe tip and the adhesive after a standard time at low pressure.

2.3.2 Peel Adhesion

Peel adhesion is the adhesive property showing the resistance to peel. It is measured by the force required to remove the adhesive tape from a substrate to which it has been applied by a standard method. Various peel methods may be employed: 180 degree peel; 90 degree peel; Drum peel (tape unwind); T–peel.

In a peel test, the adhesive may fail adhesively or cohesively, and the adhesive strength or cohesive strength of the pressure–sensitive adhesive may be derived.

Standard tack tests and peel tests for pressure–sensitive adhesives have been described in ASTM D3330, D2979, D3121.

2.4 Factors Affecting Pressure–Sensitive Adhesive Properties (Satas,D. 1982)

A liquid with a surface tension less than the critical surface tension of the substrate will spontaneously wet the surface of the substrate. Thus, to have good pressure–sensitive tack, an adhesive should have low surface energy. The interaction energy of the adhesive and the substrate is determined by the surface characteristics of the adhesive and the substrate. However, the physical (rheological) properties determine the rate and extent of contact and bond formation.

The physical properties of the adhesive are directly related to the chemical composition and the molecular structure of the adhesive. A relatively low glass transition temperature enables the deformation of the adhesive at the bonding stage. The modulus should be high to achieve good cohesive strength.

To obtain a balanced tack, adhesive and cohesive strength, one can use:

- copolymerisation to change the glass transition temperature
- regulation of molecular weight by altering initiator concentration, or addition of chain transfer agents.
- crosslinking
- compounding with tackifiers

2.5 Acrylic Polymers as Pressure Sensitive Adhesives

Acrylic polymers possess some inherent properties (Satas,D. 1982) which are superior to many other polymers used for pressure–sensitive adhesives. Firstly, unlike polybutadiene and polyisoprene, polyacrylate is saturated and resistant to oxidation. Secondly, it is transparent and does not yellow on exposure to sunlight. Thirdly, acrylic monomers can readily copolymerize with many monomers carrying various functional groups (Pradeep,K.D. et al. 1982) such as –OH, –COOH, $-NH_2$. These functional groups provide sites for crosslinking and thus improve the adhesive performance. Moreover, polyacrylates of a proper monomer composition are inherently pressure sensitive without any compounding. Thus there is no migration of low molecular weight tackifiers, plasticisers and other additives which are present in compounded adhesives. Although recently introduced, acrylic polymers have been playing an important role in pressure–sensitive adhesives. They are available in the form of solutions, emulsions, hot melts and 100% reactive solids.

Currently, acrylics account for about one–quarter of the domestic pressure–sensitive adhesive market (Temin, S.C. 1988) which traditionally has been dominated by solvent–based systems (Hagan,J.W. et al. 1979; Devadoss,E. 1985a,1985b). Stimulated by the soaring costs of energy and labour and the increasing awareness of environmental pollution, acrylic emulsions have been presenting the pressure–sensitive adhesive (PSA) market with a challenge. Besides emulsions, other alternatives for solvent–based PSAs such as radiation curing (UV and EB) and hot melt PSAs are under development by many manufacturers and research institutions.

Chapter 3

Aspects of Suspension, Emulsion and Photochemical Polymerisation

In Chapter 1, polymerisation and the techniques for polymerisation have been generally introduced. In this chapter, more specific aspects of emulsion polymerisation, suspension polymerisation, photopolymerisation and photoinitiators will be considered.

3.1 Polymerisation in Aqueous Systems

Polymerisations in aqueous systems fall into three categories: solution polymerisation of a water soluble monomer, suspension polymerisation and emulsion polymerisation. As already introduced in Section §1.2, aqueous suspension polymerisation and emulsion polymerisation refer to polymerisation of a water insoluble or sparingly soluble monomer in a heterogeneous dispersion in water, the former being initiated in monomer droplets and the latter being initiated in micelles in aqueous phase. Emulsion polymerisation usually produces a stable colloidal dispersion of polymers in an aqueous medium which is known as a synthetic latex, with particle diameters in the range 0.03 — 0.5 μm. The products of suspension polymerisation, however, are usually thermodynamically unstable due to the increased particle diameters 50 — 200 μm (Grulke,E.A., 1989). In the present work, the particle size of the products of polymerisation in a whistle reactor is in the range of 2 — 20 μm. Such dispersions share characteristics with both latexes prepared by conventional emulsion polymerisation, and polymer dispersions produced by conventional suspension polymerisation. These products are referred to as latexes, because they exhibit some degree of stability.

3.2 Droplet Formation in Suspension Polymerisation

For suspension polymerisation, the monomers are suspended, by agitation, as a discontinuous phase of droplets in a continuous phase, which is usually water. The monomer droplets are thermodynamically unstable, unlike emulsion systems in which the monomer droplets are stabilised by the adsorbed emulsifiers. If the agitation stops, the monomer droplets (50 — 200 μm) coalesce rapidly to form a distinct monomer phase (Grulke,E.A., 1989). Particle coalescence is not prevented but is retarded by a combination of protective colloids (or surfactants) and agitation design.

After polymerisation, polymer particles are formed. These products of suspension polymerisation — slurries of suspended polymer particles --- are thermodynamically unstable, unlike the polymer latexes produced by emulsion polymerisation. During storage, these polymer particles settle from the slurry as a result of density differences. If the particles are soft, they may coagulate together. After monomer recovery and dewatering, a powder product is obtained and may be stored for further use. Monomers with too high a water solubility and monomers which yield polymers of too low glass transition temperature (Tg) are unsuitable for such conventional suspension polymerisation processes due to the high tendency for particle agglomeration (Odian,G.,1981). In this present work, with ultrasonic homogenisation as the agitation, however, the tendency of particle agglomeration is suppressed in the suspension polymerisations of 2-ethylhexyl acrylate (EHA), and n-butyl acrylate (BA) whose Tgs are -85 °C and -54 °C respectively and are far below room temperature.

3.3 Particle Nucleation in Emulsion Polymerisation

Several theories exist of interpreting the mechanism of emulsion polymerisation, however no one of them can fully explain all the experimental observations. It is evident that emulsion polymerisation is a complicated process, with several mechanisms of particle nucleation.

3.3.1 Nucleation in Micelles

The Harkins Theory has long been accepted as the mechanism of emulsion polymerisation in which the principal locus for initiation is the micelles in the aqueous phase (Harkins, 1947, 1950). The principal function of the monomer droplets, according to Harkins' theory is not to be a locus of polymerisation, but to act as a storehouse of monomer from which molecules diffuse into the aqueous phase and from this into either soap micelles or polymer- monomer latex particles. The outline of Harkins theory is :

- Principal loci for the initiation of polymer particle nuclei are the micelles.
- Principal locus for the formation of polymer is the polymer particle itself.
- A free radical mechanism of polymerisation is assumed.
- Very little polymer forms within the monomer droplets, whose function is to act as highly distributed reservoirs of monomer.
- Extremely little polymer is produced in the aqueous phase.

In the studies of seeded and unseeded polymerisation of styrene using sodium dodecyl sulphate as emulsifier, Hansen and co-workers (Hansen and Ugelstad, 1979b) conclude that the micelles become the dominating loci for particle nucleation above the critical micelle concentration for the emulsifier.

3.3.2 Homogeneous Nucleation

The term “homogeneous nucleation” is used to describe particle formation in the water phase by the propagation and precipitation of oligomeric radicals. Roe (Roe,C.P., 1968) proposed a theory of particle initiation which, in outline is as follows. The interaction of a free radical and a monomer molecule (both of which are dissolved in the aqueous phase) results in the formation of a monomer radical. This reacts with additional dissolved monomer molecules to become a growing polymer chain suspended in the aqueous phase. Further development of this sort results in the adsorption of emulsifier which prevents flocculation, and thus a stable polymer particle is formed. This is then swollen with absorbed monomer. Particle formation stops when the surface of the particles has grown to such a size that the emulsifier concentration in the aqueous phase is below a critical point, somewhat lower than the critical micelle concentration.

Hansen and Ugelstad (Hansen and Ugelstad, 1978) have proposed a more qualitative theory for homogeneous nucleation. If no emulsifier is present, the radicals produced may:

- add monomeric units dissolved in the water phase;
- be absorbed into an existing polymer particle or be adsorbed onto the surface of the particle;
- terminate in the water phase with another radical;
- coagulate with other dissolved radicals; or

- precipitate as a primary polymer particle if the radical reaches the critical chain length.

If, in the water phase, there are surface active species present which may adsorb onto the precipitated primary particles, the particles may be stabilised, otherwise they will coagulate due to insufficient surface charge. The coagulation will stop when the charge density reaches a higher level where the particles are stable. The mechanism is called limited coagulation. They established a kinetic model for this simultaneous particle nucleation and limited coagulation.

Hansen et al. (Hansen and Ugelstad, 1979a) also conducted seeded emulsion polymerisation and investigated the effects of amount, size, and surface charge of the seed particles on the formation of new particles.

Arai et al. (Arai, Arai, and Saito, 1979) established a model for polymer particle formation in soapless emulsion polymerisation on the assumption that each growing radical and polymer molecule above the critical size form a fresh polymer particle. Based on the assumption that the increase in the total volume of polymer particle is caused by:

- the fresh formation of polymer particle,

- the entrance of growing radicals into polymer particle, and

- the propagation reaction in each polymer particle.

they were able to calculate the number of polymer particles. This calculated value was in good agreement with the experimental results for the soapless emulsion polymerisation of methyl methacrylate.

3.3.3 Nucleation in Monomer Droplets

Ugelstad et al.(Ugelstad, El-Asser and Vanderhoff, 1973) presented some evidence that the initiation of polymerisation may take place in monomer droplets, whose sizes are small enough to be able to compete sufficiently with monomer-swollen micelles in capturing free radicals from the aqueous phase. Hansen and Ugelstad (Hansen, Ugelstad, 1979c) studied the nucleation of polymer particles in a finely dispersed styrene monomer emulsion in competition with homogeneous and micellar mechanisms. The emulsions were prepared with a high-pressure homogenizer. Sodium dodecyl sulphate was used as emulsifier. For some experiments, the final particle sizes were found to have a bimodal distribution. This was taken as the evidence of particle nucleation both in micelles and monomer droplets.

3.4 Factors Affecting Polymer Latex Stability

There are many factors that affect the stability of polymer latex. Some of the more important of these factors are:

- particle size;
- particle surface properties;
- the physical state of particles;
- electrolyte concentration in aqueous phase.

3.4.1 Particle Size

With sufficiently small particle sizes, particles can be retained suspended in the continuous phase by random Brownian motion. With increased particle size, the effect of gravity becomes dominant and particles become concentrated at either the upper or lower part of the system, according to the density difference from the continuous phase.

3.4.2 Particle Surface Properties

In aqueous-based emulsion polymerisation, various surface groups can be formed using different initiators (Ottewill,R.H.,1982):

weak acid	–COOH	from bisazocyanopentanoic acid
strong acid	$-OSO_3^-$	from persulphate
base	$-NH_2$	from azobisisobutyramidine
nonionic	–OH	from hydrogen peroxide

Copolymerisation of monomers with functional groups (–COOH,$-SO_3H$,$-NH_2$,–OH) may also provide those groups on the particle surface.

In emulsion polymerisation, the adsorption of emulsifiers on the polymer particle surfaces is crucial to stabilise the particle against agglomeration. In suspension polymerisation, a protective film of water soluble polymer or a layer of inorganic dispersent on the surfaces of polymer particles is necessary to prevent immediate coalescence. Electrical charges will be present on the surfaces of particles with adsorbed anionic, cationic surfactants molecules, or with surface groups. Charged particles will show repulsion upon approach, but the mixing of opposite charged latexes can lead to coagulation.

3.4.3 The Physical State of Particles

One polymer particle is made of a large number of polymer chains, except in the case of highly crosslinked polymerisation in which each polymer particle is a single molecule. According to the arrangement of polymer chains inside the particles, one can classify the polymer particles into amorphous or crystalline groups. For amorphous particles, it may be elastomeric or glassy according to the Tg of the polymer. If residual monomer is present, the polymer within the particles may be soluble, swollen, or insoluble. For amorphous elastomeric particles and monomer swollen particles, if two particles approach to close-range interaction distances, there is the tendency for coagulation. For hard glassy particles there is less tendency for coagulation even when close range interactions may be significant.

3.4.4 Effect of Electrolytes

Ottewill (Ottewill,R.H. 1982) summarised the effect of electrolytes on a latex having charged particles as follows:

At intermediate electrolyte concentration (10^{-3}mol dm^{-3}) and at low volume fractions of polymer, particles occupy random positions with transient repulsive contacts. At reduced electrolyte concentration (10^{-5} mol dm^{-3}), which increases the range of the electrostatic repulsive force, or when the volume fraction of polymer is increased, the particles maintain repulsive interactions over a long period of time and remain well separated. On the other hand, if the electrolyte concentration is increased to a certain value (e.g. 0.2 mol dm^{-3}), there is a transition from a stable dispersion to an unstable state. The electrolyte concentration at which the transition occurs is termed the "critical coagulation concentration".

3.5 Particle Coagulation during Polymerisation

The number of particles formed in emulsion polymerisation is directly related to the number of primary particles and to the extent of subsequent coagulation of the primary particles.

In suspension polymerisation, polymer particles are usually directly formed upon the initiation of polymerisation in the monomer droplets. The final number of particles is determined by the equilibrium between the coagulation of the particles and the redispersion of these coagulated particles by agitation.

Particle coagulation occurs during polymerisation, even if a high level of surfactant is used. Particle coagulation may result in gel formation, particularly in suspension polymerisation. However, by the combination of the use of surfactant/protective colloid and of proper agitation design, polymerisation is able to proceed and the system remains stable throughout the polymerisation process.

Fig.3.1 illustrates the possible pathways of a primary particle during polymerisation. Coagulation leads to a decreased number of polymer particles, to increased mean particle size, and to a more wide particle size distribution.

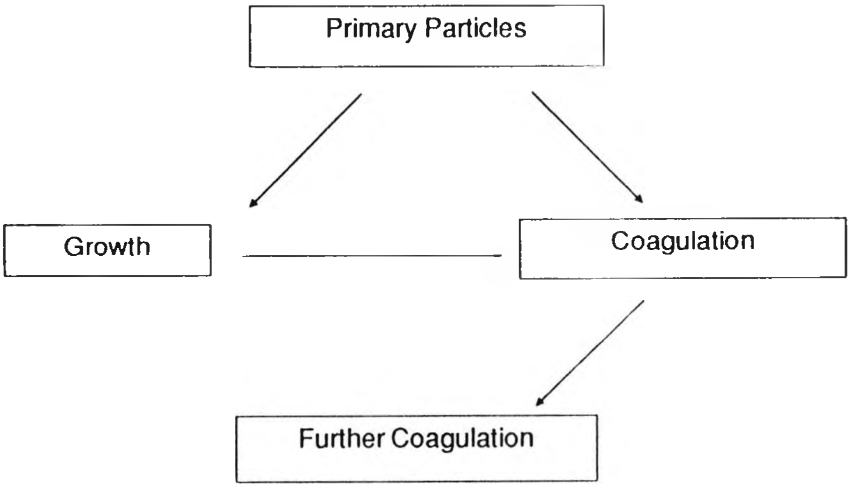


Fig.3.1 Primary Particle Pathways in Polymerisation

3.6 The Role of Poly(vinyl alcohol) (PVA) in Suspension and Emulsion Polymerisation

Partially hydrolysed polyvinyl acetate, namely polyvinyl alcohol (PVA) is one of the commonly used suspension and emulsion stabilisers.

Hatate et al. (Hatate, et al., 1981, 1985) conducted suspension polymerisation of styrene in the presence of PVA as the dispersing agent. Ultrasonic irradiation (200–800 kHz) was applied from a transducer element to the bottom of the reaction vessel. It was suggested that ultrasonic irradiation has the effect of preventing the agglomeration between droplets and the sticking of droplets to the reactor wall, in both batch and continuous reactors during suspension polymerisations of styrene. Apparently, the ability of PVA in stabilising suspension polymer particles is not as good as that of surfactant (e.g. soap), and the polymer particles produced by suspension polymerisation are usually much bigger than that of emulsion polymerisation in the presence of surfactant.

There have been some examples of emulsion polymerisations using PVA as the emulsifier (Wolf,F. and Eckert,S., 1971; Borden, 1973; Hayashi,S. et al. 1973; Brizzolara,D.F. and Garrett,R.R. 1974; Lindemann,M.K. 1976). Most of the work is in the form of patents, and the amount of PVA used was not quoted. It seems that in emulsion polymerisations, more than 5% of PVA based on the weight of aqueous phase has been used. In the emulsion copolymerisation of divinylbenzene and styrene, Wolf and Eckert used PVA as the emulsifier with the formation of oversized polymer particles in the range of 0.3-0.8 mm. It is clear that PVA alone is not a good emulsifier for emulsion polymerisation. Moreover, PVA has also been used in combination with another anionic surfactant which is more powerful than PVA (Domoto,M. et al. 1974). Domoto and co-workers conducted the emulsion copolymerisation of ethylene with vinyl acetate using a mixed emulsifier system containing PVA, glycol mono(nonyl phenyl) ether having 9 moles of ethylene oxide units, and sodium lauryl sulphate.

3.7 The Role of Agitation in Suspension and Emulsion Polymerisation

In suspension polymerisations, apart from ensuring good mixing and heat removal, agitation is used to redisperse droplet pairs and clusters (Grulke,E.A., 1989). As a result, agitation can affect the final particle size of the polymer dispersion.

In conventional emulsion polymerisations, agitation is employed to ensure good mixing of the reactants and to promote the heat transfer to the reactor jacket or coils (Poehlein,G.W.,1989). Because a relatively high level of emulsifiers is used, agitation has no direct effect on the particle size of the polymer latexes.

3.8 Photopolymerisation

The term photopolymerisation is used to describe a polymerisation process under the influence of light. It is the case that monomers and low molecular weight polymers with unsaturated carbon bonds usually undergo addition reactions on the absorption of light, without the elimination of any other molecules in the process, i.e. an addition polymerisation process. It is further known that addition photopolymerisation proceeds almost exclusively by way of free-radical polymerisation or cationic polymerisation. Thus photopolymerisation can be classified into two major groups: free-radical photopolymerisation and cationic photopolymerisation. The former is currently enjoying a lively commercial interest in a large number of applications including photo-imaging (Jacobson,1989) and UV curing of coatings and inks (Phillips, 1983).

An alternative scheme for classifying photopolymerisation has been suggested by Delzenne (Delzenne,1979 a,b), who divided photopolymerisation into two major classes, Type 1 and Type 2. In Type 1 photopolymerisation the formation of each new chemical bond requires its own photochemical activation. Practically, Type 1 photopolymerisation usually involves crosslinking between pre-existing polymer chains.

In Type 2 photopolymerisation, a photoinitiator absorbs light and converts it into chemical energy in the form of a reactive intermediate, such as free-radicals or reactive cations. On the other hand, the exited PI* may decay back to PI with the emission of light or heat, or may be deactivated by oxygen. The reactive intermediate e.g. $I^{\cdot}$ may in turn react with another radical, with oxygen , or may initiate polymerisation (see Fig.3.2).

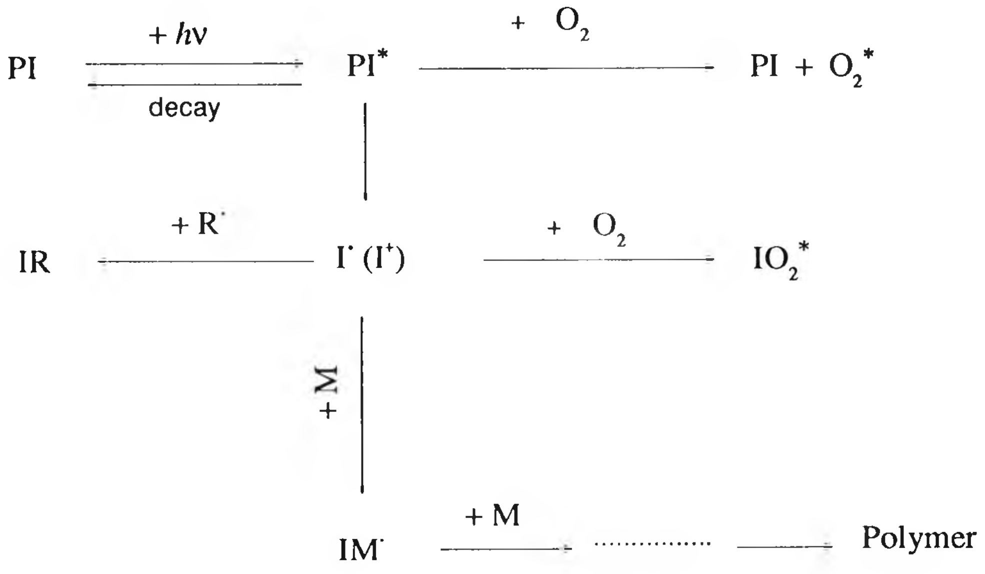


Fig.3.2 Pathways of Active Centre
in Type 2 Photopolymerisation

3.9 Photoinitiators for Free-radical Polymerisation

Photoinitiators are essential ingredients for UV initiated polymerisation systems. They can be divided into two main groups:

- Type I photoinitiators --Unimolecular Radical Generation
- Type II photoinitiators --Bimolecular Radical Generation.

3.9.1 Type I Photoinitiators

Many aromatic carbonyl compounds carrying particular functional groups undergo direct photofragmentation into radicals. This fragmentation can take place at the bond adjacent to the carbonyl group (α-cleavage),or at the bond in the β-position (β-cleavage) depending on the nature of the functional group and its location in the molecule (Hageman,1985) (see Fig.3.3).

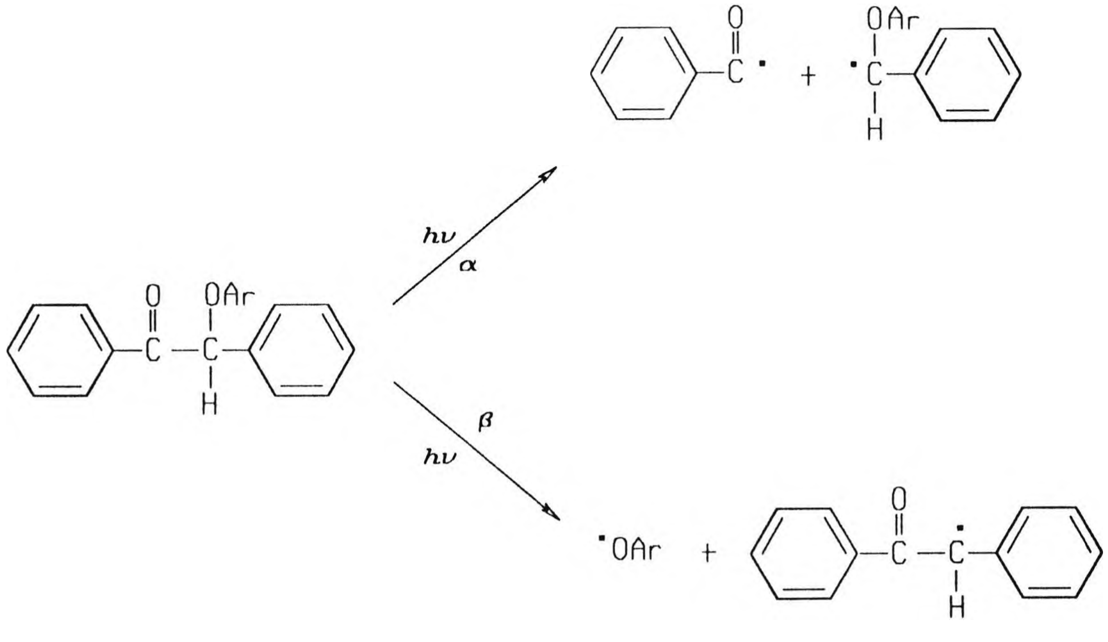


Fig.3.3 Photofragmentation of Benzoin Aryl Ether

3.9.2 Type II Photoinitiators

Photoinitiators of this type include benzophenone, Michler's ketone, etc. Unlike Type I photoinitiators, Type II photoinitiators must undergo bimolecular H-abstraction with a H-donor to give free-radicals for initiating polymerisation. Suitable H-donors include tertiary amines, alcohols and ethers.

Fig.3.4 represents the bimolecular H-abstraction between benzophenone(BP) and tertiary amines with the formation of α-aminoalkyl radicals, which are efficient in the initiation of the polymerisation of acrylates.

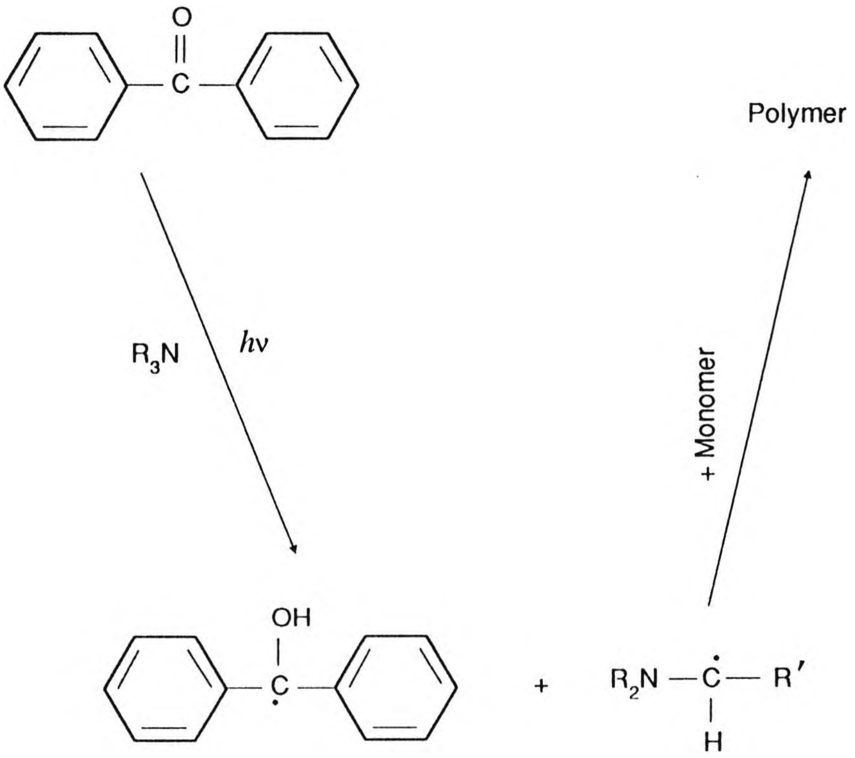


Fig.3.4 H-Abstraction between Benzophenone and Amine

3.10 Radiation-induced Emulsion Polymerisation

Radiation-induced emulsion polymerisation refers to the emulsion polymerisation initiated by a radiation source, either γ-rays or ultraviolet light (UV). Because reactive free-radicals (e.g. hydroxyl radicals) can be generated from water molecules with γ-ray irradiation, no initiator is necessary for the γ-ray induced emulsion polymerisation. Under γ-radiation, particularly using isotopes such as ^{60}Co γ-source, an essentially unlimited range of radical fluxes from zero to that equivalent to many moles per litre of chemical initiators can be produced. Photoinitiators and photosensitizers are generally used in UV-induced emulsion polymerisations. For these systems, the rate of initiation is dependent on the type and concentration of the photoinitiators as well as on the intensity of the UV-light irradiation. Another feature of the radiation initiation is that the rate of initiation is essentially temperature independent, which leads to relatively low temperature dependencies of the overall polymerisation (Stannett,V.T. 1982).

The following are some of the advantages of the radiation-induced emulsion polymerisation:

- Initiation rate and polymerisation rate may be varied over a wide range during the polymerisation processes. This allows the possibility of automatic control of molecular weight, particle size and distribution. Elimination of residual monomers can be easily performed by increasing the radiation intensity at the end of the polymerisation.

- Initiation rate is not coupled with the polymerisation temperature, so polymerisation can be initiated at any desired temperature, low or high.

- The polymerisation can be stopped at any stage of the polymerisation by the removal of the radiation source.

- There is no contamination with residual initiator for γ-ray induced polymerisation.

Chapter 4

The Uses of Ultrasound in Polymer Chemistry

The sound range that can be heard by the human ear is about 16 Hz -16 kHz. The name ultrasound is used to describe the range of sound which cannot be heard by humans. The ultrasound range is divided into two sub-ranges (Mason and Lorimer, 1988). The high frequency sub-range (1-10 MHz) involves low amplitude propagation , which is often referred to " low power ultrasound ". The low frequency sub-range (20-100 kHz) involves high energy waves, which is often called " power ultrasound ".

4.1 Ultrasonic Cleaning

Ultrasonic cleaning is a major application of power ultrasound (Cracknell,1980). It is very familiar to chemists and there are few chemistry laboratories that do not make use of an ultrasonic cleaning bath. However, apart from the ultrasonic cleaning bath, there are many examples which make use of ultrasonic cleaning, some examples are described below.

In a reactor which is quite similar to a ultrasonic cleaning bath, Hatate et al (Hatate, et al, 1981, 1985) conducted suspension polymerisation of styrene. The reaction vessel used was a separate flask. Ultrasonic irradiation

(200-800 kHz) was applied from a transducer element to the bottom of the reaction vessel (see Fig.4.1) No effect of the ultrasonic irradiation on the kinetics of styrene polymerisation has been detected. However, ultrasonic irradiation has the effect of preventing the agglomeration between droplets and the sticking of droplets to the reactor wall, in both batch and continuous reactors during suspension polymerisations of styrene.

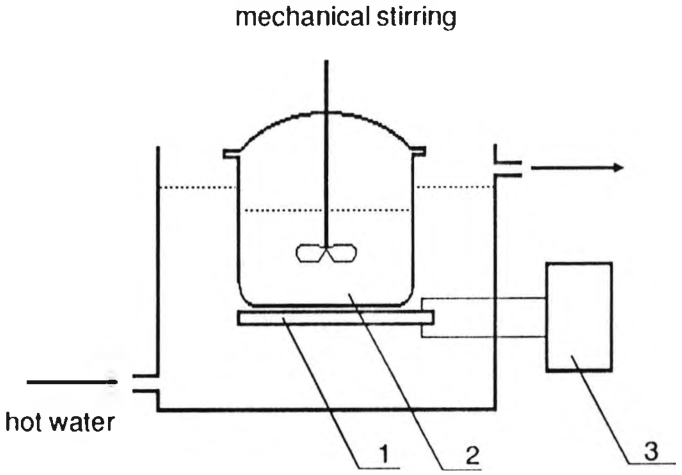


Fig.4.1 Hatate's Reactor for Suspension Polymerisation
1 ultrasonic oscillater; 2 reactor; 3 ultrasonic generator

Tategami and co-workers (Tetagami,Y. et al, 1987) have used ultrasound treatment to remove dispersant residues, scale, and emulsion polymer particles from suspension polymerised poly(methyl methacrylate-butyl acrylate-methyl acrylate) particles in order to produce highly transparent polymer compositions useful as lenses, prisms, and optical fibres.

In a patent assigned to Hitachi Chemical Co. Ltd. (Hitachi, 1982), moisture-resistant adhesive tapes are prepared by ultrasonic treatment of dried acrylic emulsion tapes in methanol for 1 minute. The tape is then dried to give an adhesive tape with greatly increased humidity resistance. This is probably also due to the removal of surface active species from the adhesive films by ultrasonic cleaning.

4.2 Monitoring Polymerisation Reactions

Low power ultrasound have been increasingly employed to follow the course of polymerisation during the last ten years. The principle of ultrasonic monitoring of polymerisation reaction, similar to SONAR, is the velocity dependence of the ultrasound upon the transmission media. SONAR uses the ultrasound velocity to determine the distance of certain subjects under water, whereas following a polymerisation process utilises the changes of ultrasound velocity caused by the changes of the bulk properties of the polymerisation system.

Sladky et al reported the use of ultrasound in the range of several hundred kHz to a few MHz for monitoring suspension polymerisation of vinyl chloride (Sladky,P. et al, 1979a, 1979b, 1982). The local phase transition and the morphology were predicted, and the degree of conversion during polymerisation was continuously monitored, by following the attenuation of the ultrasonic waves. In a patent entitled "Continuous determination of monomer conversion" (Zdrazil,J. et al, 1982), a method of following monomer conversion during suspension and emulsion polymerisation was described using the rate of propagation of the ultrasound wave by comparison with a calibration diagram relating the propagation rate of the waves to monomer conversion.

Russian workers (Dubrovskii,S.A. et al, 1982) have derived the relationship of the relative coefficient of acoustic loss to the average dimension of the suspended particles. They have used this relationship for following the dynamics of the particle dimension changes in a suspension polymerisation of ethylene oxide in heptane. Subsequent work reported on the application of ultrasound for monitoring suspension and emulsion polymerisation is from Germany in the form of patents as well as papers (Dinger,F. et al, 1982, 1983a, 1983b, Hauptmann,P. et al, 1981, 1983a, 1983b, 1984, 1985, Hergeth,W.D. et al, 1986). The process was illustrated for the emulsion, suspension and solution (in MeOH) polymerisations of vinyl acetate. The contribution of individual components of the polymerisation systems to the overall ultrasound velocity was emphasised.

4.3 Ultrasound Induced Polymerisation and Depolymerisation

Until recently, the application of ultrasound to homogeneous systems comprising only monomers and initiators to produce polymers or copolymers received little attention, due to the competition of depolymerisation with polymerisation. Another difficulty encountered in such a process is likely to be the increased viscosity during the course of polymerisation which will change the acoustic field (Mason and Lorimer, 1988). In spite of the problems associated with such systems, there has been some work reported on the use of ultrasound to initiate polymerisations in pure monomers or monomer mixtures.

Tretinnik and co-workers (Tretinnik,V.Y. et al, 1971) have used high intensity ultrasound to initiate polymerisation of acrylic monomers as a method of producing emulsion stabilisers. This is an example which makes use of the competitive reaction between polymerisation and depolymerisation under ultrasonic irradiation, which will lead to the formation of low molecular weight species useful as emulsion stabilisers.

Recently Price and co-workers (Price,G.J. et al, 1990) have successfully produced homopolymers and copolymers of styrene, methyl methacrylate, and n-butyl methacrylate. High molecular weight homopolymers were formed rapidly during the initial stage of sonication and were then subjected to degradation.

Until recently most investigations have concentrated on applying ultrasound to systems containing either a mixture of homopolymers or a mixture of polymer and monomer in order to produce graft or block copolymers (Mason and Lorimer, 1988). In the case of sonication of mixtures of homopolymers, it is assumed that the homopolymers are first degraded to form macroradicals, which are subject to recombination to form a block copolymer (see Fig.4.2). Whereas in the case of sonication of monomer/polymer mixtures, it is likely

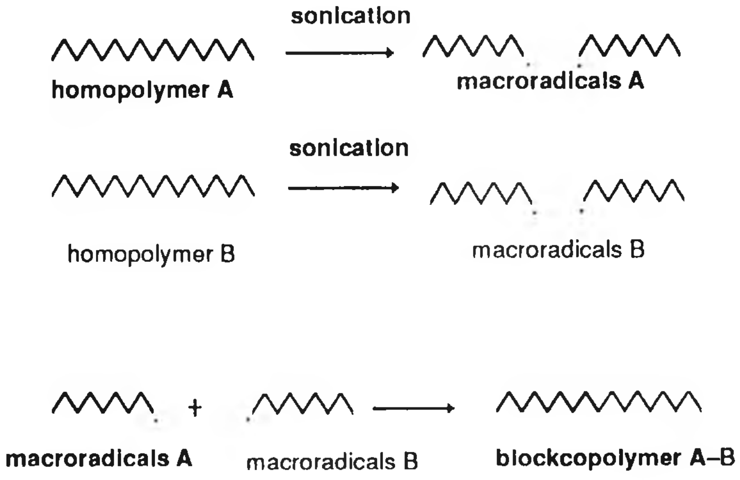


Fig.4.2 Mechanical/chemical Reaction of Polymers

that the macroradicals formed by degradation of polymer initiate the polymerisation of monomers to give block copolymers.

Few workers have studied the degradation of polymers by ultrasound in a suspension polymerisation system. In a series of papers, German workers (Simionescu,C. et al, 1977, Vasiliu-Oprea,C. et al, 1979, 1980), studied the mechanical-chemical reaction of poly(vinyl chloride) in suspension polymerisation. It was confirmed that the alterations of the fine structure (particle size distribution) and the physicochemical properties of the polymer are a result of mechanical degradation of the heterogeneous system. Fujiwara and co-worker (Fujiwara,H. et al, 1981) conducted the suspension polymerisation of methyl methacrylate in the presence of poly(vinyl alcohol) in aqueous media under ultrasonic irradiation (200 kHz, 7.4 W/cm^3). They were able to obtain a mechanochemical block copolymer of methyl methacrylate and poly(vinyl alcohol). The polymerisation was terminated with inhibitor so that there was no further homopolymerisation of methyl methacrylate.

4.4 Emulsification and Dispersing

4.4.1 The Mixing Process and the Commercially Available "Whistle Reactor"

An emulsion of two immiscible liquids is formed when the shearing stresses on the liquids are greater than the interfacial tension. Emulsification can occur as a direct consequence of agitation, even in the absence of cavitation. An example of this is the mixing together of two liquids having widely differing densities, e.g. water and mercury (Blitz,J.,1971). However, the emulsion so formed is not stable and the liquids separate after a very short time. For making a stable emulsion, surfactants or emulsifiers are generally used to prevent particle agglomeration. Clearly, if ultrasonic induced cavitation and very violent agitation breaks up the liquid particles, it aids in obtaining the emulsion (Goldman,R.,1962). The name homogenisation is often applied to this process. In the food industry, a commercially available minisonic homogenizer, or the "whistle reactor" (see Fig.4.3) is often used for the production of tomato sauce and similar items. This is an example of ultrasonic homogenisation for emulsifying and dispersing purposes. The particle size of the emulsion formed by ultrasonic homogenisation depends on the physical properties and state of the dispersed liquids, on the intensity and duration of ultrasound application, and also on the dimensions and form of the vessel in which the homogenisation is taking place (Puskar,1982).

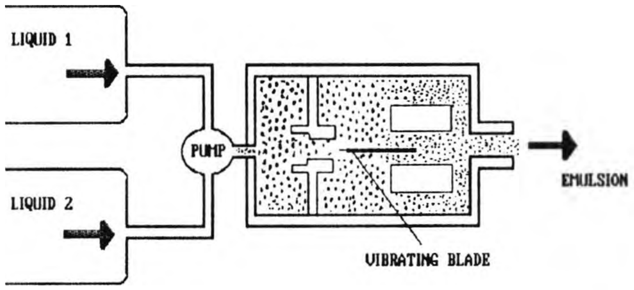


Fig.4.3 The "Whistle Reactor"

4.4.2 Homogenisation of Monomers

In practice, aqueous monomer emulsions and suspensions are generally made by mechanical stirring and shaking of the mixture of monomer with water containing surfactants (anionic, cationic, or nonionic) and suspension stabilisers. However an alternative technique is the use of ultrasonic homogenisation, i.e. pre-emulsification. It seems that pre-emulsification was first used in 1973 by Japanese workers (Uraneck,C.A.,et,al. 1973) who reported increased reactivity of tert-dodecyl mercaptan and tert-hexadecyl mercaptan modifiers in the emulsion polymerisation of butadiene with styrene as a result of pre-emulsification. Russian workers (Kokorev,D.T.,et al, 1975) observed an increased rate of emulsion polymerisation upon preliminary ultrasonic treatment of styrene. Subsequent reports of work involving pre-emulsification comes mainly from Japan, and almost all are in the form of patents.

Hansen and co-worker (Hansen and Ugelstad,1979 c) used an Ultra-Turrax homogenizer to obtain coarse emulsions and a high pressure two-stage homogenizer to obtain fine emulsions of styrene. Sodium dodecyl sulphate of a total concentration of 2 g/dm^3 , was used to stabilise the monomer emulsion against phase separation. They found that the higher degree of monomer homogenisation gives fast conversion of monomer to polymer(up to 60% with in 200 min) and smaller particle size of the final emulsion.

In a patent assigned to Asahi-Dow Ltd., Yokochi et al (Yokochi,T. et al,1977) used pre-irradiation of monomer with ultrasound for scale prevention in the emulsion polymerisation of butadiene with styrene. It is claimed that no scale formation was observed if pre-ultrasonic treatment was applied, while 50% of the polymer formed as scale if no ultrasound irradiation was applied.

In a patent assigned to Nitto Electric Industrial Co.(Nitto, 1982), pre-emulsification was used to produce acrylic acid-acrylonitrile-2-ethylhexyl acrylate copolymer emulsions with uniform particle size.

For the production of sulphonic acid-containing perfluorocarbon polymer emulsions, Japanese workers (Miyake,H. et al, 1985) also used ultrasound for the pre-emulsification of monomer in the presence of a fluorine-based emulsifier ($C_8F_{17}CO_2NH_4$).

Recently, organosiloxane emulsions with tiny and uniform particle size (mean size about 0.25 μm, polydispersity 1—2.7) have been prepared by pre-emulsification of octamethylcyclotetrasiloxane and $CH_3Si(OR)_3$ (R = methyl, ethyl) monomer, and then emulsion polymerisation in a stirred reactor (Zhang, X. et al, 1987). The monomers were emulsified with an ultrasonic homogenizer (Cole-Parmer Instrument Co., type 4710) for 1.5 minute in the presence of emulsifiers such as dodecylbenzyl sulphonic acid, dodecylmethylbenyl ammonium bromide, or dodecyldimethylbenzyl ammonium hydroxide. It is thought that the increased polymerisation rate is due to the increased hydrolysis and condensation rate of the monomer as a result of the ultrasonic homogenisation.

Emulsification by means of homogenisation has also found use in the preparation of fine solid suspensions of inorganic dispersing agents prior to monomer addition. In a patent entitled "Suspension polymerisation of vinyl compounds" (Fujikura,T., 1972), a suspension of calcium tribasic phosphate in water containing sodium dodecylbenzenesulphonate was exposed to ultrasonic waves. Monomers were added to the treated suspension and the mixture was subjected to thermal polymerisation to produce stable polymer beads with little polymer formed on the surface inside the reactor. This is probably due to the much finer solid suspension of the stabiliser formed by sonication and thus is more efficient in stabilising the polymer particles against deposition on the wall of the reaction vessel. Similar work is that of Spicuzza (Spicuzza,J.P.Jr, et al, 1977), who has claimed that polymerisation involving ultrasonic treatment of the finely divided phosphate stabiliser prior to monomer addition and thermally induced suspension polymerisation results in beads of smaller size than those prepared in untreated aqueous media.

Emulsification by homogenisation has also found use in the preparation of monomer dispersions prior to suspension polymerisation. Again most of the reported work comes from Japan, and almost all of the reports are in the form of patents. Most of the investigations involved the production of toners for developing electrostatic images (Hiyozu,Y. et al, 1987, Utsumi,H. et al, 1988a,1988b, Koyama,Y. et al, 1989). The conventional method for producing toners involved kneading a molten mixture of a pigment such as carbon black with a binder resin, cooling and grinding of the kneaded mixture, and classifying the mixture into powders having sizes between 5 and 25 µm. In contrast, Japanese workers (Hiyozu,Y. et al, 1987, Utsumi,H. et al, 1988a,1988b, Koyama,Y. et al, 1989) developed a process for producing toners by ultrasonic treatment of the monomer suspension mixtures and then suspension polymerisation in a heated stirred tank reactor (70-90 °C, 5-10 hours). Toners produced by this method comprise uniform, spherical, coloured polymer particles and do not need the grinding and classifying steps.

In a patent assigned to Kao Corp.(Kao, 1984), fine granules (average size 11.3 µm) were made by preliminary ultrasonic homogenisation of the monomer mixture (methyl methacrylate / methyl acrylate / ethylene glycol dimethacrylate) with water containing poly(vinyl alcohol) for 10 minutes and then thermally induced suspension polymerisation was conducted in a stirred reactor for 12 hours at 75°C. Without the ultrasound irradiation, the reaction mixture gelled after 1 hour of polymerisation.

Recently, Shirai and co-worker (Shirai and Takeda, 1989) also used ultrasound (US-1200, 15 kHz, 1200 W, 10 min.) to prepare monomer dispersion prior to polymerisation. Polymer particles with an average size 20.6 µm were obtained, and they were used as thermosetting powdered coating.

4.4.3 Emulsification of Polymer Solution

Emulsification by means of homogenisation has found use in the preparation of polymer dispersions that cannot be prepared directly by emulsion polymerisation (Vanderhoff, et al, 1978, Miscra, et al, 1978, El- Asser, et al, 1977 a, b). Such polymers include epoxy resins, polyurethanes, and silicones. To obtain dispersions of such polymers, one can emulsify the solutions of the polymer by homogenisation, followed by removal of the solvent by evaporation. Such polymer dispersions, with a particle size of 1-2 μm, are not stable because of the settling of the particles on storage (Ugelstad, et al, 1982).

Recently, a Japanese worker (Takeda,Y.,1990) prepared poly(N-alkylacrylamide) microgranules by firstly polymerisation of N-alkylacrylamide in benzene, followed by emulsification of the polymer solution in water using ultrasound. The prepared microgranules showed good stability without coagulation or precipitation, and are useful for pigments and coatings.

4.5 Agitation during Polymerisation

4.5.1 Agitation in Heterophase Polycondensition

Most of the chemical effects of ultrasound on the heterogeneous reaction systems can be attributed to the vast increase of the interfacial areas between different phases (Mason and Lorimer, 1988).

Ultrasonic mixing has been used as the agitation during polymerisation (Kokorev,D.T et al, 1973) for the continuous production of polycarbonate. Kokorev and co-workers used ultrasound to prepare a dispersion of an aromatic dihydroxyl compound in dichloromethane. Phosgene was then bubbled though the dispersion to give a 94% yield of polycarbonate after 25 seconds. In contrast, when using mechanical stirring (4200 rpm), 1 hour was necessary for the same yield of polycarbonate.

There is no doubt that, as a consequence of ultrasonic agitation, highly dispersed droplets of the aromatic dihydroxyl compound were formed with a vast increase of the interfacial areas between the aromatic dihydroxyl compound and phosgene bubbles. As a result, the condensation rate between the aromatic dihydroxyl compound and phosgene was greatly enhanced.

4.5.2 Agitation in Suspension Polymerisation

The use of continuous ultrasonic homogenisation instead of mechanical stirring as the means of agitation during suspension polymerisation, however, has not been reported, except for the work of Utsumi et al. who employed ultrasonic irradiation to aid agitation during suspension polymerisation. For the production of toners for developing electrostatic images (Utsumi,H. et al, 1988a, 1988b), they used ultrasound to prepare monomer (monofunctional and difunctional) dispersions. The monomer dispersion was then transferred to a reaction vessel equipped with paddle type stirring blades. The monomer dispersion was subjected to polymerisation under nitrogen and heating and stirring. As an option, they put an ultrasonic homogenizer (5 W/Litre) in the reaction vessel apart from the paddle stirring blades (see Fig.4.4). The suspension polymerisation was carried out at 80 °C for a period of 5 hours. To

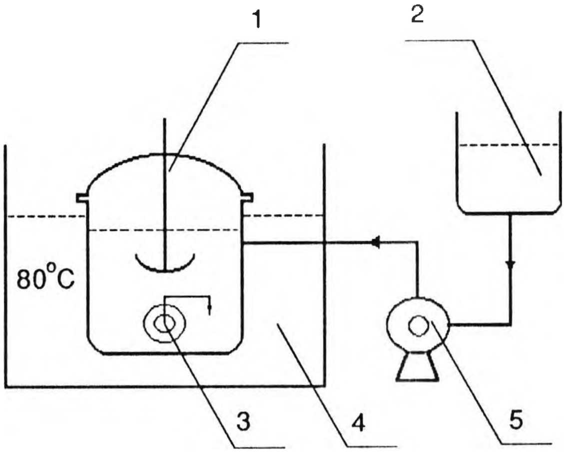
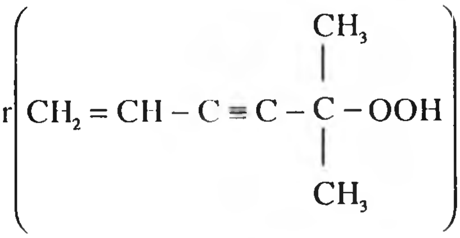


Fig.4.4 Utsumi's Reactor for Producing Toners
1 paddle stirring; 2 feed tank; 3 homogenizer;
4 water bath; 5 homogenizer for monomer charging

keep the reaction system in a dispersed state, every 30 minutes ultrasonic waves were applied for 10 minutes. This intermittently applied ultrasonic wave did not change the mean particle size, but reduced the polydispersity of the polymer particles (without the intermittently applied ultrasonic wave: 70% by volume between 3-7 µm; with the intermittently applied ultrasonic wave: 80% by volume between 3-7 µm). In Utsumi's polymerisation system, a low monomer to water ratio (monomer: 16.67% by weight) was used. Upon pre-emulsification with ultrasonic homogenizer, the mixture formed a fine dispersion. Because the monomer to water ratio was very low, there was less tendency for coagulation of the monomer droplets. But the intermittently applied ultrasonic wave had no effect either on the mean particle size or on the final toner properties, and thus the significance of such applied ultrasonic wave during polymerisation is questionable.

4.5.3 Agitation in Emulsion Polymerisation

Because in emulsion polymerisations high levels of surface active materials are generally used, the droplet particles are stabilised against agglomeration. Thus the use of continuous ultrasonic homogenisation instead of mechanical stirring as the means of agitation during emulsion polymerisation received little attention.

Lukin and co-workers(Lukin,Y.V. et al, 1986) produced magnetic latexes by emulsion polymerisation of styrene and methyl (meth)acrylate in the presence of magnetite with ultrasonic mixing (22 kHz). An oligomer (molecular weight: 10,000 - 11,100) derived from the copolymerisation of maleic anhydride, styrene and a functional monomer  $\left(\mathrm{CH_2=CH-C\equiv C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OOH}\right)$ was used as the emulsifier and initiator. The aqueous dispersion of the magnetite (stabilised with potassium oleate) was first treated with the ultrasound for 2 minutes. The emulsifier was added to the dispersion and sonication was applied for 1 minute. Then the monomers were added and the mixture was sonicated for another 10 minutes. Finally, the residual monomers were removed by distillation and the product was sonicated for 1-2 minutes. It is not stated in the patent whether the source of ultrasonic irradiation is of homogenizer type or similar to an ultrasonic cleaning bath. However, there is not doubt that the employment of ultrasound ensured good mixing and good encapsulation of the magnetite in the polymer particles.

Recently Gololobov and co-workers (Gololobov,Y.G. et al, 1989) have conducted emulsion polymerisation of alkyl 2-cyanoacrylates to produce microparticles in the presence of citric acid. A polysaccharide (nitrobenzyldextran) was used, which may function as an emulsifier. The monomer was added to a mixture of water, citric acid, heparin, and nitrobenzyldextran pretreated with ultrasound (35 kHz). The reaction system was dispersed with ultrasonic mixing for 10 minutes and a latex with a mean particle size of 0.216 µm was obtained. It is thought that the particle polydispersity is decreased as the result of the ultrasonic dispersing. No free radical initiator was used in the polymerisation system. The polymerisation of the cyanoacrylates was probably by an anionic mechanism, and thus this is not a conventional emulsion polymerisation.

In a recently published paper (Templeton-Knight,R. 1990), titanium dioxide particles were encapsulated with poly(methyl methacrylate) by acoustic emulsion polymerisation of methyl methacrylate in dispersions of titanium dioxide powder. The best encapsulation was obtained when low powers of ultrasound were applied in the initial stages of polymerisation. It is thought that the polymerisation occurred at the titanium dioxide particle-liquid interface as a result of cavitation. However, it is most likely that the polymerisation occurred by an ordinary micellar mechanism with the titanium dioxide particle captured by the monomer swollen polymer particles. There is not doubt that the employment of ultrasound ensured good mixing and good encapsulation of titanium dioxide particle in the polymer particles.

4.6 Summary

As has been reviewed above, ultrasound has been widely used in polymer chemistry. One of the most important uses is the pre-emulsification for emulsion/suspension polymerisations. It is obvious that pre-emulsification ensures good mixing of all the ingredients for polymerisation. As far as agitation during polymerisation is concerned, ultrasound employed in suspension polymerisation by Utsumi(Utsumi,H. et al, 1988a, 1988b) did not affect the particle size and property of the suspension products. For agitation in emulsion polymerisations, because emulsifiers were used in all cases to prevent particle agglomeration, the only effect of the applied ultrasound seems to be to ensure good mixing and encapsulation of solid particles.

Chapter 5

Plan of Work

The initial research work involved the synthesis and characterisation of polymers for use as solvent–based pressure–sensitive adhesives. As a very low glass transition temperature (Tg) is essential for the desired pressure–sensitive properties, 2–ethylhexyl acrylate was chosen as the monomer. For variation of the adhesive properties, a hard monomer —vinyl acetate was chosen as the co–monomer.

The adhesives were made in a batch reactor by copolymerisation of 2–ethylhexyl acrylate and vinyl acetate in ethyl acetate as solvent. After polymerisation in a constant temperature water bath, the polymers were isolated for characterisation. For use as pressure–sensitive adhesives, the polymerised product —copolymer solutions in ethyl acetate were coated on polyester films and dried. The adhesive properties were evaluated.

It was found that acrylate reacts faster than vinyl acetate so that at the end of polymerisation, some homopolymer of vinyl acetate was formed. As a result, attention was drawn to the effect of compositional heterogeneity of the copolymer on the adhesive properties. Copolymers with less compositional heterogeneity were made by stopping the reaction at low conversion. The adhesive properties of the low conversion copolymers and the high conversion copolymers were compared. No effect of the compositional heterogeneity on the adhesive properties has been detected.

Some of the inherent disadvantages of the solvent–based adhesives are well known –, the solvents are expensive, flammable, toxic. In addition during this work it was recognised that the relatively low molecular weight of the polymer prepared by solution polymerisation in a batch reactor resulted in low cohesive strength and moreover, when the monomer to solvent ratio is increased, the viscosity of the polymer solution becomes very high at high conversion. This will cause problems for agitation and product transfer. Thus the interest was further drawn to water–based pressure–sensitive adhesives.

Water–based pressure–sensitive adhesives are, in practice, normally the products of emulsion polymerisation. Some of the disadvantages of solvent–based pressure–sensitive adhesives are overcome at the expense of introducing new disadvantages for water–based adhesives. The presence of emulsifiers and stabilisers results in low water resistance and low peel strength, and coating is more difficult than with solution based adhesives. Thus an exploration of emulsions with very low or zero concentrations of surfactant was undertaken. It is inevitable that at very low or even zero concentrations of surfactant, polymer particles will agglomerate significantly. As a result, a novel polymerisation reactor —the whistle reactor was set up for surfactant–free emulsion polymerisation. The reactor comprises a jacketed reaction vessel equipped with an ultrasonic homogenizer. The reaction mixture can be circulated through the ultrasonic homogenizer so that droplet agglomeration can be prevented.

Fig.5.1 is the plan for the work on the synthesis and characterisation of pressure–sensitive adhesives. Fig.5.2 illustrates the plan of work on the study of the polymerisation in the whistle reactor.

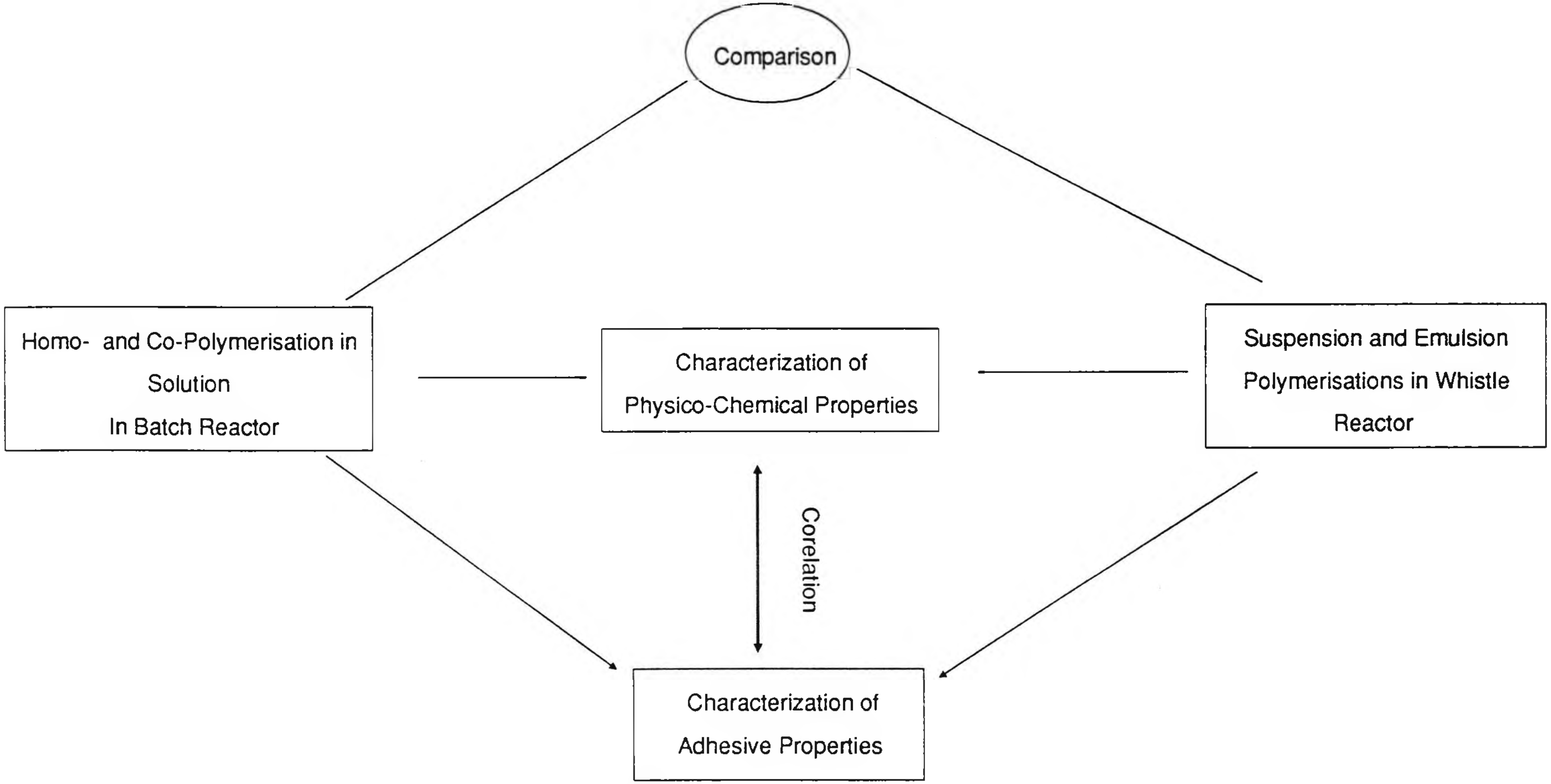


Fig.5.1 Plan of Work on Pressure-Sensitive Adhesives

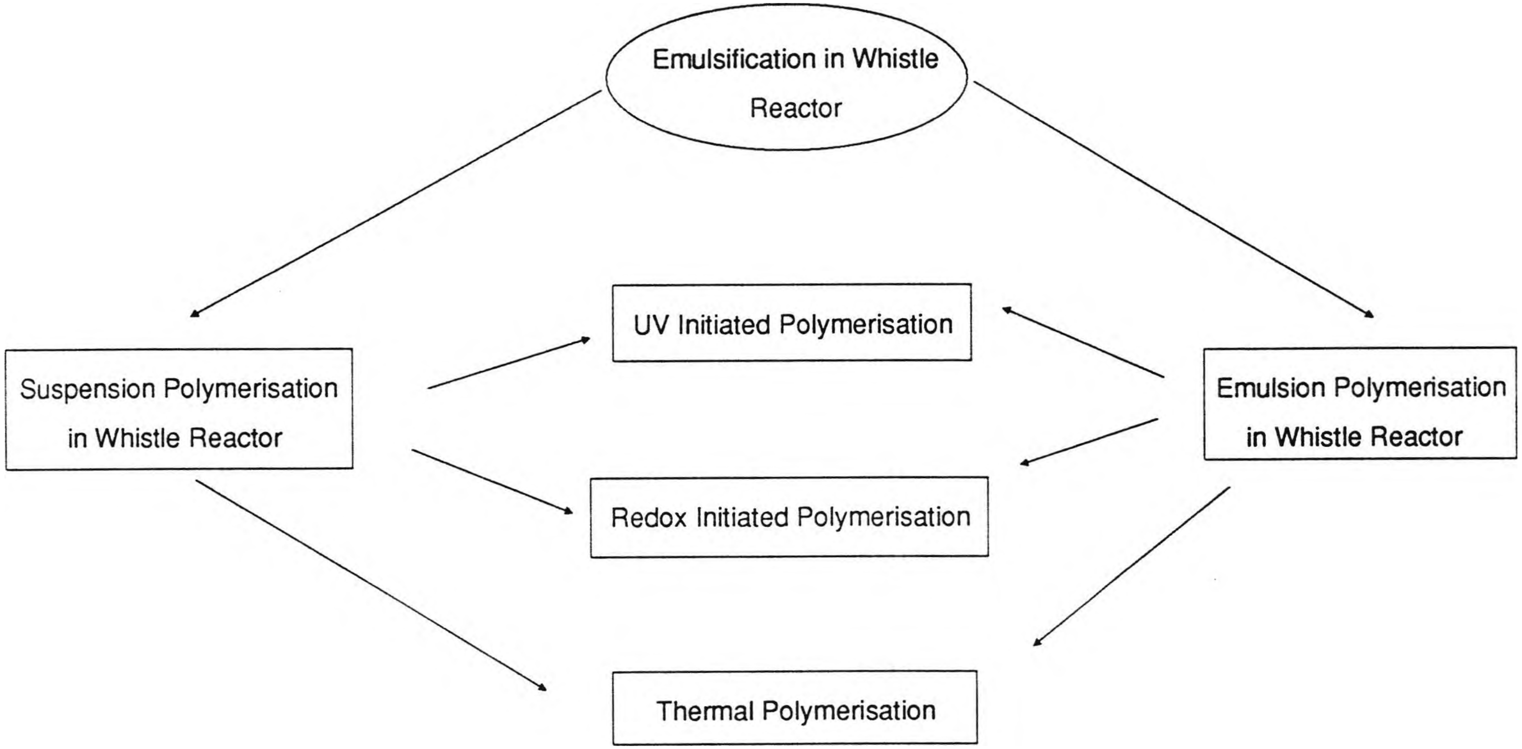


Fig.5.2 Plan of Work on the Suspension and Emulsion Polymerisation in the Whistle Reactor

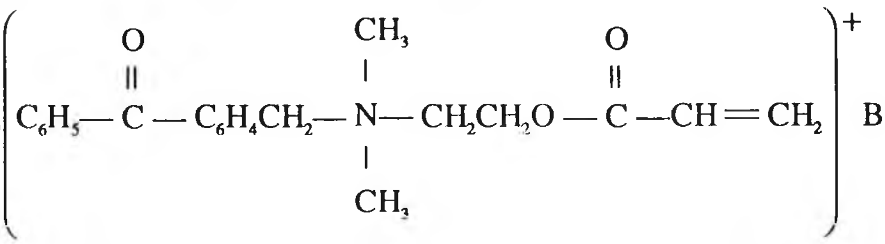
Chapter 6

Experimental

6.1 Materials And Apparatus:

6.1.1 Reagents

- Acrylic acid (AA), Aldrich, monomer, b.p. 139°C;
- (2–Acryloyloxyethyl)(4–benzoylbenzyl) dimethylammonium bromide (ABQ),

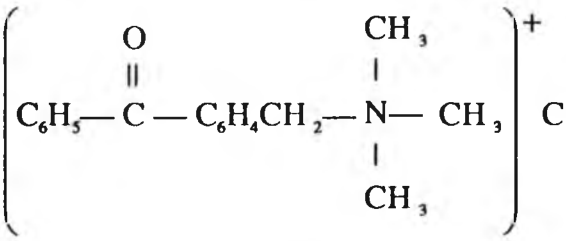


$$\left(C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_4CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-CH_2CH_2O-\overset{\overset{O}{\|}}{C}-CH=CH_2\right)^+ Br^-,$$

  International Bio–Synthetics, England, water soluble photoinitiator;
- Ammonium persulphate, Aldrich, water–soluble thermal initiator;
- 4,4′–Azobis(4–cyanovaleric acid) (AICA), Aldrich, water–soluble thermal initiator, m.p. 125°C, 25% remaining water, used without further purification;
- α,α'–Azoisobutyronitrile (AIBN), Fluka, oil–soluble thermal initiator, m.p. 125°C, used without further purification;

- Benzoin methyl ether (BME), Aldrich, oil–soluble photoinitiator, m.p. 47.5–48.5°C;

- 4–Benzoylbenzyltrimethylammonium chloride (BTC),



$$\left[C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}C_6H_4CH_2\text{—}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{N}}\text{—}CH_3 \right]^+ Cl^-$$

, International Bio–Synthetics, England, water soluble photoinitiator;

- Benzoyl peroxide (BPO), Aldrich, oil–soluble thermal initiator, remaining water 20%, used without further purification;

- N,N–Bis(2–hydroxylethyl)–p–toluidine, Fluka, UV co–initiator, m.p. 48–52°C;

- Butyl acrylate (BA), Aldrich, monomer, b.p. 145°C, used without further purification;

- N–n–Butyldiethanolamine, Fluka, UV co–initiator, b.p. 268–272°C;

- N–tert–Butyldiethanolamine, Fluka, UV co–initiator, b.p. 263–265°C;

- Butyl methacrylate, Aldrich, b.p. 160–163°C, used without further purification;

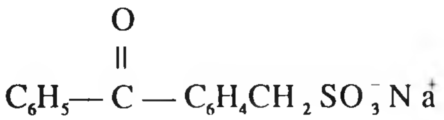
- 2–(2–Diethylamino–ethoxy)–ethanol, Fluka, UV co–initiator, b.p. 100–104°C;

- 2–Diethylaminoethyl acrylate, Fluka, b.p. 202°C;

- N,N–Dimethylethanolamine, Aldrich, UV co–initiator, b.p. 139°C;

- 1–Dodecanthiol,Aldrich, chain transfer agent, b.p.266–283°C;

- Ethyl acetate (EA), solvent;
- 2–Ethylhexyl acrylate (EHA), Aldrich, b.p. 215–219°C, redistilled for solution polymerisation, unpurified for emulsification experiments, washed with 5% NaOH aqueous solution 3 times and then washed with distilled water 3 times for emulsion and suspension polymerisations;
- Ethylene glycol dimethacrylate (EGDMA), Aldrich, monomer, b.p. 98–100°C/5mm, used without further purification;
- Igepal CO–990, Aldrich, $4-(C_9H_{19})C_6H_4O(CH_2CH_2O)_{99}CH_2CH_2OH$, nonionic surfactant;
- Isobornyl acrylate (IBA), Sartomer International Inc., monomer, used without further purification;
- N–Methyldiethanolamine, Aldrich, UV co–initiator, b.p. 246–248°C;
- Polyvinyl alcohol (PVA), BDH, protective colloid, molecular weight 115,000;
- Sodium benzophenone–4–methyl sulphonate (WB4698),

  $C_6H_5-\overset{\overset{O}{\parallel}}{C}-C_6H_4CH_2SO_3^-Na^+$, International Bio–Synthetics, England,

  water soluble photoinitiator;
- Sodium sulphite, Aldrich, redox initiator;
- Styrene, Aldrich, monomer, used without purification;
- Triethylamine, Aldrich, UV co–initiator, b.p.88.8°C;
- Triethanolamine, Aldrich, UV co–initiator, b.p.190–193°C;

- Vinyl acetate (VA), Aldrich, monomer, b.p. 72–73°C, redistilled for polymerisation.

6.1.2 Reactor Setup

The batch reactor used for solution polymerisation is shown in Fig.6.1. It comprises a stirred resin flask equipped with a condenser, a nitrogen inlet and a dropping funnel. The resin flask is supported in a constant temperature water bath.

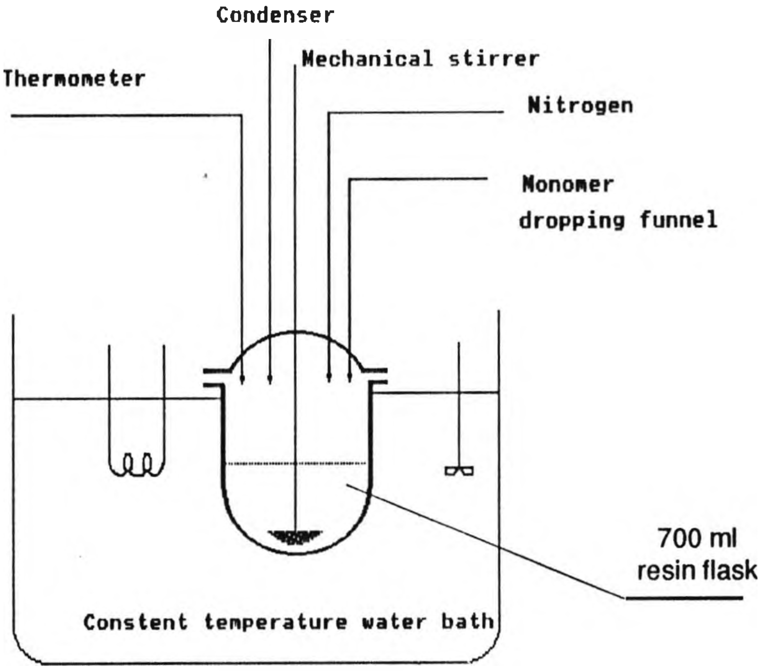


Fig.6.1 Batch Reactor for Solution Polymerisation

As illustrated in Fig.6.2, the reactor used for UV–induced suspension and emulsion polymerisations is a glass reaction vessel equipped with an ultrasonic laboratory homogenizer (Type 4005, Lucas Dawe Ultrasonics),and a 400 watts medium pressure UV lamp and its power supply.

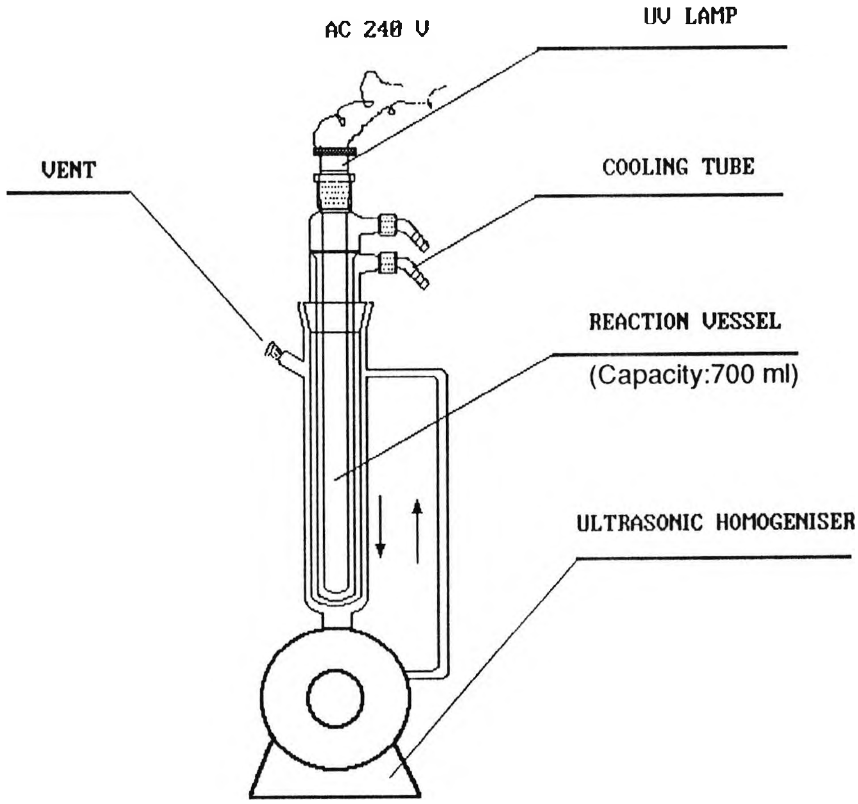


Fig.6.2 Photochemical Reactor

Fig.6.3 represents the reactor used for thermal emulsion and suspension polymerisations. It is a jacketed glass vessel equipped with an ultrasonic homogeniser (Type 4005, Lucas Dawe Ultrasonics), a mechanical stirrer, a condenser and a nitrogen inlet.

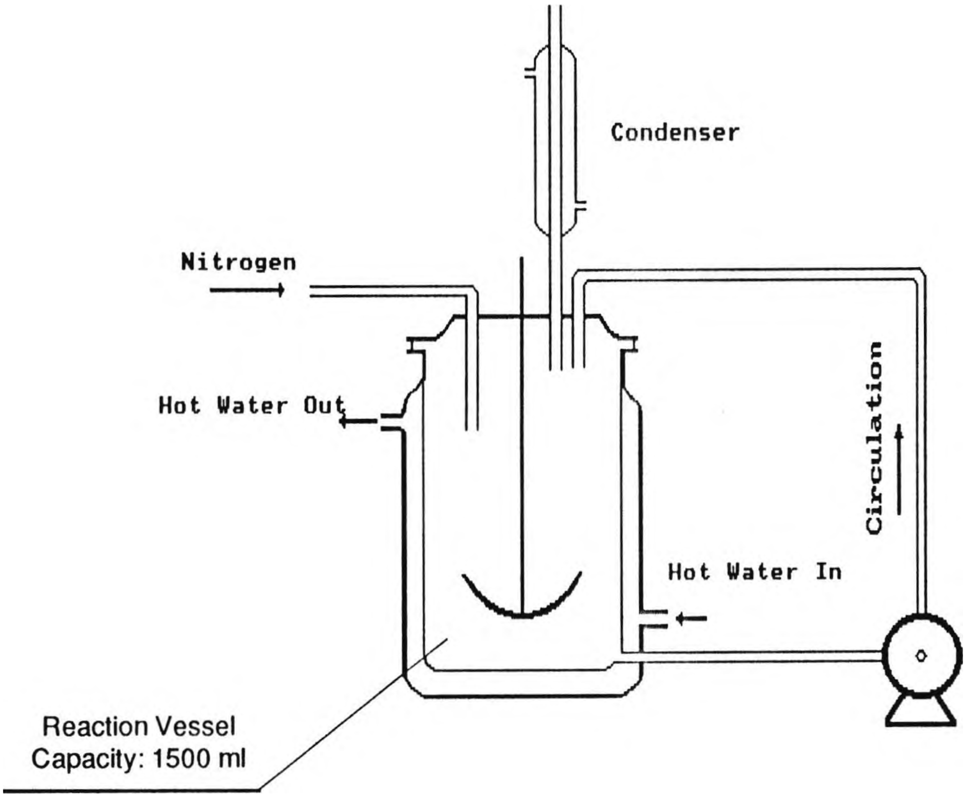


Fig.6.3 Thermal Reactor

Finally, the reactor used for redox-induced polymerisation is a jacketed glass vessel equipped with an ultrasonic homogenizer (Type 4005, Locus Dave Ultrasonics) and nitrogen inlet (see Fig.6.4).

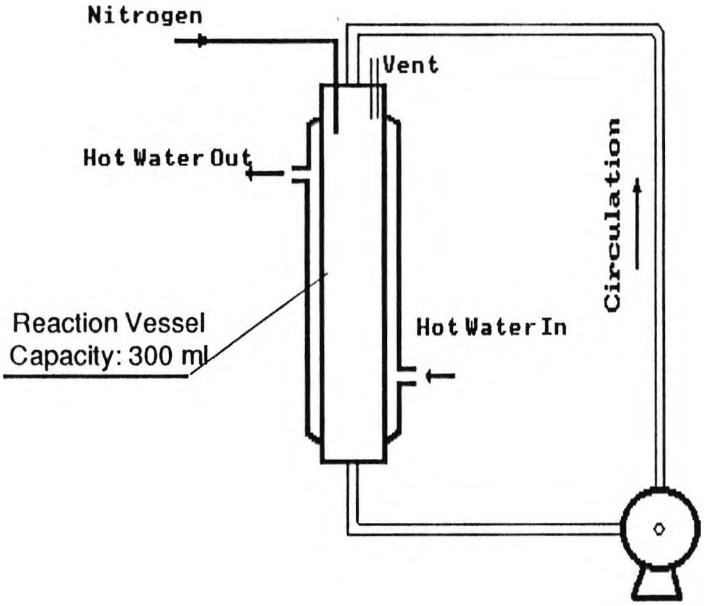


Fig.6.4 Redox Reactor

6.2 General Characterisations

^{1}H n.m.r. spectra were recorded on either a Jeol MH 100 spectrometer or a Jeol PMX 60 spectrometer. Tetramethylsilane (TMS) was used as the internal reference and the chemical shifts are quoted in δ. Copolymer compositions were calculated based on integration of the character peaks and the numbers of the corresponding protons.

The DSC traces were obtained using a Stanton Redcroft STA–785 thermal analyser. Alumina was used as the reference. The glass transition temperatures (Tgs), which were determined based on the DSC traces, are in degrees centigrade.

The peel strengths were measured on an Instron 1026 tensile tester at a crosshead speed of 200 mm/min using load cells AM or BM.

The particle size distributions (PSD) were measured on a Malvern 2600/3600 particle sizer at an obscuration between 0.2 to 0.3 using either 63 mm, 100 mm or 300 mm focus length lenses. The mean particle sizes (MPS) were computed by a Basic Programme (see Appendix IV).

The SEM photographs of polymer latexes were taken from a Steroscan Mark 2A scanning electron microscope at 0.5 to 2.0 k magnification and 3.0 kV of the gun potential and 45° tilt of the sample plate.

The gel permeation chromatograms of the polymers were obtained through the Department of Chemistry, University of Kent. The GPC results are based on a poly(methyl methacrylate) calibration.

6.3 Solution Polymerisation: Synthesis and Characterisation of Homo-and Co-polymers of Vinyl Acetate and 2-Ethylhexyl Acrylate

6.3.1 Synthesis of Polymers

1.0g of AIBN (initiator) was dissolved in 200g ethyl acetate (solvent), and this was mixed with mixtures of EHA and VA (see Table 6.1 for EHA/VA ratios). The reaction mixture was put into a 700ml flask equipped with condenser, mechanical stirrer, nitrogen inlet, thermometer and dropping funnel, supported in a constant temperature water bath. The reaction was carried out at about 70°C under a nitrogen atmosphere, with gentle stirring and solvent reflux for about 2.5 hours. The reaction was terminated with hydroquinone as needed for the preparation of low conversion copolymer. The polymerised product was a viscous solution of polymer in ethyl acetate and unreacted monomer(s). The residual monomers and solvent were removed by distillation using a rotary evaporator, and further drying in a vacuum oven.

The dried product was transparent. Homopolymers and copolymers of high and low conversions were prepared with the feeds shown in Table 6.1.

Table 6.1 Solution Polymerisation of EHA and VA (* yields for polymers No. 1–11 were not measured but they are very high due to a relatively long reaction time)

Polymer No.		Feed (grams)				Time of Reaction (min)	Yield* (%)
		EHA	VA	EA	AIBN		
high conversion	1		200	200	1	150	
	2	20	180	200	1	150	
	3	40	160	200	1	150	
	4	60	140	200	1	150	
	5	80	120	200	1	150	
	6	100	100	200	1	150	
	7	120	80	200	1	150	
	8	123.7	53	176.7	0.884	150	
	9	160	40	200	1	150	
	10	146.8	16.3	163	0.816	150	
	11	200		200	1	150	
low conversion	12	10	190	200	1	10	13.4
	13	20	180	200	1	12	16.9
	14	30	170	200	1	10	23.7
	15	37.5	149.5	180	0.833	15	23.6
	16	60	140	200	1	15	33.9
	17	80	120	200	1	15	45.6
	18	110	90	200	1	16	60.5
	19	150	50	200	1	17	70.4
	20	170	30	200	1	10	81.7
	21	180	20	200	1	10	73

6.3.2 Copolymer Composition Analysis Using ^{1}H n.m.r.

The gross compositions of the copolymers were determined by using the ^{1}H n.m.r. spectrum of about 20% of solutions of copolymers in deuterated chloroform. TMS (tetramethylsilane) was used as the reference, and the experiments were carried out at room temperature. The major features of the ^{1}H n.m.r. spectrum of the copolymers are due to the 2–ethylhexyl ester groups in EHA units and the methine groups in VA units. The strongly deshielded methines in VA units were observed as a broadened multiplet near 4.88 ppm, and the methylene group in the EHA unit adjacent to the ester moiety appeared as a doublet at 3.96 ppm. The weight percentages of EHA units (F_{EHA}) in copolymers were calculated from the integrations (I_{VA} near 4.88ppm and I_{EHA} near 3.96ppm) and the numbers of the corresponding protons using the following equation: $F_{EHA} = \dfrac{1}{2\left(\dfrac{I_{VA}}{I_{EHA}}\right)\left(\dfrac{M_{VA}}{M_{EHA}}\right)+1} \times 100\%$ where M_{VA} and M_{EHA} are the molecular weights of VA and EHA, respectively. The results are listed in Table 6.2.

Table 6.2 The Characterised Copolymer Compositions by ^{1}H n.m.r.

Polymer No. (low conversion)	Composition (% Weight of EHA)	Polymer No. (high conversion)	Composition (% Weight of EHA)
1	0	12	43.8
2	14.7	13	59.0
3	28.7	14	62.3
4	38.2	15	67.5
5	44.4	16	74.4
6	62.7	17	77.6
7	71.6	18	84.1
8	83.1	19	92.0
9	90.5	20	92.2
10	94.1	21	94.0
11	100		

6.3.3 Tg Measurement Using DSC

About 10 mg of copolymer sample and 5 mg of reference alumina were placed in two aluminium sample pans which were carefully put into the furnace . A nitrogen atmosphere was created inside the furnace using 30% nitrogen flow rate. Prior to the measurement, the furnace was heated to 100°C to melt the copolymer sample. After the temperature of the furnace dropped to room temperature, the furnace was cooled by liquid nitrogen to -125 °C. The DSC trace was obtained while the sample was heated at a rate of 10°C/min. For some copolymers, two glass transitions were observed within the temperature range scanned. The DSC analysis results are listed in Table 6.3.

Table 6.3 Glass Transition Temperature of Polymers Determined using DSC.

Polymer No.	Tg$_1$(^{o}C)	Tg$_2$(^{o}C)	Polymer No.	Tg$_1$(^{o}C)	Tg$_2$(^{o}C)
1	......	26	7	-57	34
2	-38	38.5	8	-60	......
3	-40	38	9	-65	......
4	-46	37	10	-66	......
5	-48	36	11	-73	......
6	-51	38			

6.3.4 Peel Adhesion Testing

Copolymers and homopolymers were dissolved in ethyl acetate to form solutions containing 20% copolymer by weight. The copolymer solutions were then coated on Melinex backings using a glass rod as the roller. The initial thickness of the adhesive layers was controlled at 0.5 mm, which became 0.1 mm after drying. The samples were dried for 72 hours in a vacuum oven having a vacuum of 900 mbar and a temperature of 80°C. The substrate aluminium panels were briefly washed firstly in soap solution, and then washed using an ultrasonic bath for 5 minutes in soap solution and finally washed for 5 minutes in stabilised 1,1,1–trichloroethane. The pressure sensitive films were applied to the clean aluminium panels by using a 3.5 kg roller. These samples were kept at room temperature for 4, 24, 94, and 120 hours. The peel strengths of these copolymers were then measured on an Instron 1026 Tensile Tester using a crosshead speed of 200 mm/min and the results are shown in Table 6.4.

6.4 Emulsification in the Whistle Reactor

6.4.1 General Procedure

The general procedure for the emulsification of monomer EHA and water was as follows: Polyvinyl alcohol was dissolved in distilled water with heating (70°C) and stirring. The aqueous solution of polyvinyl alcohol was mixed with 2–ethylhexyl acrylate in a large beaker. The mixture was then transferred to the homogeniser and homogenised. 5–25 minutes of homogenisation was needed to get a stable fine monomer emulsion. The particle size distributions of the monomer emulsions were measured.

6.4.2 Emulsification Using Different Durations of Ultrasonic Application

▪ EHA	200g
▪ Water	300g
▪ PVA	4g

Table 6.4 Peel Adhesion Results *

Polymer No.	Peel Strength (g/½ inch)			
	after 4 hrs aging	after 24 hrs aging	after 94 hrs aging	after 120 hrs aging
5	100ss	100ss	100ss	100ss
6	690a	720a	750a	780a
7	770a	790a	750a	760a
8	690c	705c	670c	590c
9	310c	300c	210c	200c
10	160c	150c	105c	80c
11	35c	35c	27c	25c
12	50ss	50ss	50ss	50ss
13	50ss	50ss	50ss	50ss
14	400ss	710a	700a	700a
15	700a	720a	720a	750a
16	725a	725a	805a	810a
17	780a	780a	760a	760a
18	660c	690c	610c	640c
19	135c	130c	100c	90c
20	35c	40c	30c	25c

* ss: stick slip failure; a: adhesive failure between adhesive and substrate; c: cohesive failure within the adhesive layer.

The above mixture was homogenised at 1000 ml/min throughput. After pumping from one glass vessel to the other 3 times, a monomer emulsion with a mean particle size of 6.19 μm was obtained. The monomer emulsion was further homogenised, by circulating the emulsion in the homogeniser for 25 minutes, during which samples were taken for particle size measurements. The results are listed in Table 6.5.

Table 6.5 Mean Particle Size Obtained at Different Durations of Ultrasonic Homogenisation

Duration (minutes)	Mean Particle Size (μm)
5	4.63
10	4.01
15	3.91
20	3.78
25	3.72

6.4.3 Emulsification Using Different Pump Operating Pressure (Pump Flow Rate)

EHA	60g
Water	690g
PVA	4.93g

The above mixture was mixed in the whistle reactor followed by homogenisation at (i) 560 ml/min pump throughput for 25 minutes, (ii) 800 ml/min for 20 minutes, (iii) 1085 ml/min for 20 minutes, (iv) 1210 ml/min for 15 minutes, (v) 1700 ml/min for 10 minutes and (vi) 2200 ml/min for 5 minutes. The results are listed in Table 6.6.

Pump Flow Rate (ml/min)	Mean Particle Size (μm)
560	6.63
800	5.04
1085	4.13
1210	3.57
1700	2.85
2200	2.36

Table 6.6 Mean Particle Size Obtained by Ultrasonic Homogenisation using Different Pump Flow Rate

6.4.4 Emulsification Using Different Levels of PVA

Mixtures of EHA monomer and water containing different amounts of PVA were homogenised at 1000 ml/min throughput for 25 minutes. The results are listed in Table 6.7.

Table 6.7 Mean Particle Size Obtained by Ultrasonic Homogenisation using Different Amount of PVA

Homogenisation Mixture (g)			Mean Particle Size (μm)
EHA	Water	PVA	
200	300	0.5	42.4
200	300	1.0	31.2
200	300	2.0	5.56
169	253	5.07	2.77

6.4.5 Emulsification Using Different Monomer/Water Ratios

Mixtures of EHA monomer and water of different monomer/water ratios were homogenised at 1000 ml/min throughput for 25 minutes. The results are listed in Table 6.8.

Table 6.8 Mean Particle Size Obtained by Ultrasonic Homogenisation using Different Monomer/Water Ratios

Homogenisation Mixture (g)			Mean Particle Size (μm)
EHA	Water	PVA	
50	450	4	3.25
100	400	4	3.42
250	250	4	3.74
300	200	4	4.41

6.4.6 Emulsification of Polymer Solution with Water

Instead of pure EHA monomer, a solution of polymer in the monomer was homogenised with water. The mixture of

EHA homopolymer	25g
EHA	175g
Water	300g
PVA	4g

was homogenised for 25 minutes at 1000 ml/min throughput. A monomer emulsion with an average particle size of 2.77 μm was obtained.

6.4.7 Emulsification by Mechanical Stirring: Comparative Experiment to Section §6.4.2

The same mixture as that of Section §6.4.2 was mechanically stirred in a resin flask at about 300 rpm for 25 minutes. A monomer emulsion with a mean particle size of 56.1 μm was obtained compared with 3.72 μm by homogenisation in the whistle reactor.

6.4.8 Emulsification in the Presence of a Nonionic Surfactant

Instead of polyvinyl alcohol, a nonionic surfactant Igepal CO–990 was used for the homogenisation of EHA monomer with water. The mixture of EHA 200g, Water 300g, and Igepal CO–990 4g was homogenised for 25 minutes at 1000 ml/min throughput. A monomer emulsion with an average particle size of 2.02 µm was obtained, compared with 3.72 µm by homogenisation in the whistle reactor.

6.5 Suspension Polymerisation

In the present work, suspension polymerisations were carried out using two different methods:

- polymerisation of pre–emulsified monomer in a reactor without continuous applied ultrasonic homogenisation.
- polymerisation in the whistle reactor under continuous applied ultrasonic homogenisation

Of the two the former is referred to as conventional polymerisation and the latter the polymerisation in the whistle reactor (see Section §6.1.2 for the setups of the whistle reactor).

6.5.1 UV–Induced Suspension Polymerisation

6.5.1.1 Suspension Polymerisation of Pre–emulsified EHA

300 g of distilled water containing 4.0 g of polyvinyl alcohol was homogenised with 200 g of 2–ethylhexyl acrylate containing 1g (0.0044 mole) of benzoin methyl ether using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into a photochemical reactor and irradiated (UV–400 watts) during which no ultrasonic homogenisation was used. Samples were taken during the reaction.

The particle size distributions of the samples were measured. The conversions of these samples were determined by solid content. A stable polymer suspension with 95.6% yield and a mean particle size of 3.87 μm was obtained after 60 minutes of UV–irradiation. The resultant polymer suspension was examined by scanning electron microscopy (SEM).

6.5.1.2 Suspension Polymerisation of EHA under Continuous Homogenisation:Comparative Reaction to Section §6.5.1.1

The same reaction mixture and procedure as that of Section §6.5.1.1 was used, except that ultrasonic homogenisation was used during the reaction process. Samples were taken during the reaction. The particle size distributions of the samples were measured. The conversions of the samples were determined by solid content. A stable polymer suspension with 85.5% yield and a mean particle size of 3.76 μm was obtained after 60 minutes of irradiation. The resultant polymer suspension was examined by SEM.

6.5.1.3 Suspension Copolymerisations of EHA and VA

400 g of distilled water containing 4.0 g of polyvinyl alcohol was homogenised with mixtures of EHA and VA monomers (see Table 6.9) containing 1g (0.0044 mole) of benzoin methyl ether using the ultrasonic homogeniser at 1000 ml/min throughput for 15 minutes. The mixture was then pumped into a photochemical reactor and irradiated (UV–400 watts) during which continuous ultrasonic homogenisation was used. A stable polymer suspension with high yield was obtained after 15 minutes of irradiation. The copolymer composition was determined by ^{1}H n.m.r. analysis. The resultant polymer suspension was not long term stable and it phase–separated after 5

weeks of storage. The results of copolymerisations using different EHA/VA ratios are listed in Table 6.9.

Table 6.9 Results of Suspension Copolymerisations of EHA and VA

EHA (g)	VA (g)	Conversion (%) after 15 minutes of Irradiation	Polymer Composition (wt.% of EHA)
60	140	37.0	75.8
80	120	35.8	81.5
110	90	53.5	85.0
150	50	72.5	90.6

6.5.1.4 Suspension Polymerisations and Copolymerisations of Other Monomers

(i) n–Butyl Acrylate

450 g of distilled water containing 5.0 g of polyvinyl alcohol was homogenised with 250 g of n–butyl acrylate containing 1.3g (0.00572 mole) of benzoin methyl ether using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into a photochemical reactor and irradiated (UV–400 watts) during which continuous ultrasonic homogenisation was used. A stable polymer suspension with 72.5% yield was obtained after 30 minutes of irradiation. The resultant polymer suspension was examined by SEM.

(ii) Isobornyl Acrylate

The same reaction procedure as that for (i) was used, except that the monomer was replaced by isobornyl acrylate. A stable polymer suspension with 89.4% yield was obtained after 20 minutes of irradiation. The resultant polymer suspension was examined by SEM.

(iii) Methyl Methacrylate

The same reaction procedure as that for (i) was used, except that the monomer was replaced by methyl methacrylate. The polymerisation ran out of control due to a rapid exothermic reaction. The polymerisation system gelled after 30 minutes of reaction. The polymerisation product was examined by SEM.

(iv) n–Butyl Methacrylate

The same reaction mixture and procedure as that for (i) was used, except that the monomer was replaced by n–butyl methacrylate. A stable polymer suspension with 32.0% yield was obtained after 60 minutes of irradiation. The resultant polymer suspension was examined by SEM.

(v) Styrene

The same reaction procedure as that for (i) was used, except that the monomer was replaced by styrene. The reaction system gelled after 40 minutes of irradiation. The resultant polymer suspension was examined by SEM.

(vi) EHA/Acrylic Acid(AA)

450 g of distilled water containing 6.0 g of polyvinyl alcohol was homogenised with a monomer mixture (EHA 285g, AA 15g) containing 1.5g (0.0066 mole) of benzoin methyl ether using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into a photochemical reactor and irradiated (UV–400 watts) during which continuous ultrasonic homogenisation was used. A polymer suspension with high yield was obtained after 30 minutes of irradiation. The polymer suspension was examined by SEM. The polymer suspension phase–separated after about 4 weeks of storage.

(vii) EHA/Ethylene Glycol Dimethacrylate (EGDMA)

The same reaction procedure as that for (vi) was used, except that AA was replaced by EGDMA. A polymer suspension with 99.8% yield was obtained after 30 minutes of irradiation. When precipitated with acetone and dried in the oven, a white, brittle polymer was obtained which swelled up in toluene but did not dissolve. The polymer suspension was examined by SEM. The polymer suspension phase separated after about 4 weeks of storage.

(viii) Isobornyl Acrylate(IBA)/Vinyl Acetate

430 g of distilled water containing 4.0 g of polyvinyl alcohol was homogenised with a monomer mixture (IBA 100g, VA 150g) containing 1.3g (0.00572 mole) of benzoin methyl ether using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into a photochemical reactor and irradiated (UV–400 watts) during which continuous ultrasonic homogenisation was used. A polymer suspension with 49.3% yield and a copolymer composition of 21.8% by weight of VA units was obtained after 40 minutes of irradiation. The polymer suspension was

examined by SEM. The polymer suspension phase–separated after about 4 weeks of storage.

6.5.2 Thermal Polymerisation

6.5.2.1 BPO as Initiator

200g of distilled water containing 4g of polyvinyl alcohol was homogenised with 90g of 2–ethylhexyl acrylate and 60g of vinyl acetate containing 0.75 grams of benzoyl peroxide at 1200 ml/min pump throughput for 25 minutes. The homogenised mixture was transferred to a 700ml resin flask supported on a temperature constant (70 °C) water bath, and gently stirred (about 150 rpm) under nitrogen atmosphere for 70 minutes. A polymer suspension with 58.9% conversion and a mean particle size of 3.64 µm was obtained. The polymer suspension was examined by SEM.

6.5.2.2 BPO as Initiator: Comparative Reaction to Section §6.5.2.1

The same reaction mixture and procedure as that for Section §6.5.2.1 was used, except that the homogenised monomer emulsion was transferred to a jacketed thermal reactor (nitrogen atmosphere, 70 °C) where the reaction mixture was subjected to continuous circulation with the homogeniser. A stable polymer suspension with 41.1% yield and a mean particle size of 2.06 µm was obtained after 70 minutes of reaction. The polymer suspension was examined by SEM.

6.5.2.3 AIBN as Initiator

450g of distilled water containing 9g of PVA and monomer mixture (EHA 270g, VA 30g) containing 3g of AIBN was homogenised for 10 minutes at 1000 ml/min pump throughput and then transferred to a jacketed thermal reactor (70°C, nitrogen atmosphere) where the mixture was subjected to continuous circulation with the homogeniser. A stable polymer suspension with 92.0% yield and a mean particle size of 4.23 μm was obtained after 35 minutes of reaction. The resultant polymer emulsion was examined by SEM.

6.5.2.4 AIBN as Initiator: Comparative Reaction to Section §6.5.2.3

A comparative reaction to Section §6.5.2.3 with only 4.5g of PVA as protective colloid gave a polymer emulsion with 71.0% yield and a mean particle size of 7.88 μm. The resultant polymer emulsion was examined by SEM.

6.6 Emulsion Polymerisation

6.6.1 UV-induced Polymerisation

6.6.1.1 Emulsion Polymerisation of Pre-emulsified EHA

300 g of distilled water containing 4 g of polyvinyl alcohol and 3.0g (0.01 mole) of WB4698 was homogenised with 200 g of 2-ethylhexyl acrylate containing 7.5g (0.063 mole) of N-methyldiethanolamine using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into the reaction vessel and irradiated (UV-400 watts) for 65 minutes during which no ultrasonic homogenisation was used. Samples were taken during the reaction. The particle size distributions of the samples were measured. The conversions of the samples were determined by their solid contents. A polymer emulsion with a mean particle size of 8.52 μm and 26.5% yield was obtained after 65 minutes of irradiation. The resultant polymer emulsion was examined by SEM. The polymer emulsion was not long term stable and it phase-separated after 2 weeks of storage.

6.6.1.2 Emulsion Polymerisation of EHA under Continuous Homogenisation: Comparative Reaction to Section §6.6.1.1

The same reaction mixture and procedure as that for Section §6.6.1.1 was used, except that ultrasonic homogenisation was used during the reaction process. Samples were taken during the reaction. The particle size distributions of the samples were measured. The conversions of the samples were determined by solid content. A stable polymer emulsion with a mean particle size of 2.09 μm and 52.0% yield was obtained after 40 minutes of irradiation. The resultant polymer emulsion was then examined by SEM. The polymer emulsion had a shelf life of at least 18 months.

6.6.1.3 Emulsion Polymerisation of EHA Using Different Co–initiator Amines and Using WB4698 as Initiator

(i) N–Methyldiethanolamine as Co–Initiator

450 g of distilled water containing 4 g of polyvinyl alcohol and 3.5g (0.0117 mole) of WB4698 was mixed with 300 g of 2–ethylhexyl acrylate containing 7.0g (0.0587 mole) of N–methyldiethanolamine in a large beaker. The mixture was transferred to one of the glass vessels of the homogeniser and pumped to the other glass vessel at 1300 ml/min throughput. The mixture was then pumped back and the homogenisation was repeated 5 times. Then one of the homogeniser glass vessels was replaced with a photochemical reactor to which the reaction mixture was pumped and where the mixture was irradiated (UV–400 watts). During the reaction, continuous ultrasonic homogenisation was applied. Samples were taken at different reaction times and the polymers were coagulated by the addition of acetone. The conversions were determined by solid content measurements. A stable polymer emulsion with a mean particle size of 3.64 μm and 78.0% yield was obtained after 60 minutes of irradiation.

(ii) N,N–Dimethylethanolamine as Co–Initiator

The same reaction procedure as that for (i) was used, except that 5.24g (0.0587 mole) N,N–dimethylethanolamine was used instead of N–methyldiethanolamine. A stable polymer emulsion with a mean particle size of 3.57 μm and 88.4% yield was obtained after 60 minutes of irradiation.

(iii) Triethanolamine as Co–Initiator

The same reaction procedure as that for (i) was used, except that 8.76g (0.0587 mole) of triethanolamine was used instead of N–methyldiethanolamine. A stable polymer emulsion with a mean particle size of 5.80 μm and 80.7% yield was obtained after 60 minutes of irradiation.

(iv) Triethylamine as Co–Initiator

The same reaction procedure as that for (i) was used, except that 5.94g (0.0587 mole) of triethylamine was used instead of N–methyldiethanolamine. A stable polymer emulsion with a mean particle size of 3.47 μm and 83.0% yield was obtained after 60 minutes of irradiation.

(v) N–n–Butyldiethanolamine as Co–Initiator

The same reaction procedure as that for (i) was used, except that 9.47g (0.0587 mole) of N–n–butyldiethanolamine was used instead of N–methyldiethanolamine. A stable polymer emulsion with a mean particle size of 2.26 μm and 85.1% yield was obtained after 60 minutes of irradiation.

(vi) N,N–Bis(2–hydroxyethyl)–p–toluidine as Co–Initiator

The same reaction procedure as that for (i) was used, except that 11.48g (0.0588 mole) of N,N–bis(2–hydroxyethyl)–p–toluidine was used instead of

N–methyldiethanolamine. However, the total conversion after 80 minutes of irradiation was only 5%.

(vii) N–tert–Butyldiethanolamine as Co–Initiator

The same reaction procedure as that for (i) was used, except that 9.47g (0.0587 mole) of N–tert–butyldiethanolamine was used instead of N–methyldiethanolamine. Stable polymer emulsion with a mean particle size of 2.87 μm and 62.3% yield was obtained after 80 minutes of irradiation.

(viii) 2–Diethylaminoethyl Acrylate as Co–Initiator

The same reaction procedure as that for (i) was used, except that 10.05g (0.0587 mole) of 2–diethylaminoethyl acrylate was used instead of N–methyldiethanolamine. The rate of polymerisation was very slow and only 18% conversion was obtained after 80 minutes of irradiation.

(ix) 2–(2–Diethylamino–ethoxyl)–ethanol as Co–Initiator

The same reaction procedure as that for (i) was used, except that 9.47g (0.0587 mole) of 2–(2–diethylamino–ethoxyl)–ethanol was used instead of N–methyldiethanolamine. A stable polymer emulsion with a mean particle size of 2.36 μm and 49.8% yield was obtained after 50 minutes of irradiation.

6.6.1.4 Emulsion Polymerisation Using BTC as the Initiator

(i)N–Methyldiethanolamine as Co–Initiator

500 g of distilled water containing 4 g of polyvinyl alcohol and 2.898g (0.01 mole) of BTC was mixed with 200 g of 2–ethylhexyl acrylate containing 11.916g (0.1 mole) of N–methyldiethanolamine in a large beaker. The mixture was transferred to one of the glass vessels of the homogeniser and pumped to

another glass vessel at 1000 ml/min throughput. The mixture was then pumped back and the homogenisation was repeated 3 times. The mixture was circulated and homogenised for 25 minutes. Then one of the homogeniser glass vessels was replaced with a photochemical reactor to which the reaction mixture was pumped and where the mixture was irradiated (with 400 watts UV lamp). During the reaction, continuous ultrasonic homogenisation was applied. Samples were taken at different reaction times and the polymers were coagulated by the addition of acetone. The conversions were determined by solid content measurements. A polymer emulsion with 61.2% yield was obtained after 35 minutes of irradiation. The polymer emulsion phase–separated after a week of storage.

(ii) N,N–Dimethylethanolamine as Co–Initiator

The same reaction mixture and procedure as that for (i) was used, except that 8.914g (0.1 mole) of N,N–dimethylethanolamine was used instead of N–methyldiethanolamine. A polymer emulsion with 96.0% yield was obtained after 50 minutes of irradiation. The polymer emulsion was not stable and phase–separated after 4 days of storage.

6.6.1.5 Emulsion Polymerisation of EHA in the Presence of a Nonionic Surfactant

(i) WB4698 as Initiator

450g of distilled water containing 6g of Igepal CO–990 and 4.5g (0.015 mole) of WB4698 was homogenised with 300 g of EHA containing 11.25g (0.0944 mole) of N–methyldiethanolamine using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into the reaction vessel and was subjected to irradiation (UV–400 watts) and continuous circulation with the homogeniser. Samples were taken during the reaction. The conversions of these samples were determined by solid content.

Polymer emulsions with 8.6%, 29.06%, 53.1%, 78.04%, 89.8% and 96.4% yield were obtained after 5, 10, 20, 30, 40 and 60 minutes of irradiation. The polymer emulsion obtained after 60 minutes of reaction had a mean particle size of 1.26 μm. The resultant polymer emulsion was examined by SEM.

(ii) ABQ as Initiator

The same reaction procedure as that for (i) was used, except that 6.3g (0.015 mole) of ABQ was used to replace WB4698 as initiator. Samples were taken during the reaction. The conversions of these samples were determined by solid content. Polymer emulsions with 5.3%, 25.0%, 50.9%, 62.0%, 63.3% and 65.0% yield were obtained after 10, 20, 30, 40, 50 and 60 minutes of irradiation. The polymer emulsion obtained after 60 minutes of reaction had a mean particle size of 1.96 μm. The resultant polymer emulsion was then examined by SEM.

6.6.1.6 Emulsion Copolymerisation of EHA and VA

(i) WB4698 as Initiator

330 g of distilled water containing 4 g of polyvinyl alcohol and 3.0g (0.01 mole) of WB4698 was homogenised with a monomer mixture (EHA 120g and VA 80g) containing 7.5g (0.063 mole) of N–methyldiethanolamine using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into the reaction vessel and irradiated (UV–400 watts) for 120 minutes during which continuous ultrasonic homogenisation was used. A stable polymer emulsion with 80.0% yield was obtained. The polymer emulsion phase–separated after 10 weeks of storage.

(ii) ABQ as Initiator

300 g of distilled water containing 4 g of polyvinyl alcohol and 4.2g (0.01 mole) of ABQ was homogenised with a monomer mixture (EHA 120g and VA 80g) containing 7.5g (0.063 mole) of N–methyldiethanolamine using the ultrasonic homogeniser at 1000 ml/min throughput for 25 minutes. The mixture was then pumped into the reaction vessel and irradiated (UV–400 watts) for 180 minutes during which continuous ultrasonic homogenisation was used. A polymer emulsion with 58.6% yield was obtained. The polymer emulsion was not long term stable and phase–separated after 6 weeks of storage.

6.6.2 Thermal Polymerisation

6.6.2.1 Ammonium Persulphate Initiated Polymerisation of EHA

200g of distilled water containing 3g of PVA and 0.6g ammonium persulphate was put into a resin flask equipped with a condenser and nitrogen atmosphere, and supported in a water bath at 80°C. 100g of monomer 2–ethylhexyl acrylate was added through a dropping funnel with stirring. The reaction mixture soon became milky indicating the formation of polymer particles. The system gelled(emulsion unstable) after 15 minutes of reaction.

6.6.2.2 Ammonium Persulphate Initiated Polymerisation of Pre–emulsified EHA: Comparative Reaction To Section §6.6.2.1

The same reaction mixture and procedure as that for Section §6.6.2.1 was used, but the reaction mixture was homogenised at 1000 ml/min throughput for 25 minutes and then transferred to the resin flask to react. A polymer emulsion with a mean particle size of 13.87 µm was obtained after 30 minutes of reaction. The polymer emulsion was not stable and phase–separated after 3 days.

6.6.2.3 Ammonium Persulphate Initiated Polymerisation of EHA under Continuous Homogenisation: Comparative Reaction to Section §6.6.2.1 and Section §6.6.2.2

200g of distilled water containing 3g of PVA and 0.6g ammonium persulphate was homogenised with 100g of EHA at 1000 ml/min throughput for 25 minutes. The monomer emulsion was then pumped to a jacketed thermal reactor (nitrogen atmosphere, condenser, 80°C) where the mixture was subjected to continuous circulation through the homogeniser. The reaction mixture soon became milky indicating the formation of polymer particles. Polymer emulsions with mean particle sizes of 4.57, 4.56, 5.70, 5.39 and 9.28 μm were obtained after 10, 20, 30, 40 and 55 minutes of reaction. The polymer emulsion appeared stable after polymerisation but phase–separated after 4 weeks.

6.6.2.4 AICA Initiated Copolymerisation of EHA and VA

450g of distilled water containing 9g of polyvinyl alcohol and 4g (25% remaining water) of AICA and a monomer mixture (EHA 270g, VA 30g) were placed in a 700ml resin flask supported on a constant temperature water bath at 70 °C and stirred at about 500 rpm for 4 minutes, and then gently stirred (about 150 rpm) under a nitrogen atmosphere for 35 minutes. A polymer emulsion with 83.3% conversion and with a mean particle size of 16 μm was obtained. The polymer emulsion was not stable

6.6.2.5 AICA Initiated Copolymerisation of Pre–emulsified EHA and VA: Comparative Reaction to Section §6.6.2.4

The same reaction mixture and procedure as that for Section §6.6.2.4 was used, except that the reaction mixture was homogenised for 10 minutes at 1000 ml/min pump throughput and then transferred to the resin flask where the mixture was gently stirred. A stable polymer emulsion with 84.1% yield and a mean particle size of 4.87 μm was obtained after 35 minutes of reaction.

Another comparative reaction with only 4.5g of PVA as protective colloid gave a polymer emulsion with 68.2% yield and a mean particle size of 7.55 µm together with some polymer particle agglomerates. The polymer emulsions were examined by SEM.

6.6.2.6 AICA Initiated Copolymerisation of EHA and VA under Continuous Homogenisation: Comparative Reaction to Section §6.6.2.4 and Section §6.6.2.5

The same reaction mixture and procedure as that for Section §6.6.2.4 and Section §6.6.2.5 was used, except that the reaction mixture was homogenised for 10 minutes at 1000 ml/min pump throughput and then transferred to a jacketed thermal reactor (70°C, nitrogen atmosphere) where the mixture was subjected to continuous circulation through the homogeniser. A stable polymer emulsion with 93.2% yield and a mean particle size of 3.25 µm was obtained after 35 minutes of reaction. Another comparative reaction with only 4.5g of PVA as protective colloid gave a stable polymer emulsion with 76.0% yield and a mean particle size of 4.56 µm. The polymer emulsions were examined by SEM.

6.6.2.7 AICA initiated Copolymerisation of EHA and VA in the Presence of a Chain Transfer Agent

The same reaction mixture and procedure as that for Section §6.6.2.4 was used, except that 0.3g (0.001482 mole) of 1–dodecanthiol was added to the monomer mixture and the reaction mixture was homogenised for 10 minutes at 1000 ml/min pump throughput and then transferred to a jacketed thermal reactor (70°C, nitrogen atmosphere) where the mixture was subjected to continuous circulation with the homogeniser. A stable polymer emulsion with 71.4% yield and a mean particle size of 3.16 µm was obtained after 20 minutes of reaction. The polymer emulsion was examined by SEM.

6.6.3 Redox–Induced Polymerisation

6.6.3.1 Polymerisation of EHA

0.3g ammonium persulphate was dissolved in 142g distilled water (containing 4g PVA). The aqueous solution together with 100g EHA was transferred to a 500ml resin flask supported on a water bath(30 °C) and mechanically stirred at about 300 rpm under a nitrogen atmosphere for 5 minutes. Then 0.2g sodium sulphite (in 8g distilled water) was added dropwise to the flask, and the mixture was stirred under a nitrogen atmosphere for 15 minute. An emulsion product with 81% conversion was obtained. The polymer emulsion was unstable and phase–separated soon after the reaction.

6.6.3.2 Polymerisation of Pre–emulsified EHA : Comparative Reaction to Section §6.6.3.1

The same reaction mixture and procedure as that for Section §6.6.3.1 was used, but the reaction mixture was homogenised at 1000 ml/min throughput for 25 minutes and then transferred to the resin flask to react. A stable polymer emulsion with 91% conversion and a mean particle size of 5.42 µm was obtained after 15 minutes of reaction. In another experiment with 1.5 g of PVA, an unstable polymer emulsion with 83.5% yield was obtained. The resultant polymer emulsions were examined by SEM.

6.6.3.3 Polymerisation of EHA under Continuous Homogenisation Comparative Reaction to Section §6.6.3.1 and Section §6.6.3.2

The same reaction mixture as that for Section §6.6.3.2 was used. The reaction mixture was homogenised at 1000 ml/min throughput for 25 minutes and then pumped to a jacketed reactor (nitrogen atmosphere, 30°C). After addition of sodium sulphite(in 8g of water), the mixture was circulated in the whistle reactor. A stable polymer emulsion with 96% conversion and a mean particle size of 3.51 µm was obtained after 15 minutes of reaction. In another experiment using 1.5 g of PVA, a stable polymer emulsion with 68% yield and a mean particle size of about 10 μm (estimated from the SEM photograph) was obtained. The resultant polymer emulsions were examined by SEM.

6.6.3.4 Polymerisations of EHA using Different Amounts of PVA

Redox–induced polymerisations of EHA under continuous homogenisation have been described in Section §6.6.3.2, in which 1.5 g and 4.0 g of PVA were used. To show the effect of the amounts of PVA, polymerisations were carried out using the same reaction mixture and procedure as that of Section §6.6.3.2, except that the amount of PVA was varied. The results of polymerisations with different amount of PVA are summarised as follow: With 0.5 g of PVA, an unstable emulsion with 32% yield and a shelf life of 1 week was obtained 15 minutes after the addition of sodium sulphite; with 1.5 g of PVA, a stable emulsion with 68% yield was obtained 15 minutes after the addition of sodium sulphite, and the emulsion phase–separated after 4 months of storage (see also Section §6.6.3.2); with 2 g of PVA, a stable emulsion with 45.3% yield was obtained 15 minutes after the addition of sodium sulphite, and after 4 months of storage some agglomerates appeared; with 4 g of PVA, a stable emulsion with 96% yield was obtained 15 minutes after the addition of sodium sulphite, and the emulsion was still stable after 4 months of storage (see also Section §6.6.3.2); with 8 g of PVA, a stable emulsion with very high yield was obtained 15 minutes after the addition of sodium sulphite, and the emulsion still stable after 4 months of storage. The resultant polymer emulsions were examined by SEM.

6.7 Characterisation of Polymer Latexes Produced by Suspension and Emulsion Polymerisation

6.7.1 Solid Content and Conversion Measurements

In a small sample bottle, 1 gram of acetone was added to about 1 gram of the latex produced by suspension or emulsion polymerisation. The mixture was shaken gently to allow the polymer to coagulate. The polymer coagulates were isolated and washed with a small amount of acetone. After drying in the oven for 24 hours at 80 °C, the weight of the polymer was measured. The weight percentage of the polymer within the polymer latex was taken as the solid content. The conversion of total monomer was then calculated according to the following equation:

$$C = \frac{S\,(M+W+P\,)-P}{M}$$

where C is the conversion, S is the solid content, M is the weight of monomer, W is the weight of water, and P is the weight of PVA.

6.7.2 Particle Size Distribution Analysis

See Section §6.2.

6.7.3 Scanning Electronic Microscopy

See Section §6.2. A highly diluted polymer latex was made by the addition of a small drop of the latex to approximately 5 ml of distilled water into a sample bottle. A specimen plate was cleaned by washing with acetone. Then a small drop of the highly diluted polymer latex was put onto a clean specimen plate, which was then put into the specimen chamber for examination.

6.7.4 Tack Test

2 g of polymer latexes were coated on hard paper card boards to an area of about 3 in^2. The coated samples were dried in an oven at 80 °C for 48 hours. A brass rod with a weight of 100 g and a cross–section area of 0.442 inch^2 was put on the dried samples at room temperature (see Fig.6.5a). A weight of 500 g was applied onto the brass rod for 10 minutes (see Fig.6.5b). The samples were turned over and sat on a steel ring (see Fig.6.5c). The brass rod was slowly loaded with weights (see Fig.6.5d). The weight at which the brass rod fell from the paper card board was taken as the tack value of the polymer latex. The results of the tack tests for some polymer latexes are summarised in Table 6.10.

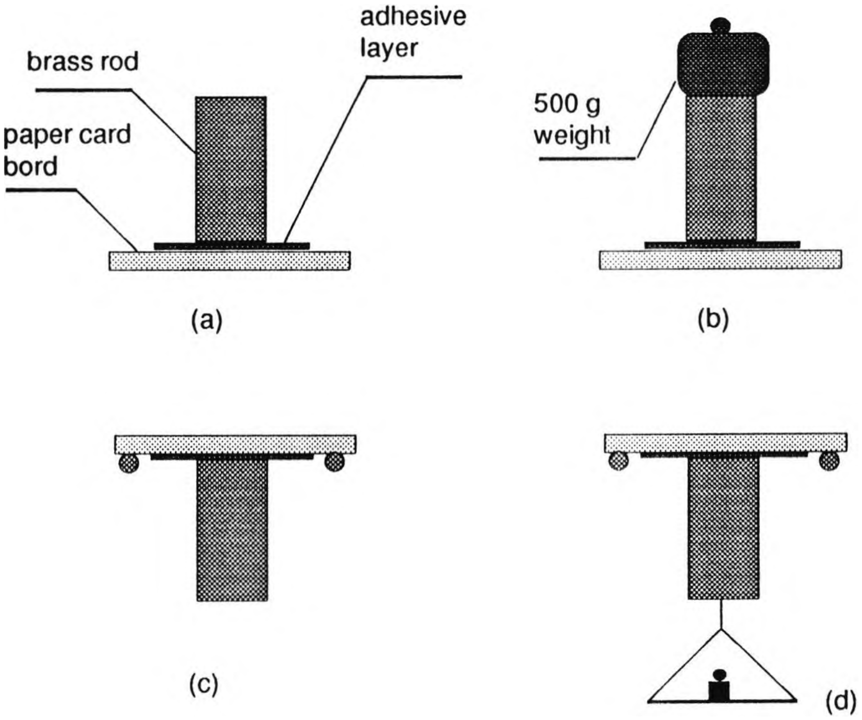


Fig.6.5(a-d) Illustration of Tack Test

6.7.5 Peel Adhesion Test

In Section §6.3.4, a glass rod roller was used for coating the polymer solution onto the substrates. However, it was found that the polymer latexes are difficult to coat evenly by using the glass rod roller. Instead of the glass rod roller, a simple doctor blade was used to coat the polymer latexes onto Melinex polyester backings. These coated samples were dried for 72 hours in an oven at 80°C. The dried adhesive films had thicknesses in the range of 54± 3 μm. The substrate aluminium panels were briefly washed firstly in soap solution, and then washed using an ultrasonic bath for 5 minutes in soap solution and finally washed for 5 minutes in 1,1,1–trichloroethane. The pressure sensitive films were applied to the clean aluminium panels by using a 3.5 kg roller. These samples were kept at room temperature for 4 hours. The peel strengths of these copolymers were then measured on an Instron 1026 Tensile Tester using a crosshead speed of 200 mm/min. The results are shown in Table 6.10

Table 6.10 Tack and Peel Test Results

Latex Produced in	Polymer Latex No.	Tack (g)	Peel Strength (g/½inch)
§6.5.1.1	1	negligible	negligible
§6.5.1.2	2	209	138
§6.6.1.3(v)	3	1123	405
§6.6.1.5(i)	4	1977	225
§6.6.1.5(ii)	5	1909	250
§6.6.2.6	6	182	negligible
§6.6.2.7	7	469	50

Chapter 7

Solution Polymerisation in a Batch Reactor

7.1 The Changes of Copolymer Composition with Conversion in the Homo– and Co–polymerisations of EHA and VA

The experimental details for the synthesis and characterisation of homo- and co-polymers of EHA and VA have been described in Section §6.3. The method adopted is a conventional batch solution polymerisation which has been commonly employed for the preparation of solution-based PSAs. Fig.7.1 shows the plots of overall copolymer compositions (F_{EHA}) as a function of initial feed composition (f_{EHA}) for both low and high conversion reactions (see Table 6.1). It can be seen from Fig.7.1 that the low conversion copolymers contain more EHA units than the high conversion copolymers with the same initial feed composition, especially when less EHA monomer is present in the initial feed. As the amount of EHA in the monomer mixture increases, the composition difference between low and high conversion copolymers decreases. When more than 80% of EHA comonomer is used, eventually the copolymer compositions are the same for low and high conversion copolymerisations. This is partially due to the fact that in the preparation of

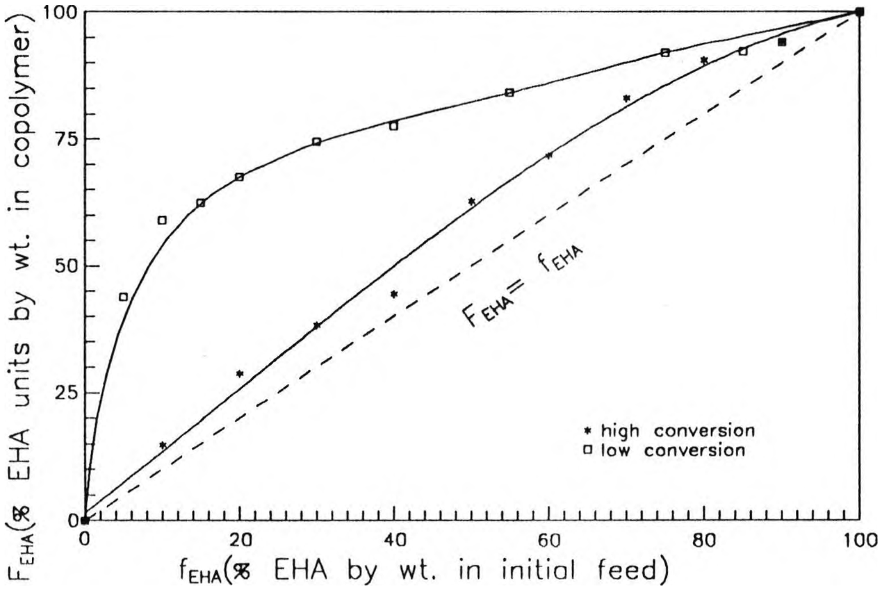


Fig.7.1 Plots of Copolymer Compositions against Initial Feed Compositions in Solution Copolymerisation of EHA and VA (according to data from Tables 6.1 and Table 6.2)

low conversion copolymers more than 70% conversion was obtained after 10 minutes of reaction, and as a result these copolymers are also high conversion copolymers.

A generalised equation relating F_{EHA} and f_{EHA} can be deduced as follow:

Let C be the total monomer conversion by weight;

let W_{EHA}^{0} and W_{EHA}^{t} be the weights of EHA in the feed at the start of the reaction and time t respectively;

let F_{EHA} be the overall copolymer composition;

let f_{EHA} be the initial feed composition, thus

$$F_{EHA} = \frac{W_{EHA}^{0} - W_{EHA}^{t}}{C\left(\frac{W_{EHA}^{0}}{f_{EHA}}\right)}$$

As can be seen from Fig7.1, the curve for F_{EHA} versus f_{EHA} at high conversion is more flat than that at low conversion. At 100% conversion, $C = 1$ and $W_{EHA}^{t} = 0$ and thus the equation becomes $F_{EHA} = f_{EHA}$, which corresponds to the dashed straight line of Fig.7.1. This means that the overall copolymer composition (F_{EHA}) changes throughout the course of the copolymerisation, and only if it proceeds to complete conversion ($C = 1$) can the overall copolymer composition (F_{EHA}) equal the initial feed composition (f_{EHA}).

7.2 Recalculation of Monomer Reactivity Ratios (MRRs) of EHA and VA

As already mentioned in Sections §2.2 and §2.4, copolymerisation can combine two dissimilar polymers, and this makes it an effective means of tailoring a polymer for a specific property or application (Krenceski,M.A. et al. 1986). EHA and VA are two monomers frequently used in formulating PSAs. However, in copolymerisation reactions, EHA has a much higher reactivity than VA (Avetisyan,I.S. 1969; Moser,K. et al. 1970) and the fast consumption of EHA monomer during copolymerisation will lead to a change in the feed composition. High conversion copolymers of EHA and VA may have quite different compositions from the low conversion copolymers produced using the same monomer feed(see §7.1). This difference in reactivity causes severe compositional heterogeneity of the high conversion copolymer.

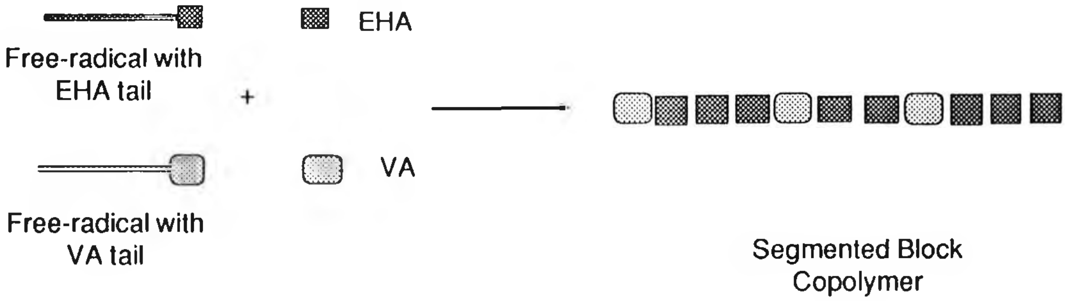
The monomer reactivity ratios of EHA and VA have been reported in the literature. Avetisyan (1969) measured the reactivity ratios of EHA and VA in an emulsion polymerisation system ($r_1 = 2.1, r_2 = 0.28$), while Moser (1970) did the same in benzene solution using peroxide as initiator ($r_1 = 7.5, r_2 = 0.04$). The temperatures at which the reactivity ratios were measured were not recorded in these two references. Apparently, the values of reactivity ratios are significantly dependent on the reaction conditions. Despite undergoing the same mechanism of free radical copolymerisation, the rate coefficients of initiation, propagation, chain transition and termination can be affected by different polymerisation systems (bulk, emulsion, solution and suspension), different types of solvent, different kinds of initiators, and different temperatures and pressures. Moreover, there are errors due to either experimental measurement or inadequate evaluation methods. As a result, recalculations of MRRs of EHA and VA seem justified.

A computer programme based on the integral copolymer equation was written to evaluate the reactivity ratios. The limits of uncertainty of the derived MRRs are estimated using their standard deviation (see Appendix I and Appendix II for the algorithm and the BASIC programme). The calculated MRRs and those reported in the literature are compared in Table 7.1.

Table 7.1 Monomer Reactivity Ratios (MRRs) of EHA (r_1) and VA (r_2)

	r_1	r_2
Based on the experimental results of present work	6.16± 0.024	0.024± 0.010
Reported by Avetisyan (1969)	2.1	0.28
Reported by Moser (1970)	7.5	0.04

The values of the recalculated monomer reactivity ratios are closer to those reported by Moser who also used a solution polymerisation system for the determination of MRRs. Whereas the results of the present work are quite different from the values reported by Avetisyan who used an emulsion polymerisation system. It seems, from these MRRs, that VA can more easily copolymerize into the polymer in emulsion polymerisation than in solution polymerisation. In the case of $r_1 > 1$ (i.e. $k_{11} > k_{12}$) and $r_2 < 1$(i.e. $k_{21} > k_{22}$), free radicals with monomer 1 (EHA) or monomer 2 (VA) at its end will show high reactivity to monomer 1(EHA). As a result, a segmented copolymer with long blocks of EHA units and short blocks of VA units is obtained by copolymerisation.



Scheme 7.1
Copolymerisation of EHA and VA (r_1>1, r_2<1)

7.3 Compositional Heterogeneity of Poly(2–ethylhexyl acrylate–co–vinyl acetate)

The copolymers of EHA and VA produced in a batch reactor have severe compositional heterogeneity due to the great difference in monomer reactivity, with the extreme case of the mixing of homopolymer in the copolymer product (see Sections §7.1 and §7.2). The DSC analysis of the high conversion homo-and co-polymers has been described in Section §6.3.3. The T_gs obtained are -73°C for poly(2-ethylhexyl acrylate) and 26°C for poly(vinyl acetate). However, two characteristic glass transition temperatures (see Fig.7.2) were observed for those copolymers produced using more VA in the monomer feed. The lower of the two T_gs (T_{g1} < -35°C) corresponds to EHA components and the higher (T_{g2} > +30°C) corresponds to VA components. The DSC analysis results strongly support the observed high compositional heterogeneity of the copolymers obtained at high conversion.

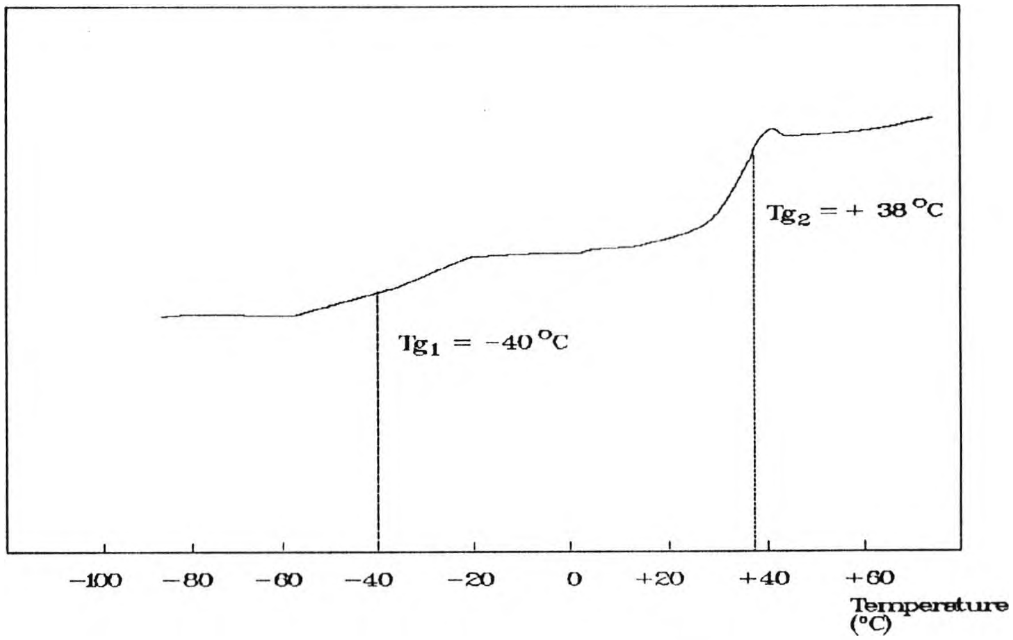


Fig.7.2 DSC Trace of Polymer No.3

7.4 Effect of Copolymer Composition on the Peel Adhesion

The peel adhesion measurements have been described in Section §6.3.4 and the peel adhesion results are listed in Table 6.4. For those copolymers with more VA units, stick-slip failures (see Fig.7.3) were observed. The stick-slip failures are associated with the high rigidity of these polymers. On the other hand, cohesive failures (see Fig.7.4) were observed for those copolymers with more EHA units, which soften the bulk of these polymers. For copolymers with 60--80% by weight of EHA units, adhesive failures were observed. Most commercial PSAs are intended to fail adhesively, so that the PSA tapes can be removed without leaving adhesives on the substrates. As a result, those polymers with 60--80% by weight of EHA units have desirable pressure-sensitive properties.

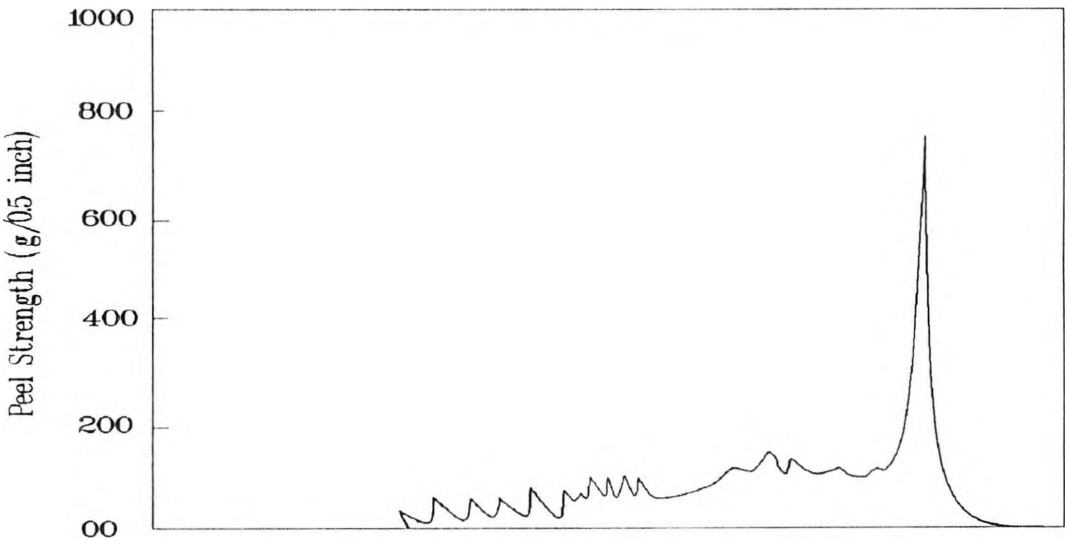


Fig.7.3 Stick-slip Failure of Polymer No.5

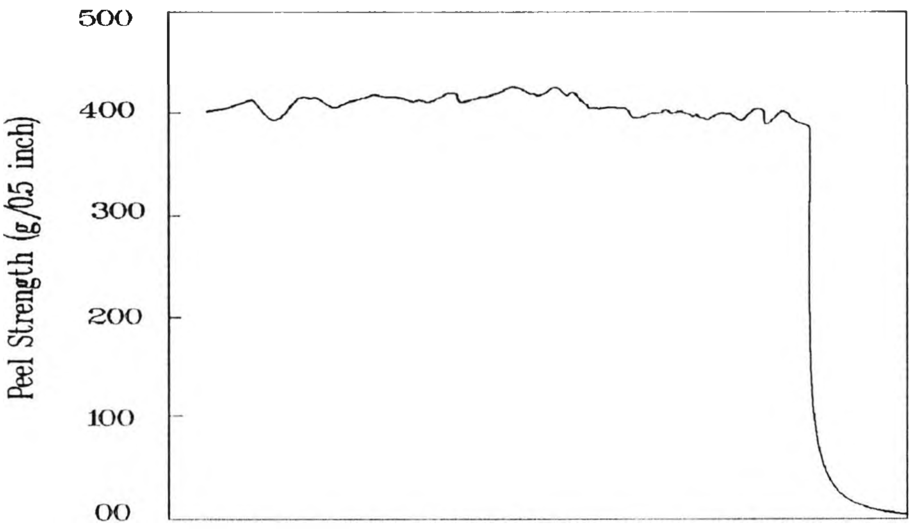


Fig.7.4 Cohesive Failure of Polymer No.9

7.5 Effect of Copolymer Compositional Heterogeneity on the Peel Adhesion

The peel adhesions of high conversion copolymers with higher compositional heterogeneity are compared with that of low conversion copolymers which have relatively lower compositional heterogeneity in Fig.7.5. It seems that the peel adhesion is not affected by the variation of heterogeneity of the copolymer, and low and high conversion copolymers show little differences in their peel strengths. For both low and high conversion polymer series a maximum value of peel adhesion is obtained near 72-74% EHA units by weight. Thus one may say that the peel adhesions of the copolymers depend on its copolymer composition rather than its compositional heterogeneity.

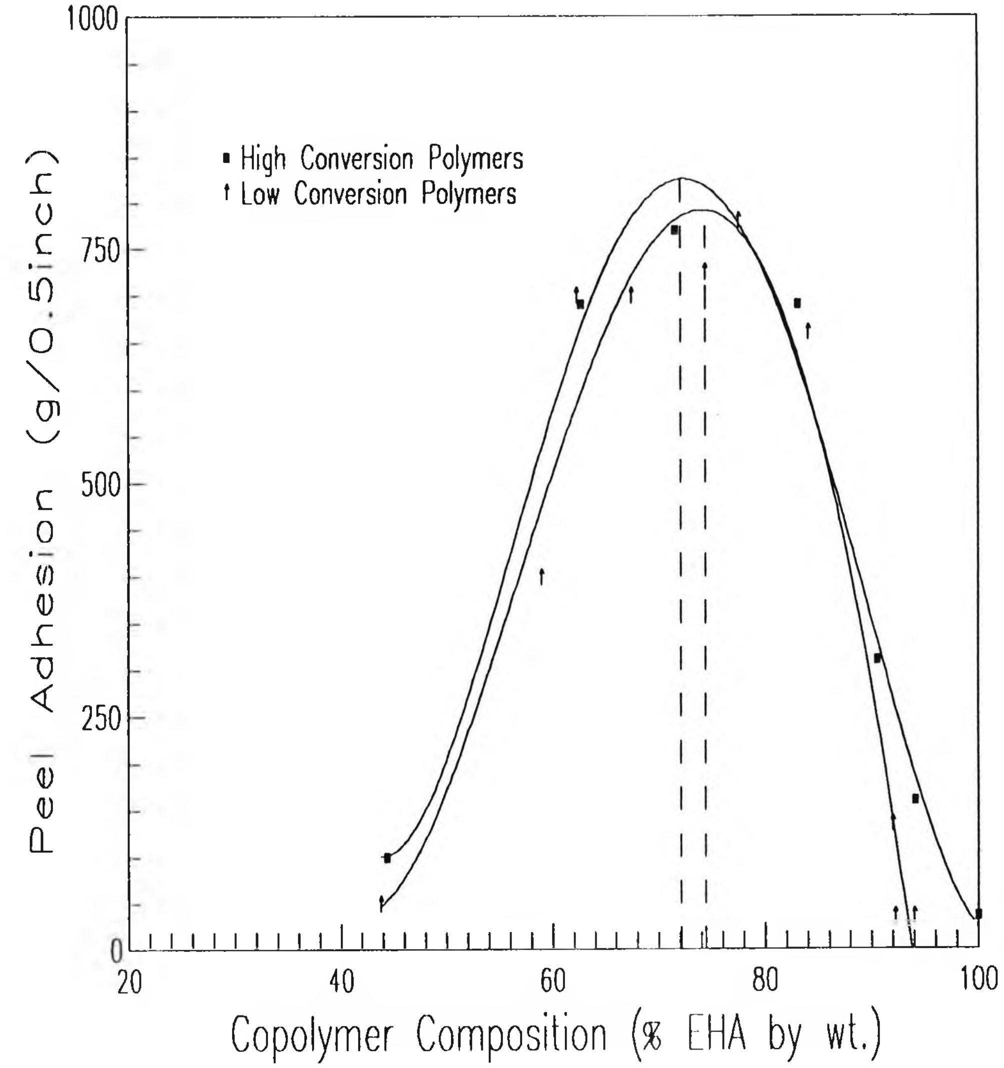


Fig.7.5 Plots of Peel against Copolymer Composition (according to data of Tables 6.2 and 6.4)

On the other hand, the average molecular weight (see also Chapter 11) will also affect the peel adhesion of a polymer. In the present work, the number average molecular weight of solution polymerised EHA is about 250,000. Polymers with such molecular weight have been proved to be suitable for pressure-sensitive adhesive application. Fig.7.6 illustrates the molecular weight distribution of Polymer No. 11.

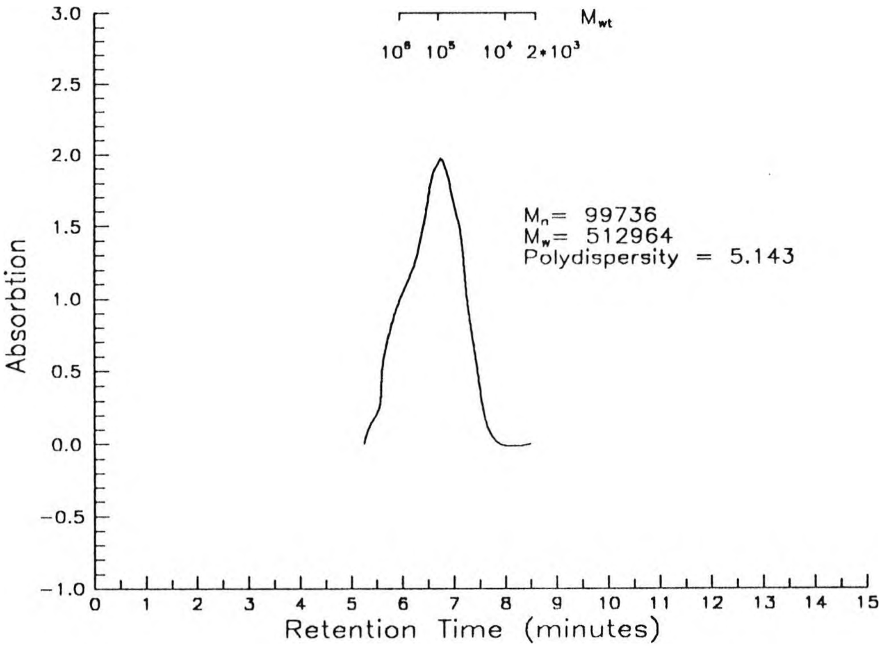


Fig.7.6 GPC Trace of Polymer No.11

7.6 Changes of the Peel Adhesion with Time

The peel adhesions of copolymers of EHA and VA with time have been summarised in Table 6.4. Some of the results are plotted in Fig.7.7. Those copolymers which failed cohesively showed some decrease in the peel adhesion with time. On the other hand, a slight increase in the peel adhesion was observed for some of those copolymers which failed adhesively. The reasons for such changes in the peel adhesion are not clear. However it should be noted that these peel adhesion results are obtained at room temperature, and thus variations of the room temperature will affect the value of peel adhesion.

7.7 Summary

- The characterisation of copolymer composition using ^{1}Hn.m.r. is a feasible and fairly straightforward method. The ^{1}Hn.m.r. characterisation results show that the weight percentages of EHA in the copolymers are higher than that in the monomer feed due to the higher reactivity of the acrylate.

- Two separate T_gs observed in the DSC analyses indicate the severe compositional heterogeneity of the batch-produced polymers. The recalculation of the MRRs of EHA and VA gives values $r_1= 6.16$, $r_2= 0.0236$. The great difference in monomer reactivity is responsible for the severe heterogeneity, with the formation of homopolymer of vinyl acetate at high conversion as the extreme case.

- Poly(2–ethylhexyl acrylate) alone is too soft and fails cohesively when peeled. Its performance can be improved by copolymerisation with VA which raises the Tg. Conversely, poly(vinyl acetate) is too hard and fails in a peel test in a stick-slip fashion and its performance can be improved by copolymerisation with EHA which will lower the Tg (Satas, D., 1982).

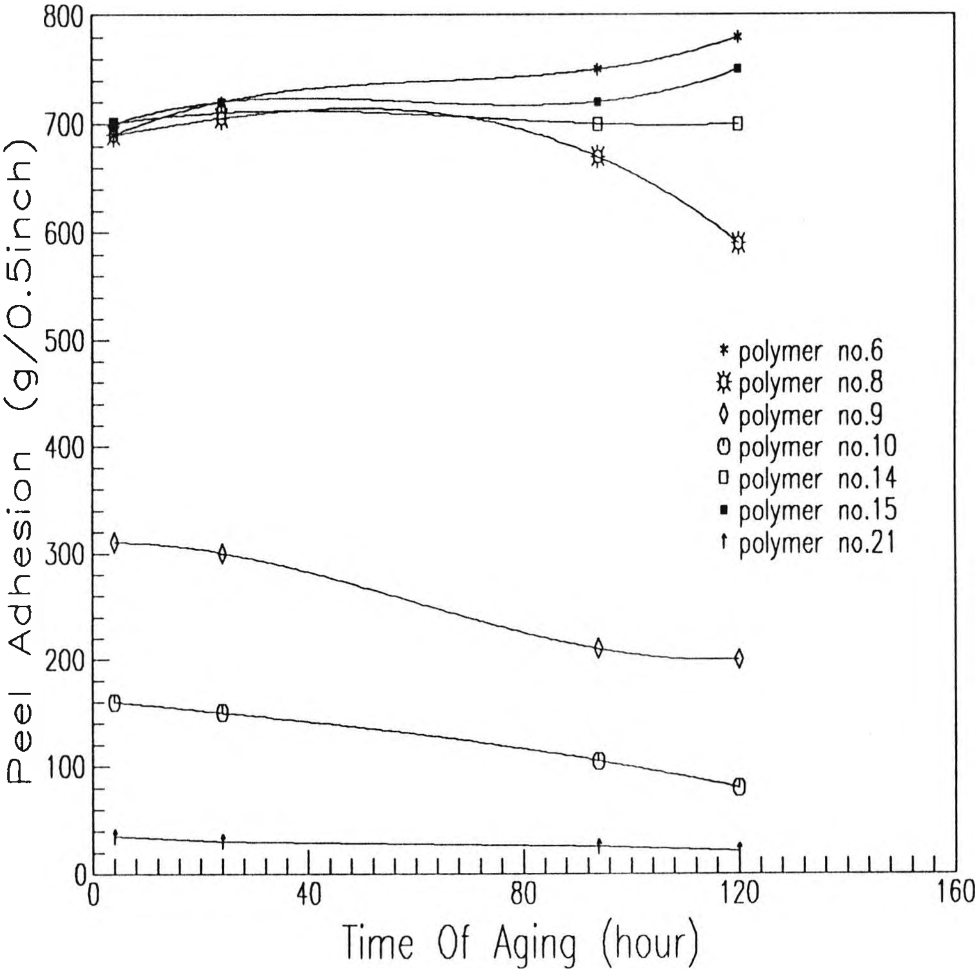


Fig.7.7 Variation of Peel with Aging
(according to data of Table 6.4)

A maximum value of peel adhesion is observed for copolymers with a composition near 72-74% of EHA in weight. One has to choose a proper composition of the copolymerisation in order to obtain balanced cohesive and adhesive properties.

- A comparison of the peel adhesion of high conversion copolymer (which is more heterogeneous) and low conversion copolymer (which is less heterogeneous) did not yield any interesting results. One may say that compositional heterogeneity will not affect peel adhesion if its components are compatible and miscible at the temperature of peel test.

Chapter 8

Emulsification in the Whistle Reactor

8.1 Introduction

The experimental details for the emulsification in the whistle reactor have been described in Section §6.4. The method adopted was the homogenisation of monomer in water in the presence of a water-soluble polymer (eg. PVA, commonly used as a suspension stabiliser).

It is known that the particle size of the emulsion formed by ultrasonic homogenisation depends on the physical properties and state of the dispersed liquids, on the intensity and duration of ultrasound application, and also on the dimensions and form of the vessel in which the homogenisation is taking place (Puskar,1982). In the present work, when EHA and water were homogenised in the whistle reactor, a suspension was formed. However, the suspensions so formed are not stable and phase separation begins soon after homogenisation. This is probably caused by the density difference between EHA and water and the rapid agglomeration of EHA droplets . When polyvinyl alcohol, a suspension stabiliser (or protective colloid) was used, the stability of the suspension was greatly increased since the rapid agglomeration of EHA droplets was suppressed. It is well accepted that the stabilisation mechanism of PVA upon suspensions is by enveloping the droplets in a "shell" of

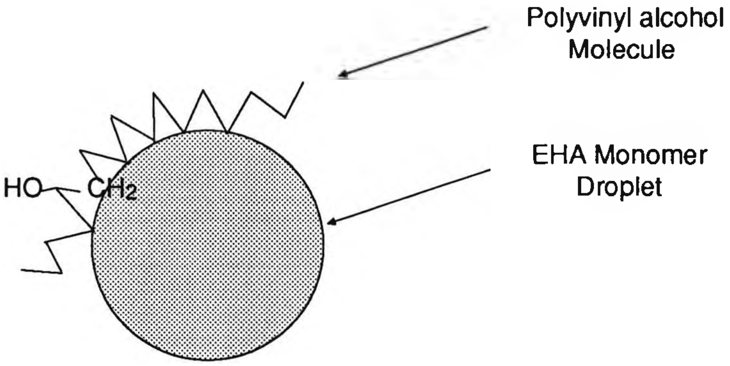


Fig.8.1 Stabilization of Monomer Droplet by PVA

water-soluble colloid, which discourages effective contact of the interiors of the droplets when they collide (see Fig.8.1).

In this chapter, the study of the emulsification of EHA with water in the whistle reactor in the presence of PVA is reported.

8.2 Effect of the Duration of Ultrasound Application

The particle size obtained in an ultrasonic homogenisation experiment depends not only on the formulation of the homogenising mixture, but also on the total energy input into the homogenising product. The total amount of the energy input, however is determined both by the duration of ultrasonic application and the pump operating condition. The effect of the duration of ultrasound application on the mean particle size and particle size distribution is described in this section. The effect of the pump operating condition is described later.

Fig.8.2(a-f) illustrates the particle size distributions of EHA monomer emulsions at different homogenisation times (see Section §6.4.2 for experimental details). It can be seen from these bar graphs that the mean particle size decreases and the particle size distribution becomes narrower with increasing duration of homogenisation. In Fig.8.3 the mean particle size is plotted against the duration of ultrasound application

When the mixture of EHA and water was pumped through the homogenizer, a coarse suspension of the EHA droplets in water was obtained. During further circulation of the coarse suspension through the homogenizer, the monomer droplets have a mean residence time (τ_m) which depends on the total volume of the EHA/water mixture (V_m) and the pump flow rate (Q_m):

$$\tau_m = \frac{V_m}{Q_m} \quad \text{(equation 8.1)}$$

At time t, the average number of circulations (n) of a droplet through the homogenizer will be $\frac{t}{\tau_m}$. As the duration of the homogenisation (t) increases, the value of n increases, and this is responsible for the decreased mean particle size at increased duration of homogenisation. On the other hand, as the duration of the homogenisation (t) increases, the numbers of circulations for different droplets tend to be the same, and this is responsible for narrower particle size distribution at increased duration of homogenisation. From Fig.8.3, one can see that the mean particle size decreased sharply from 6.2 μm to 4.0 μm during the first 10 minutes of homogenisation and then decreased slowly to 3.7 μm during another 15 minutes of homogenisation. It appears that for the homogenisation of this system in a particular homogenizer, there is a minimum particle size limit below which the particle size is not decreased by longer homogenisation.

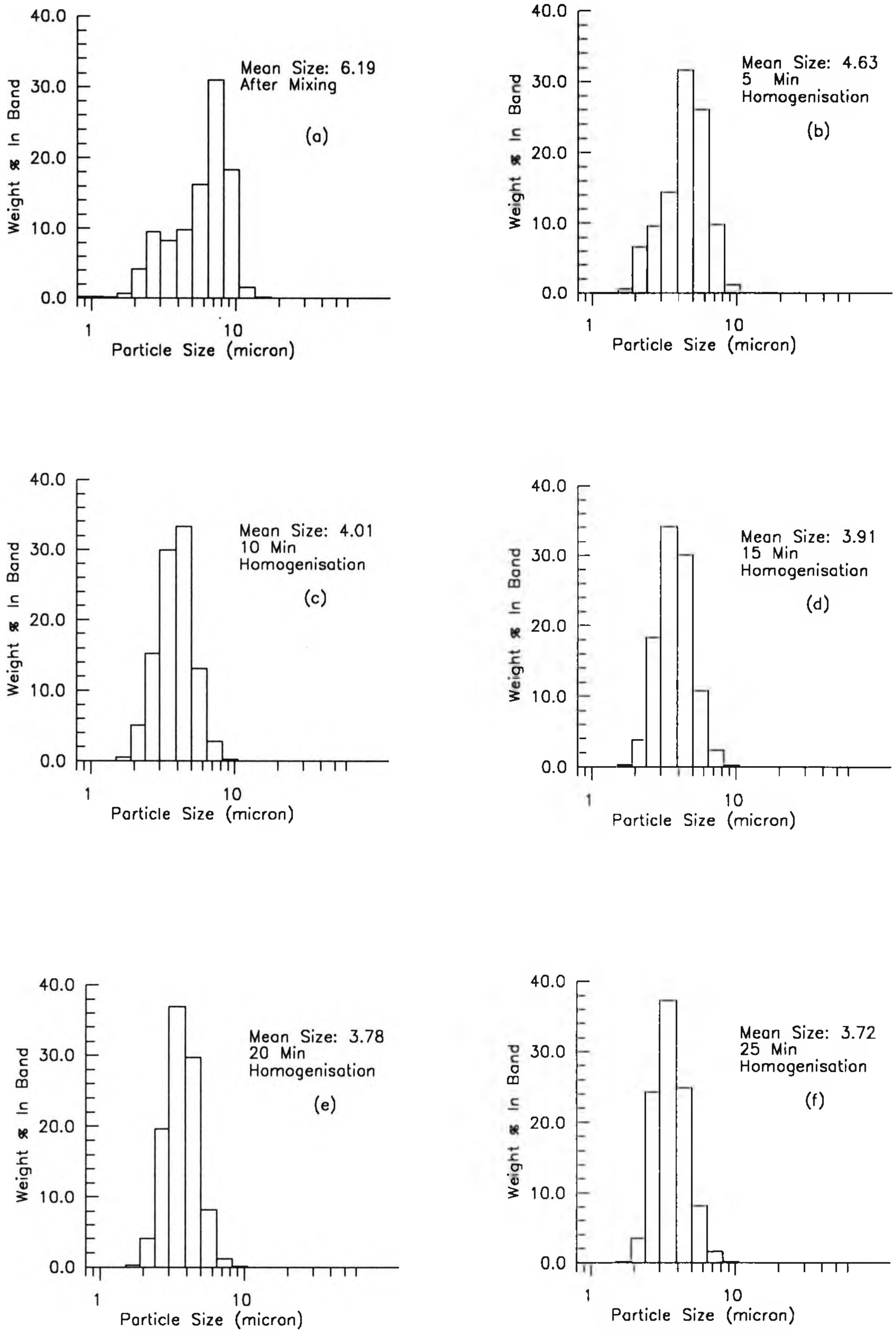


Fig.8.2(a-f) Particle Size Distribution
Effect of Duration of Ultrasound Application
(Mixture used:EHA 200g, water 300g, PVA 4g; Pump flow rate: 1000 ml/min)

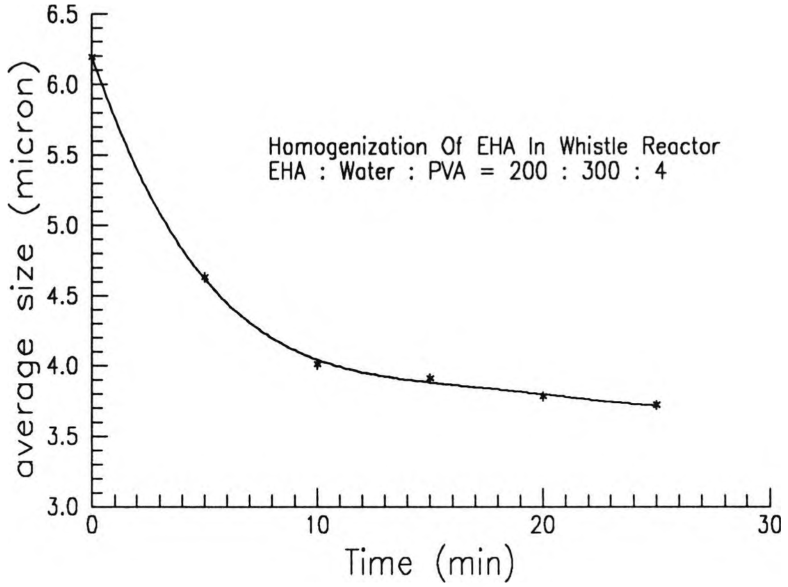


Fig.8.3 Plot of Mean Particle Size against Time
Effect of Duration of Ultrasound Application
(Mixture used:EHA 200g, water 300g, PVA 4g; Pump flow rate: 1000 ml/min)

8.3 Effect of the Pump Operating Pressure

Fig.8.4(a-f) are the bar graphs showing the mean particle size and distribution of EHA monomer emulsion by homogenisation under different flow rates (see Section §6.4.3 for experimental details). Fig.8.5 is the plot of the mean particle size against pump flow rate. It is evident from Fig.8.4(a-f) and Fig.8.5 that homogenisation under higher pump operating pressure gives small particles and narrow particle size distribution. An increase in the operating pressure of the pump will cause a higher throughput (i.e. pump flow rate Q_m) of the ultrasonic homogenizer. This will affect both the performance of the homogenizer and the mean residence time (τ_m) of the homogenisation medium (see equation 8.1). As the pump flow rate (Q_m) increases, the average number of circulations of monomer droplets (n) increases (see equation 8.1), and this is responsible for the decreased mean particle size at increased pump operating pressure. On the other hand, as the pump operating pressure

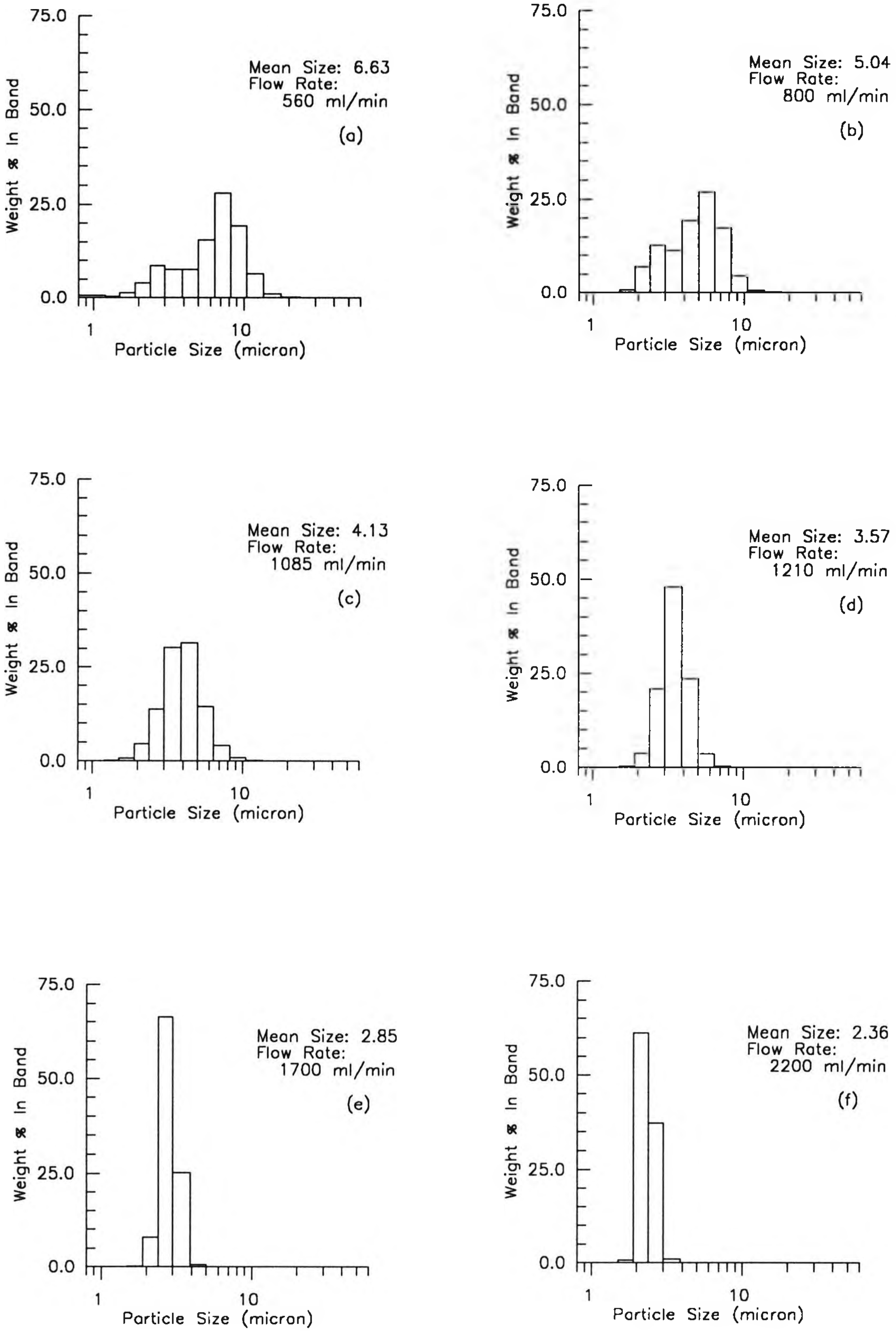


Fig.8.4(a-f) Particle Size Distribution
Effect of Pump Operating Pressure (Mixture used: EHA 60g, water 690g, PVA 4.93g;
Duration: 25 min at 560 ml/min, 20 min at 800 ml/min, 20 min at 1085 ml/min)

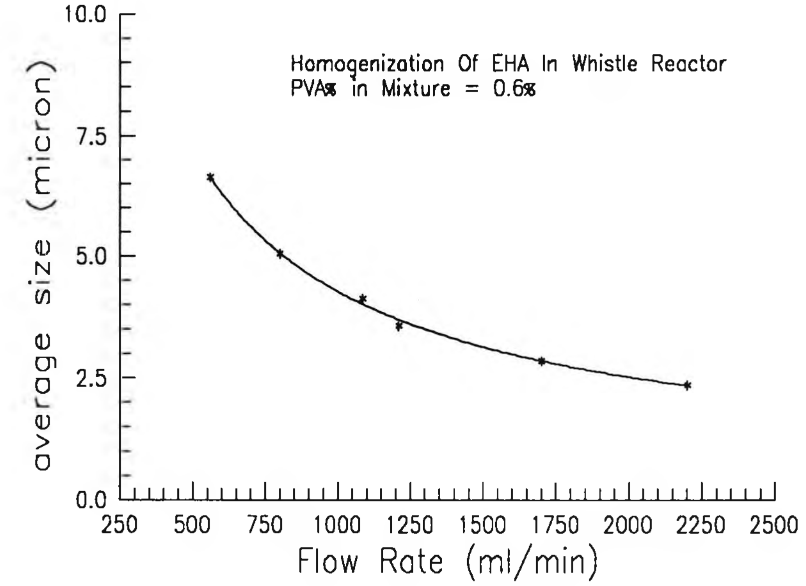


Fig.8.5 Plot of Particle Size against Pump Flow Rate
Effect of Pump Operating Pressure (Mixture Used: EHA 60g, water 690g, PVA 4.93g; Duration: 25 min at 560 ml/min, 20 min at 800 ml/min, 20 min at 1085 ml/min, 15 min at 1210 ml/min, 10 min at 1700 ml/min and 5 min at 2200 ml/min)

increases, the numbers of circulations for different droplets tend to be the same, and this is responsible for narrower particle size distribution at increased pump operating pressure.

It is also clear from Fig.8.5 that the mean particle size first decreases sharply with an increase in the pump operating pressure and then tends to level off with a further increase in the pump operating pressure. One can expect that there will be a minimum size limit below which the further break-up of particles by homogenisation is not possible even at increased operating pressure.

8.4 Effect of PVA Concentration

Fig.8.6(a-e) illustrates the mean particle sizes and the particle size distribution of EHA monomer emulsion prepared with different concentrations of PVA (for experimental details see Section §6.4.4). It can be seen from the graphs that the mean particle size decreases and the particle size distribution becomes narrower with increase in PVA concentration.

Fig.8.7 is the plot of the mean particle size against the PVA concentration used. It may be noticed that if the PVA concentration is below about 1% by weight of the EHA, a slight decrease of the PVA concentration will cause a very sharp increase in the mean particle size. Thus if the amount of PVA used is insufficient to saturate the interfaces between EHA droplets and water, the EHA droplets will agglomerate to reduce the area of their interfaces with water. Once these interfaces are saturated, an increase in the amount of PVA has little effect. It is worth noting here that the stabilising ability of polyvinyl alcohol may vary with its degree of hydrolysis and molecular weight. PVA with 5-15% of residual acetate groups is a more effective protective colloid then pure PVA in most applications (Hopff,H. et al. 1965). PVA with 14% residual acetate groups (i.e. 86% hydrolysis) was used for the present work.

8.5 Effect of Monomer to Water Ratio

Fig.8.8(a-d) illustrates the mean particle sizes and the particle size distribution of EHA monomer emulsion prepared with different ratios of EHA to water after 25 minutes of homogenisation (for experimental details see Section §6.4.5). It can be seen from these graphs that the mean particle size increases and the particle size distribution becomes wider with increasing EHA to water ratio. Fig.8.9 is the plot of the mean particle size against the ratio between EHA and water. When the EHA ratio to water is increased, there is some increase in the average particle size. This is attributed to the increased

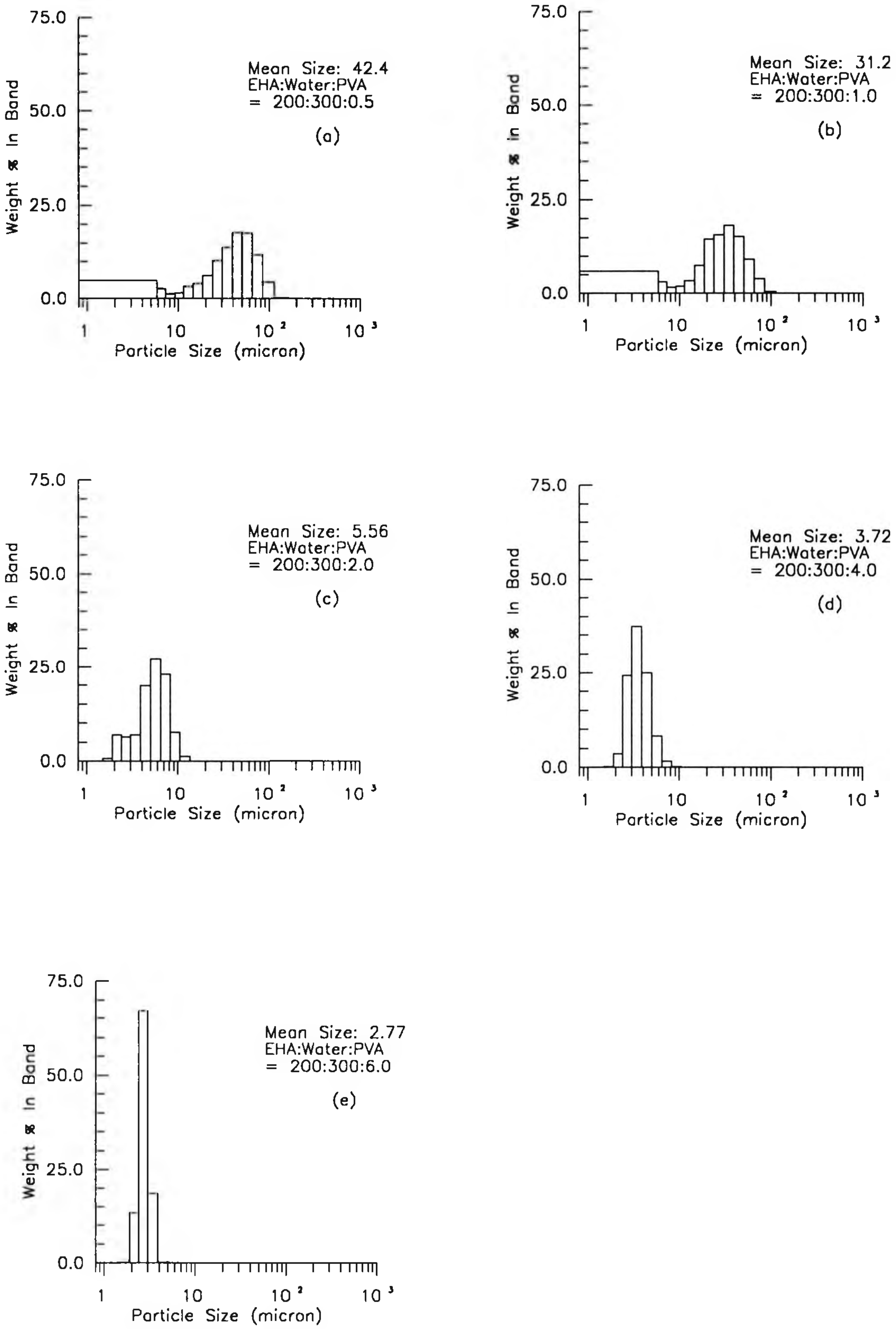


Fig.8.6(a-e) Particle Size Distribution
Effect of PVA Concentration (Pump:1000 ml/min; Duration: 25 min)

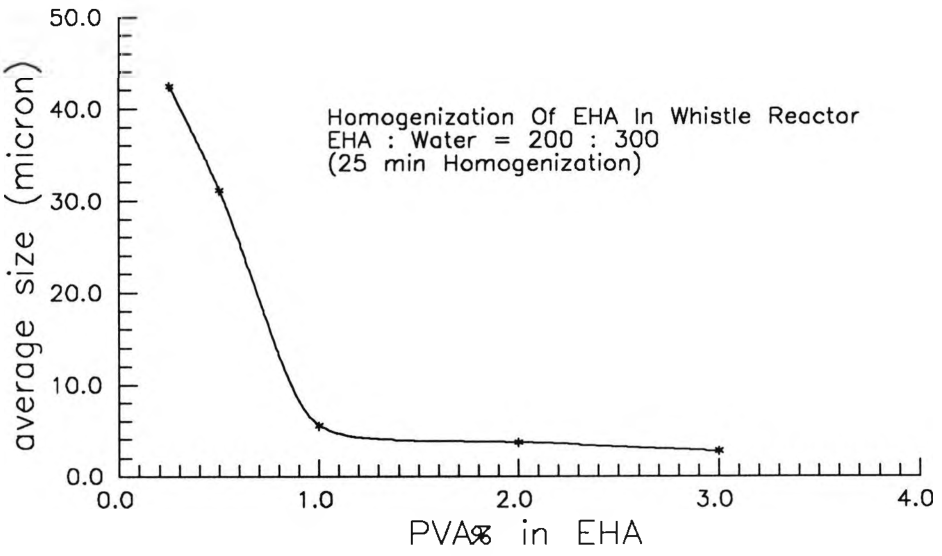


Fig.8.7Plot of Particle Size against PVA Concentration

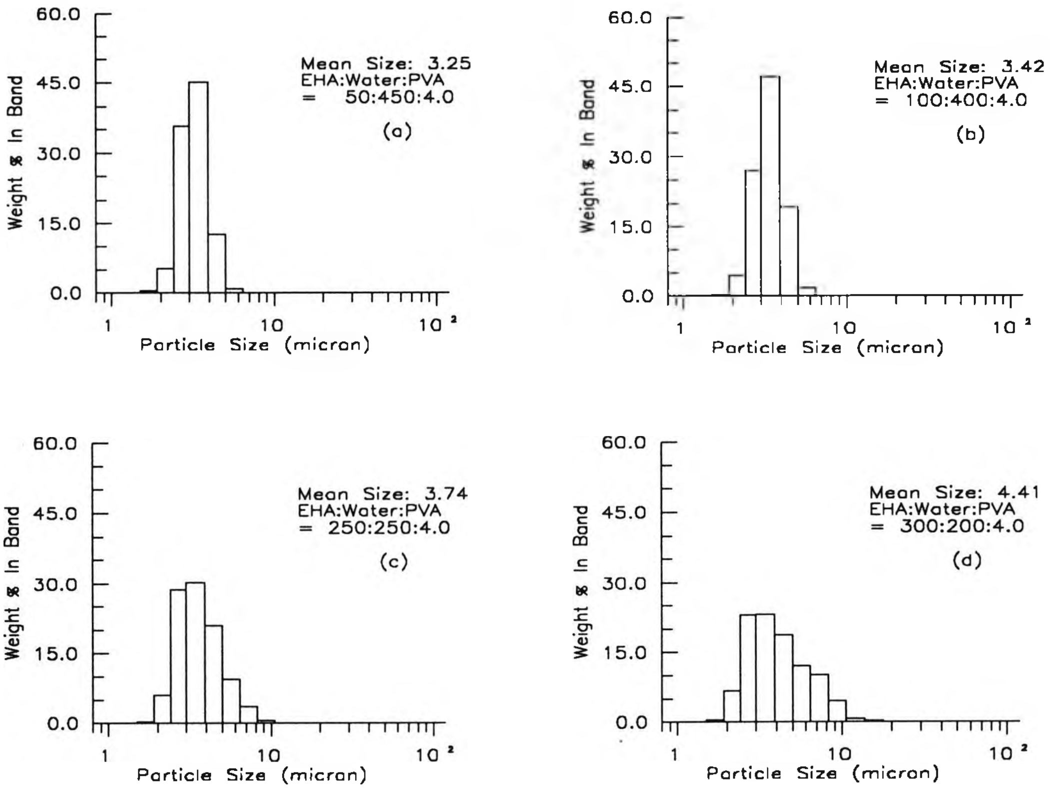


Fig.8.8(a-d) Particle Size Distribution
Effect of Monomer to Water Ratio (Pump:1000 ml/min; Duration: 25 min)

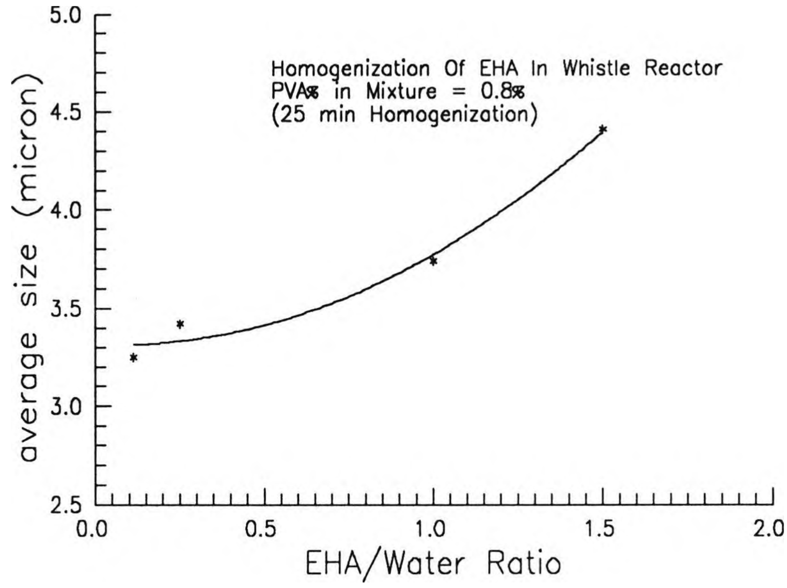


Fig.8.9 Plot of Particle Size against EHA/water Ratio
(Pump:1000 ml/min; Duration: 25 min)

probability of particles colliding when the ratio between EHA and water is increased. It was also noticed that there is a rapid increase in the viscosity of the suspension when the ratio between EHA and water is increased.

8.6 Emulsification of a Solution of a Polymer

As has been described, monomer emulsions were made by homogenisation of EHA in water. To evaluate the effect of added polymer on the particle size, poly(2-ethylhexyl acrylate) was dissolved in EHA monomer, and this solution was homogenised with water using the whistle reactor (for experimental details see Section §6.4.6). Fig.8.10 shows the mean particle sizes and the particle size distribution of the resultant emulsion after 25 minutes homogenisation. A suspension having an average particle size of 2.77 μm with 9.4% by weight of small particles below 1.2 μm was obtained compared with 0.0% below 1.2 μm when pure EHA was used. This might be because pure

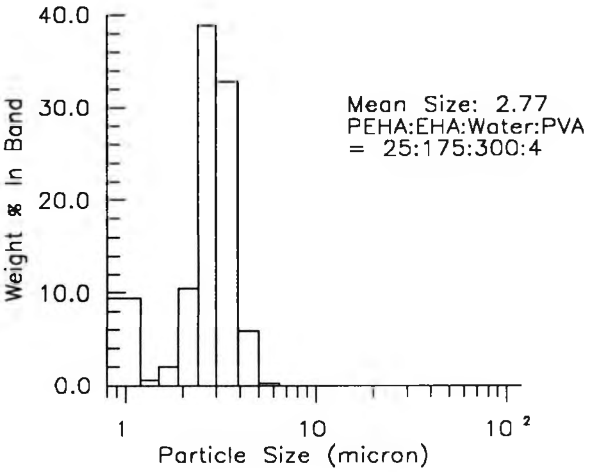


Fig.8.10 Particle Size Distribution
Effect of Dissolved Polymer in the Monomer Phase
(Pump:1000 ml/min; Duration: 25 min)

EHA droplets are softer compared with EHA polymer solution droplets, and thus easier to collapse when they collide. As a result, pure EHA gives bigger particle size than EHA polymer solution when homogenised with water.

8.7 Emulsification by Mechanical Stirring

To compare the efficiency of emulsification by ultrasonic homogenisation and mechanical stirring, the same mixture as has been used before (EHA:Water:PVA = 200:300:4) was stirred with a mechanical stirrer in a resin flask (for experimental details see Section §6.4.7). As shown in Fig.8.11 a suspension with a mean particle size of 56.1 μm was obtained after 25 min stirring. As described before (see Fig8.2(f)), a much smaller particle size (3.72 μm) was obtained with ultrasonic homogenisation. So it can be concluded that

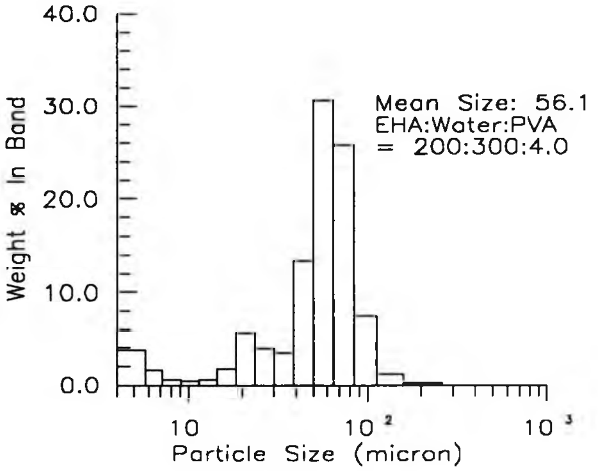


Fig.8.11 Particle Size Distribution
Emulsification by Mechanical Stirring
(at about 300 rpm for 25 min)

the ultrasonic homogenizer is much more efficient for the emulsification of EHA monomer in water with PVA as the protective colloid.

8.8 Effect of Added Surfactant

It is also expected that low molecular weight surfactants can efficiently stabilise the suspension, thus a commercially available surfactant Igepal CO-990 (nonyl phenol ethylene oxide condensate) was used to replace PVA (for experimental details see Section §6.4.8). As shown in Fig.8.12, a suspension with a small average particle size of 2.02 μm, with all particles below 5 μm was obtained. By comparison with Fig8.2(f), one can see that PVA is less effective than the surfactant Igepal CO-990 in stabilising the suspension.

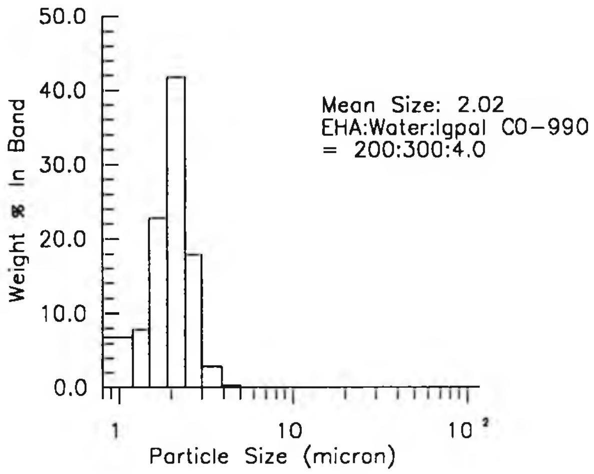


Fig.8.12 Particle Size Distribution
Effect of Added Surfactant
(Pump:1000 ml/min; Duration: 25 min)

8.9 Characteristics of the Resultant Monomer Emulsions

Because EHA is lighter than water, when an emulsion is stored, the EHA droplets tend to accumulate in the upper half of the storage bottles and a clear layer of water appears at the bottom. For EHA suspensions with good stability, the EHA droplets can be re-dispersed by hand shaking because they have not coalesced. For those suspensions with poor stability, EHA and water become two separate phases and cannot be re-dispersed by hand shaking to form an emulsion.

8.10 Summary

The present work has shown that ultrasonic homogenisation is an effective method for the emulsification of EHA monomer with water under the stabilisation of polyvinyl alcohol. Monomer emulsions have been prepared using ultrasonic homogenisation. Such monomer emulsions can remain stable for days without phase separation. For the successful preparation of stable monomer emulsions, the following are the key points to watch:

- Suitable monomer to water ratio.
- Suitable protective colloid concentration.
- Suitable pump operating pressure.

Chapter 9

Suspension Polymerisation in the Whistle Reactor

9.1 Introduction

One of the commonly used protective colloids (or dispersing agents) for suspension polymerisation is polyvinyl alcohol (PVA), the dispersing power of which depends on its molecular weight and degree of hydrolysis (Marten, F.L., 1989). For the present work, polyvinyl alcohol having a molecular weight of 115,000 and a degree of hydrolysis of 86% was used. As shown in Chapter 8, if the concentration of the PVA in water is below 1% of the weight of monomer EHA, there will be a sharp increase in the mean particle size of the emulsified monomer dispersion. In order to get a stable and fine monomer dispersion, polyvinyl alcohol was used at a level of 1 to 2% based on the weight of monomer in the present work. The amount of PVA commonly employed in conventional suspension polymerisation varies between 0.1 to 2% based on monomer depending on the final application of the suspension polymer product.

Some aspects of suspension polymerisation have been introduced in Chapter 3. Experimental details of suspension polymerisations have been described in

Section §6.5. In this chapter, the experimental results of the suspension polymerisations will be discussed.

9.2 UV-Induced Polymerisation

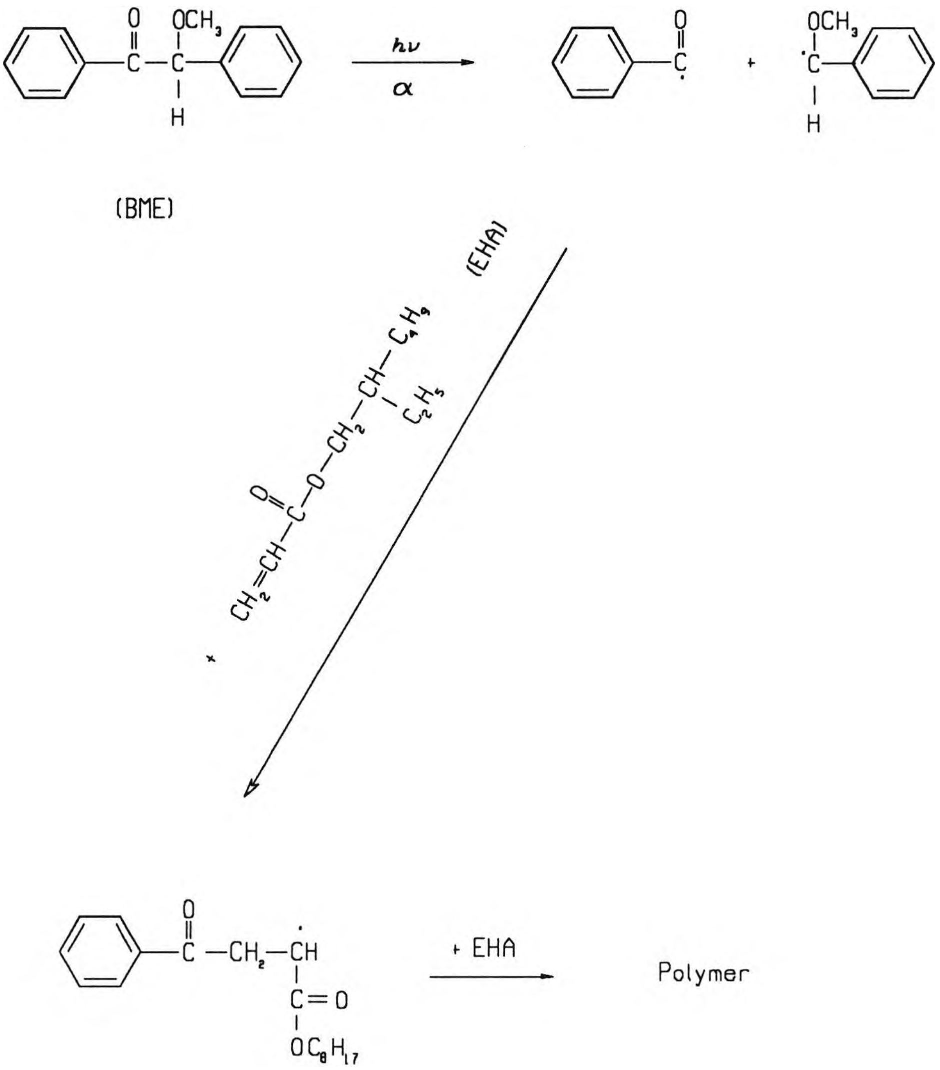
9.2.1 Introduction

The initiator benzoin methyl ether (BME) used for the UV–induced suspension polymerisation is a Type I photoinitiator which undergoes α-cleavage upon UV-irradiation. It is believed that the benzoyl radicals formed by the α-cleavage of BME molecules are responsible for the initiation of polymerisation (Hageman, 1985). The photoinitiation and photopolymerisation of 2–ethylhexyl acrylate (EHA) can be illustrated by Scheme 9.1. Two different methods have been used in the UV-induced suspension polymerisations of EHA:

- emulsification of the monomer with water by the homogenizer followed by polymerisation of the pre-emulsified EHA without continuously applied ultrasonic homogenisation, and

- emulsification of the monomer with water by the homogenizer followed by polymerisation of the monomer emulsion under continuously applied ultrasonic homogenisation.

Of the two methods, the former may be regarded as conventional polymerisation, while the latter is the polymerisation in the whistle reactor. Several aspects of these two different polymerisation methods are compared and discussed in the following section, whereas the suspension copolymerisations of EHA and VA, and suspension polymerisations of other monomers will be considered in later sections.



Scheme 9.1 The Polymerisation of 2-Ethylhexyl Acrylate Initiated by Benzoin Methyl Ether

9.2.2 Polymerisations of EHA with and without Continuous Homogenisation

The experimental details of the suspension polymerisations of EHA with and without continuous homogenisation have been described in Section §6.5.1.2 and Section §6.5.1.1, respectively.

The properties of the polymer suspension produced with and without continuous homogenisation are compared in Table 9.1.

Table 9.1 Properties of Polymer Suspensions Produced with and without Continuous Homogenisation

Properties	with Continuous Homogenisation	without Continuous Homogenisation
Solid Content (%)	34	38.2
Mean Particle Size (μm)	3.80	3.87
Shelf Life (months)	≈ 6	≈ 6

9.2.2.1 Rates of Polymerisations

Fig.9.1 shows the plots of conversion against reaction time in the polymerisations of EHA with and without continuously applied ultrasonic homogenisation. It can be seen from Fig.9.1 that the polymerisations began soon after the introduction of UV-irradiation. As shown in Fig.9.1, about 75% conversion was obtained after 10 minutes of UV-irradiation in the polymerisation under continuous homogenisation, compared with 25% conversion for the polymerisation without continuously applied ultrasonic homogenisation. This is probably caused by the fast initiation rate associated with better exposure of the reactants in the mixture to the UV-irradiation under continuous circulation through the homogenizer. The conversion of the polymerisation without continuously applied ultrasonic homogenisation after 60 minutes of reaction, however, is not as high as that of the polymerisation

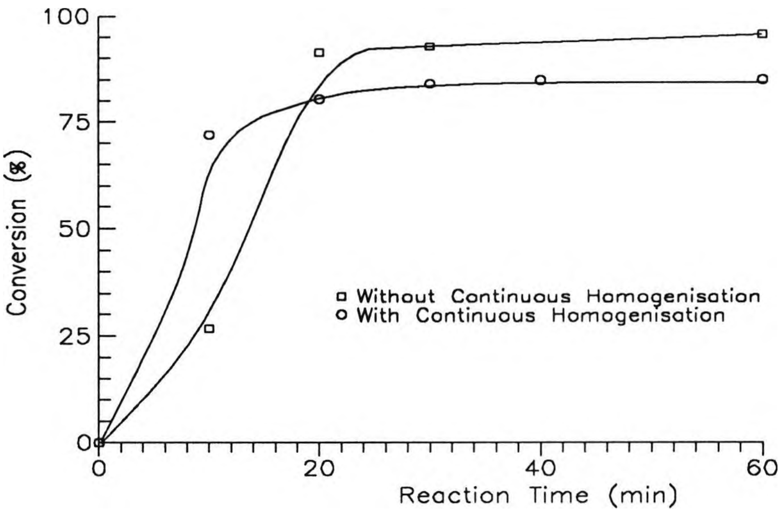


Fig.9.1 Plots of Conversion against Reaction Time
in Suspension Polymerization of EHA

of EHA without continuous homogenisation. This is probably due to the early depletion of initiator during the polymerisation with continuous homogenisation.

In the following Sections Section §9.2.2.2 and Section §9.2.2.3, the particle size distributions of the resultant polymer suspensions and molecular weight distributions of polymers produced will be discussed. Clues may then be obtained from the particle size distributions and the molecular weight distributions for the reasons for the increase in the rate of polymerisation under continuous homogenisation.

9.2.2.2 Changes of Particle Size Distribution During Polymerisation

Fig.9.3(a-f) and Fig.9.2(a-f) represent the particle size distributions and mean particle sizes of samples taken at different reaction times in suspension polymerisations of EHA with and without continuously applied ultrasonic homogenisation, respectively. Fig.9.4 illustrates the mean particle sizes at different conversions. It can be seen from Fig.9.2(a-f) and Fig.9.3(a-f) that there were significant changes of the particle size distributions during both

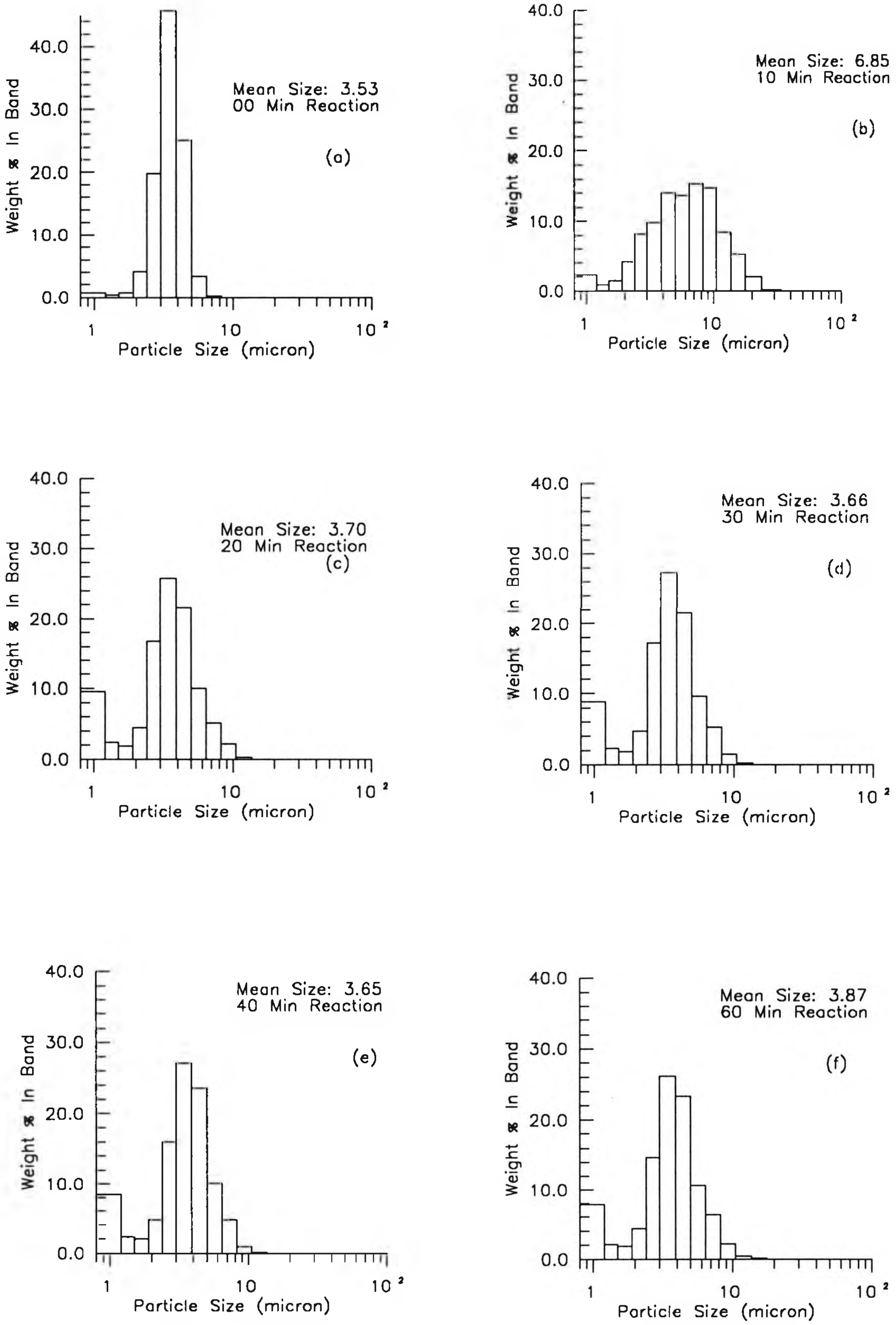


Fig.9.2(a-f) Particle Size Distribution
at Different Reaction Times in Suspension Polymerisation
of EHA without Continuous Homogenisation

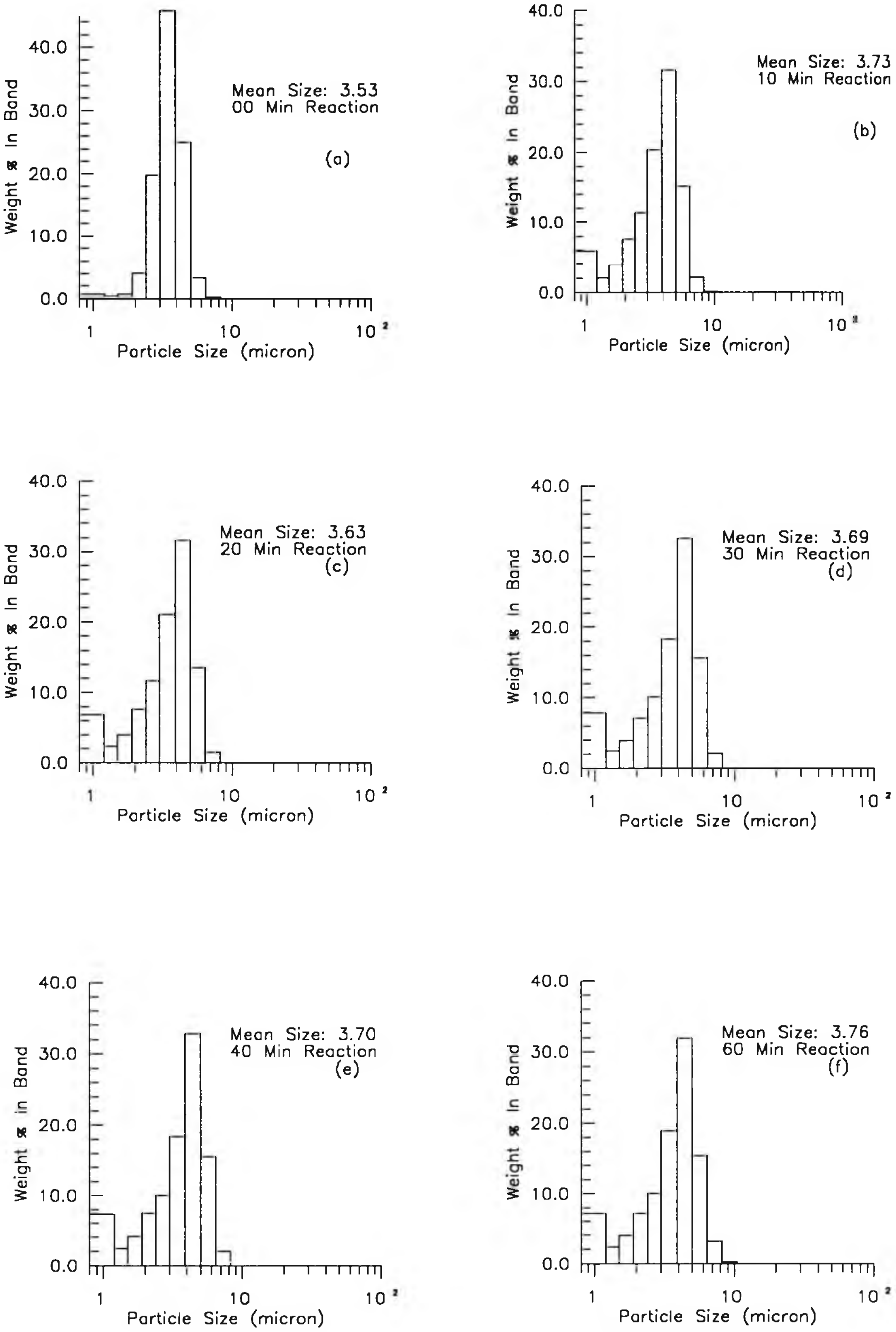


Fig.9.3(a-f) Particle Size Distribution
at Different Reaction Times in Suspension Polymerisation
of EHA with Continuous Homogenisation

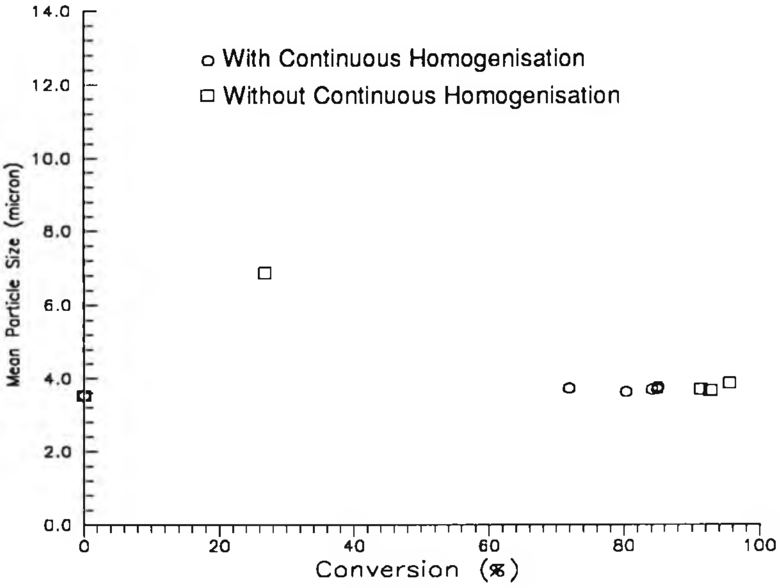


Fig.9.4 Plot of Particle Size against Conversion in Suspension Polymerisations of EHA with and without Continuous Homogenisation

polymerisations with and without continuous homogenisation. For the polymerisation without continuous homogenisation, the mean particle size increased from 3.77 μm at the beginning of the reaction to 6.58 μm at about 25% conversion. It is well accepted that the tendency for particle agglomeration varies at different stages of the polymerisation. The stage of about 25% conversion is referred to as the "tacky" stage when the particles are viscous solutions of polymer in monomer and thus very tacky and easy to agglomerate. In spite of the increased mean particle size due to particle agglomeration, the weight percentage of small monomer/polymer particles (M/P particles) below 1.2 μm increased, as illustrated in Fig.9.2b. There are two possible ways in which the weight percentage of small M/P particles below 1.2 μm increases:

- growth of the existing small M/P particles (which are about 0.8% at the beginning of the reaction as shown in Fig9.2a) by diffusion of EHA monomer from large M/P particles to these small M/P particles, followed by polymerisation in the small particles. At this stage, the sizes of the small M/P particles are still below 1.2 μm.

- formation of new M/P particles (i.e. primary particles) by homogeneous nucleation, followed by growth of the small M/P particles.

The initiator BME has limited solubility in water. However, the presence of PVA in the water phase may enhance the solubility of BME in water. As a result, free-radicals might be generated in the aqueous phase, which could then initiate polymerisation by homogeneous nucleation. On the other hand, the free- radicals generated in monomer droplets and M/P particles might escape to the aqueous phase to initiate polymerisation by homogeneous nucleation.

There is no evidence to support the assumption that some of the small particles were formed by homogeneous nucleation. If homogeneous nucleation occurred, the following emulsion polymerisation in these homogeneously nucleated particles would, in principle, give a fraction of polymer with different molecular weight from the polymer produced in those M/P particles by true suspension polymerisations. The molecular weight distributions of the polymers are discussed in Section Section §9.2.2.3. Nevertheless, it is evident from the changes of the particle size distributions during suspension polymerisations that a significant amount of the EHA monomer did not react in the monomer droplets and the large M/P particles, but diffused to small M/P particles where they polymerised. It seems that during the courses of polymerisations, there is simultaneous polymerisation in monomer droplets (i.e. true suspension polymerisation) and diffusion of monomer to small M/P particles followed by polymerisation in the small M/P particles (i.e. emulsion polymerisation).

In small M/P particles, there is a lower mobility of the monomer. Accordingly, one expects the diffusion of the growing polymer chains to be significantly decreased (Ruckenstein, E. and Kim, K. J., 1988). The bimolecular termination is, therefore, delayed and the rate of polymerisation is increased in the small M/P particles. Moreover, if a primary particle is nucleated in the aqueous phase, chain propagation will start when the first free-radical enters this particle, and bimolecular termination is only possible if a second free-radical enters. This, similar to that in emulsion polymerisation, delays bimolecular termination and thus increases the rate of polymerisation i.e. fast consumption of monomer. The fast consumption of monomer in these small polymer particles was probably responsible for the diffusion of monomer during the suspension polymerisations.

At moderate conversion, M/P particles become sticky and tend to agglomerate, resulting in the increased overall mean particle size (see Fig.9.2b). Further polymerisation leads to more diffusion of EHA monomer from large M/P particles to small ones, and this could account for the decreased mean particle size by further polymerisation (see Fig.9.2b-c). Moreover, the decreased mean particle size may be partially caused by the shrinkage of M/P particles as polymerisation proceeds. The mean particle size tends to become level at high conversion when almost all of the monomer has polymerised and there is little monomer in the reaction system for further polymerisation (see Fig9.2e-f and Fig.9.4).

At the beginning of the polymerisation with continuous homogenisation there is an increase in the weight percentage of small M/P particles, similar to the suspension polymerisation of EHA without continuous homogenisation(see Fig9.3a-f). There is also an increase in the overall mean particle size at the beginning of polymerisation. From Fig.9.4, one can see that there is little difference in the mean particle sizes at high conversions of polymerisations with and without continuous homogenisation. A comparison between Fig.9.3(a-f) with Fig.9.2(a-f) shows that the amount of particles above 6.5 μm is higher for the suspension polymerisation without continuous homogenisation. These oversized particles present after 60 minutes of reaction are responsible for the slightly higher mean particle size of the polymer suspension produced without continuous homogenisation. It seems that the continuously applied ultrasonic homogenisation partially suppressed the polymer particle agglomeration at low conversion, resulting in a reduced number of oversized polymer particles in the final polymer latex. The speed of polymerisation was very fast, resulting in a rapid increase in the viscosity of the M/P particles, and thus the break-up of large polymer particles cannot be achieved by the continuously applied ultrasonic homogenisation at high conversion. Consequently, there was no significant decrease in the mean particle size during further polymerisation at high conversion. The observed slight decrease in the mean particle size at high conversion in the polymerisation with continuous homogenisation is probably due to shrinkage of M/P particles as polymerisation proceeds.

Fig.9.5(a-b) shows the SEM photographs of the final polymer suspensions obtained. It can be seen that the polymer particles are in the range of 0.5-10 μm for suspension polymerisations with and without continuous homogenisation. There are less oversized polymer particles in the polymer suspensions produced both with and without continuous homogenisation. It can also be seen from the SEM photographs that the small particles are more spherical than the large particles, and most of the large particles are likely to contain small particles. Thus it is evident from the SEM photographs and the particle size distributions that particle agglomeration can account for the formation of oversized polymer particles especially during the early stages of suspension polymerisation.

9.2.2.3 Molecular Weight Distributions

Fig.9.6 illustrates the molecular weight distributions of poly(2-ethylhexyl acrylate) produced by suspension polymerisation with and without continuous homogenisation. It shows clearly that the average molecular weight is lower for the polymer produced with continuous homogenisation. As discussed

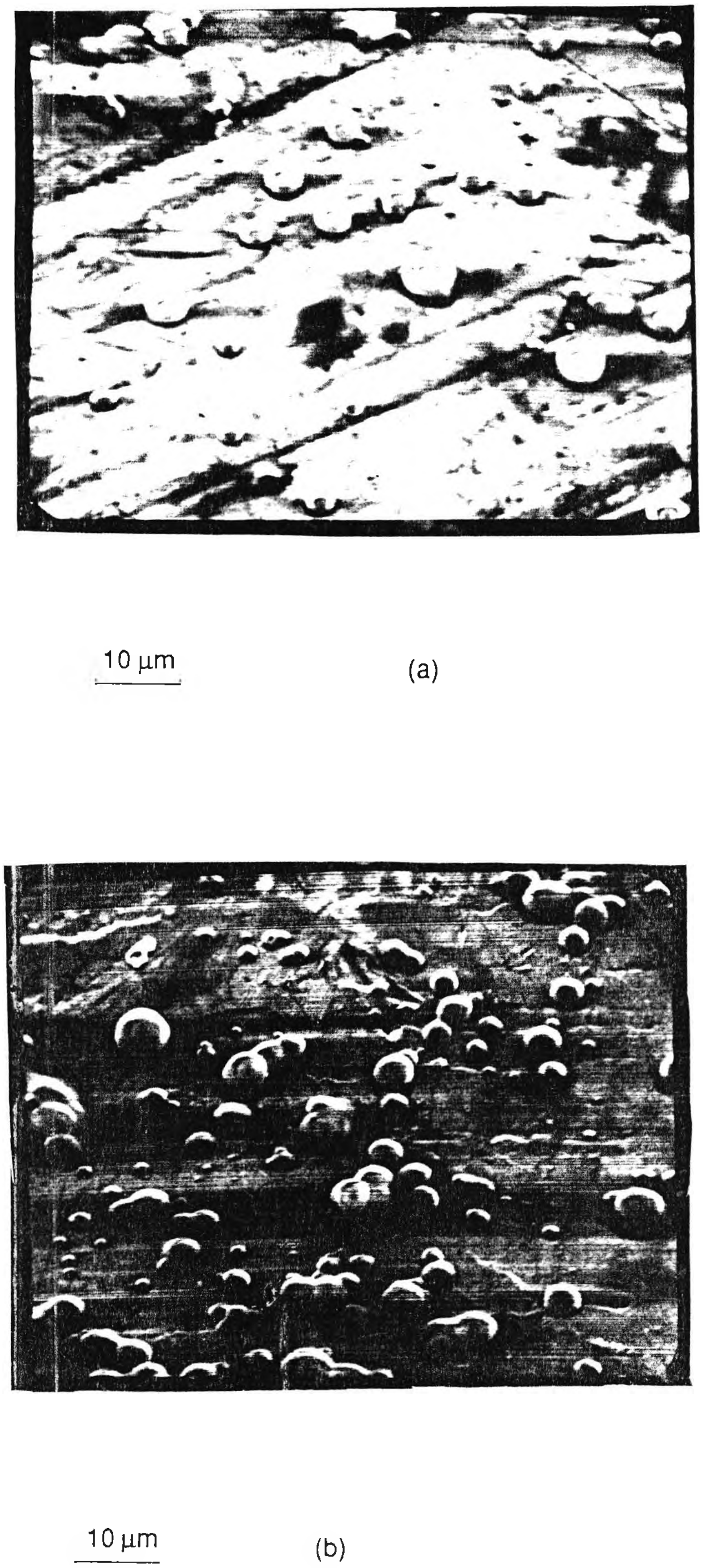


Fig.9.5(a-b) SEM Photographs of Polymer Suspensions by Suspension Polymerisations of EHA (a) with Continuous Homogenisation; (b) without Continuous Homogenisation

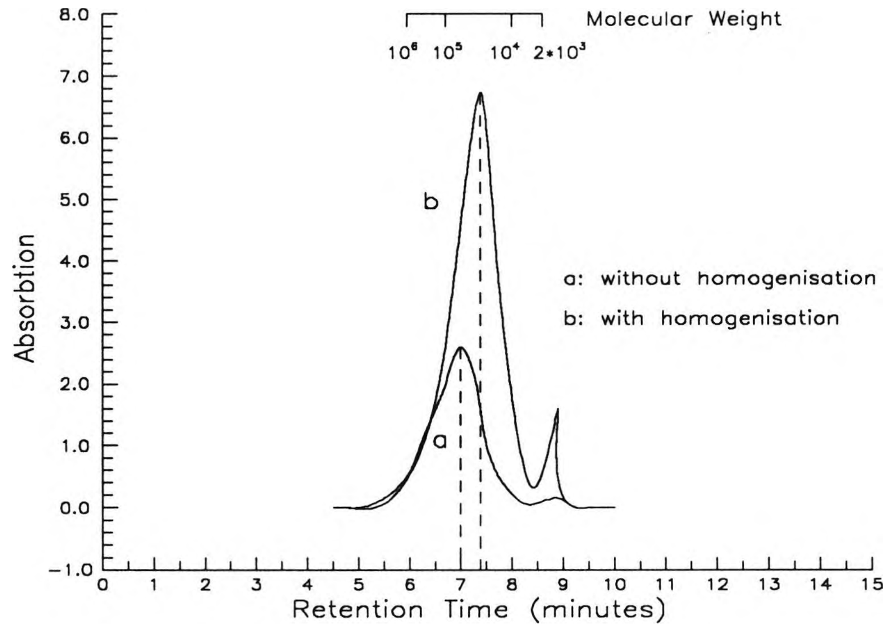


Fig.9.6 GPC Traces of Polymers Produced by Suspension Polymerisations

previously in Section §9.2.2.1, the rate of polymerisation at the early stage of the reaction is higher when continuous homogenisation is employed. The conversion in the first 10 minutes of reaction is 75%, which is three times the value that without continuous homogenisation. During suspension polymerisation under continuous homogenisation, the reaction mixture was continuously circulated within the reactor. This ensured good mixing and good exposure of reactants to the UV- irradiation. Thus more free-radicals can be generated per unit time per unit volume of reaction mixture during continuous homogenisation. The high rate of polymerisation under continuous homogenisation is most likely a result of the fast rate of free-radical generation in the monomer droplets and M/P particles.

In a monomer droplet, if more free-radicals and growing polymer chains are present there will be more possibilities for bimolecular termination. As a result, the kinetic chain length and the molecular weights of the polymer molecules will be reduced in suspension polymerisation at high rate of polymerisation. The low molecular weight of the polymer obtained when using continuous homogenisation is probably associated with the high rate of polymerisation and is unlikely to be due to ultrasonic degradation because the viscosity inside the M/P particle is too high to form cavitation bubbles (Mason, T.J. and Lorimer, J.P. 1988) even at low conversion.

GPC traces in Fig.9.6 are characterised by one large peak near 7 minutes elution time (corresponding to a molecular weight of the order of 10^4 to 10^5order) and a small peak near 8.9 minutes elution time (corresponding to a molecular weight of the order of 10^3 order). The small peaks represent small molecular weight oligomers. In such suspension polymerisations, fragmentation of an initiator BME molecule gives two free-radicals i.e. the benzoyl radical and the benzylic radical. The free-radical pair must diffuse apart from each other to avoid recombination. If this diffusion is not fast, there will be bimolecular termination of the growing oligomeric radical by the unreactive benzylic radical. The benzylic radicals act as a terminator during polymerisation. The bimolecular terminations of growing oligomeric radicals by the unreactive benzylic radical are probably responsible for the formation of most of the oligomers during suspension polymerisation.

As discussed previously in Section §9.2.2.2, there were possibly two reaction processes, namely suspension polymerisation and emulsion polymerisation in such reaction systems and, in principle, the emulsion polymerisation would give a fraction of polymer with different molecular weight compared with the polymer produced by true suspension polymerisation. However, there is only one large peak in the GPC trace for both suspension polymerisation with and without continuous homogenisation. It may be the case that the two polymerisation processes i.e. suspension polymerisation and emulsion polymerisation give polymers of identical molecular mass. In Chapter 10, the molecular weight distributions of some emulsion polymerisations will be discussed, and a comparison of the molecular weight can be made for emulsion polymerisations and suspension polymerisations

9.2.3 Suspension Copolymerisations of EHA and VA

Experimental details of the UV-induced suspension copolymerisations of EHA and VA using different monomer feed ratios have been described in Section §6.5.1.3. The method used is emulsification of the monomer/water mixtures followed by UV-irradiation under continuous homogenisation. The EHA/VA ratio was varied but the time of UV-irradiation was 15 minutes for all experiments. The conversions and the copolymer compositions were determined using ^{1}H n.m.r. (see Fig.9.7 for the spectra) and they are listed in Table 9.2. It can be seen from Table 9.2 that when more VA is used, the polymerisation rate is reduced. All resultant copolymers contain more EHA units then VA units, showing that VA is not easy to copolymerize with EHA in these systems. The shelf lives of these copolymer suspensions are shorter than that of the homopolymer suspension of EHA produced under similar

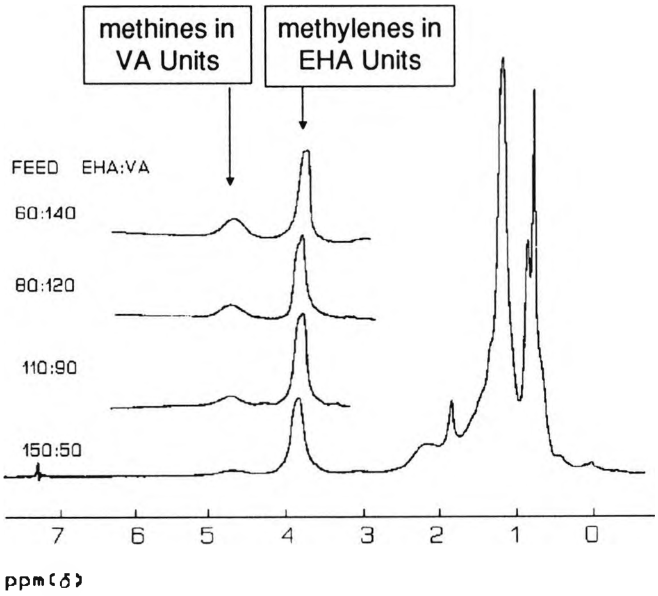


Fig.9.7 NMR Spectra of Copolymers
by UV-Induced Suspension Copolymerisation of EHA and VA in the Whistle Reactor

conditions (see Table 9.1). As can be seen from Table 9.2, the shelf life and stability of the suspension latex increases with increasing conversion of monomers to polymer. If the conversion is low, more residual monomers will be retained in polymer particles, and as a result the polymer particles will be soft and tacky i.e easy to agglomerate. This is probably responsible for the decreased shelf life and stability of the suspension copolymer latex of EHA and VA. It should also be noted that in such EHA and EHA/VA suspensions, the density difference between M/P particle and water decreases with increasing conversion of monomers to polymer. The smaller the density difference between M/P particle and water, the less the tendency for accumulation of M/P particles in the upper part of the storage vessels, and the more stable the suspension i.e. the stability increases with increase in conversion.

Table 9.2 Properties of Polymer Latexes Produced by Suspension Copolymerisations of EHA and VA Using different Monomer Ratios

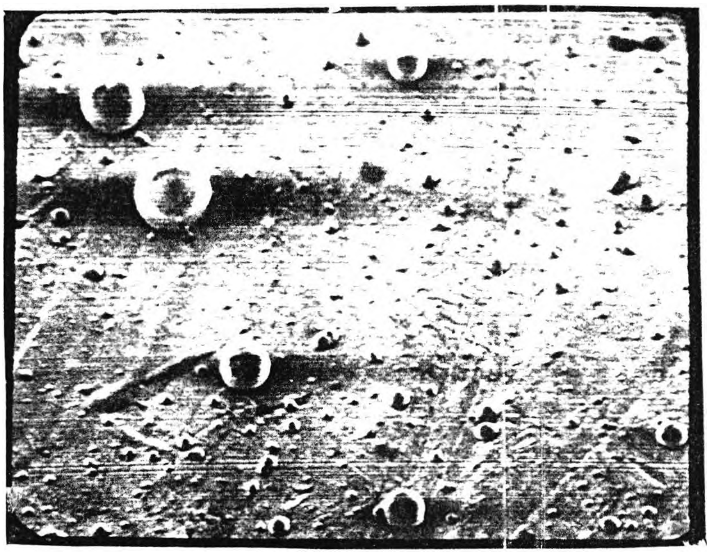
Monomer Feed (g)		Conversion After 15 Minutes Reaction	wt.% of EHA in Copolymers	Shelf Life (months)
EHA	VA			
60	140	37.0	75.8	≈ 0.5
80	120	35.8	81.5	≈ 0.5
110	90	53.5	85.0	≈ 1
150	50	72.5	90.6	≈ 1

9.2.4 Experimental Results with Other Monomers

The experimental details for the UV-induced suspension polymerisations of n-butyl acrylate (BA), methyl methacrylate (MMA), n-butyl methacrylate (BMA), isobornyl acrylate (IBA) and styrene, and the suspension copolymerisations of EHA and VA, EHA and acrylic acid (AA), EHA and ethylene glycol dimethacrylate (EGDMA), and isobornyl acrylate and vinyl acetate have been described in Section §6.5.1.4. The procedure adopted was also emulsification of the monomer/water mixtures followed by UV-irradiation under continuous homogenisation. During the suspension polymerisation of MMA and the suspension polymerisation of styrene, the polymerisation system gelled after 30 minutes of UV-irradiation. This is probably due to the rapid exothermic reaction of MMA. Other monomers polymerised smoothly to high conversion without phase separation or gellation. The results with these monomers are listed in Table 9.3. For polymer suspensions of n-butyl acrylate and 2-ethylhexyl acrylate-co-vinyl acetate, the shelf lives are 3 months. The shelf lives of the polymer suspensions of other monomers are only 1 or 2 weeks. For these polymer suspensions, the phase separation is likely as a result of the density difference between the polymer and the water phase. For additional information, the SEM photographs of these polymer suspensions are shown in Fig.9.8—Fig9.13. The SEM photographs show that these polymer suspensions are stable and that the majority of the polymer particles retain a single identity after the polymerisation.

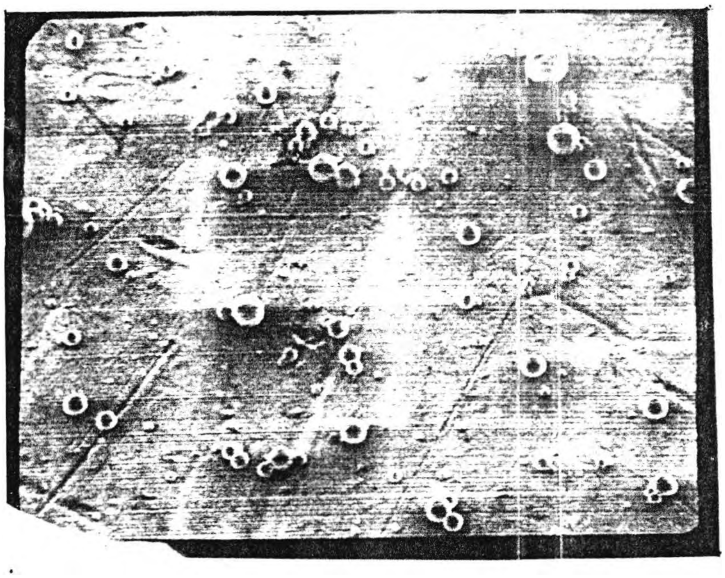
Table 9.3 Properties of Polymer Latexes Produced by Suspension Polymerisations with Different Monomers (*estimated from SEM)

Monomer	Co- monomer	Reaction Time (minutes)	Conversion (%)	Mean Particle Size (μm)	Shelf Life (months)	wt.% of VA in Copolymer
n-Butyl acrylate		30	72.5	5.91	3	
n-Butyl methacrylate		60	32	4*	2	
Isobornyl acrylate		20	89.4	3*	0.25	
Isobornyl acrylate	Vinyl acetate	40	49.3		0.5	21.8
2-Ethylhexyl acrylate	Vinyl acetate	120	75		3	21.1
2-Ethylhexyl acrylate	Ethylene glycol dimethyl acrylate	120	100	8*	0.25	
2-Ethylhexyl Acrylate	Acrylic Acid	120	80	7*	0.25	



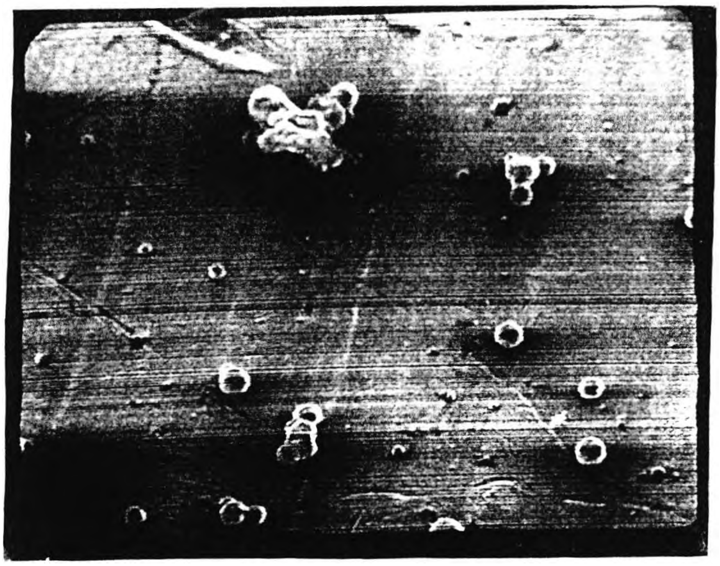
10 μm

Fig.9.8 SEM Photograph of Polymer Latex Produced by Suspension Polymerisation of Butyl Acrylate



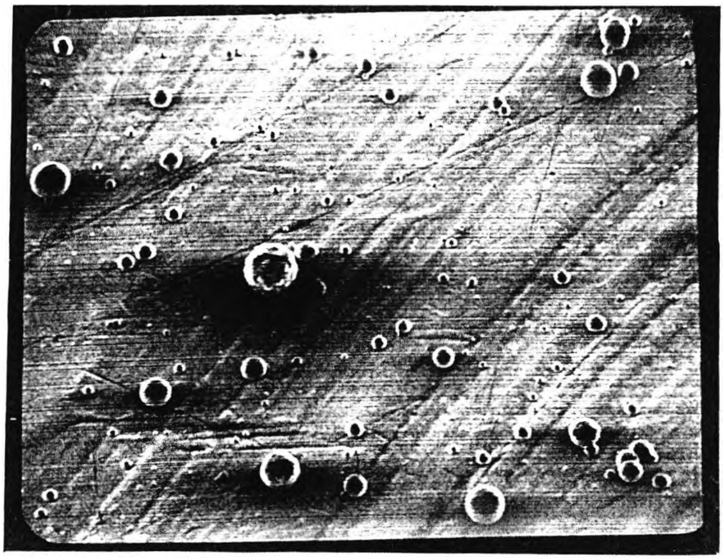
10 μm

Fig.9.9 SEM Photograph of Polymer Latex Produced by Suspension Polymerisation of Isobornyl Acrylate



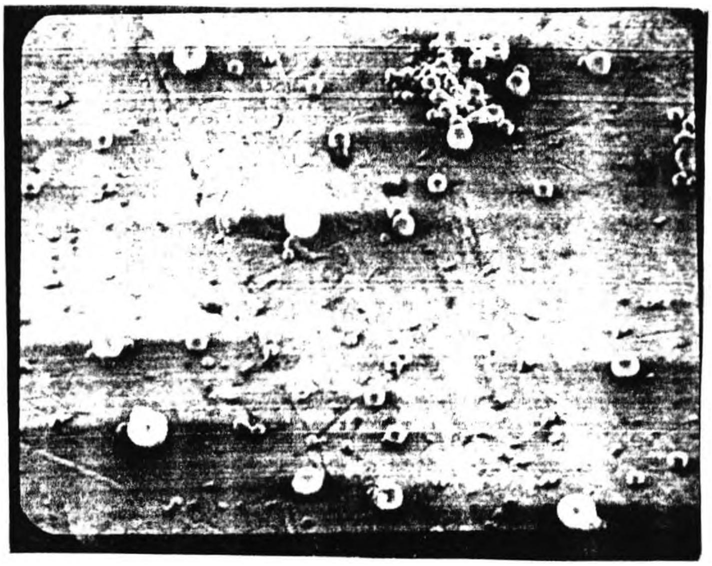
10 μm

Fig.9.10 SEM Photograph of Polymer Latex Produced by Suspension Polymerisation of Butyl Methacrylate



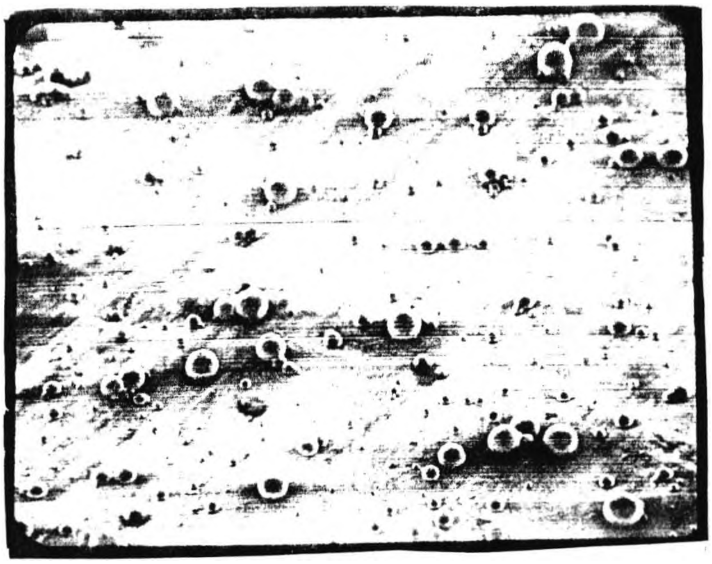
20 μm

Fig.9.11 SEM Photograph of Polymer Latex Produced by Suspension Copolymerisation of EHA and EGDMA



10 μm

Fig.9.12 SEM Photograph of Polymer Latex Produced by Suspension Copolymerisation of Isobornyl Acrylate and Vinyl Acetate



20 μm

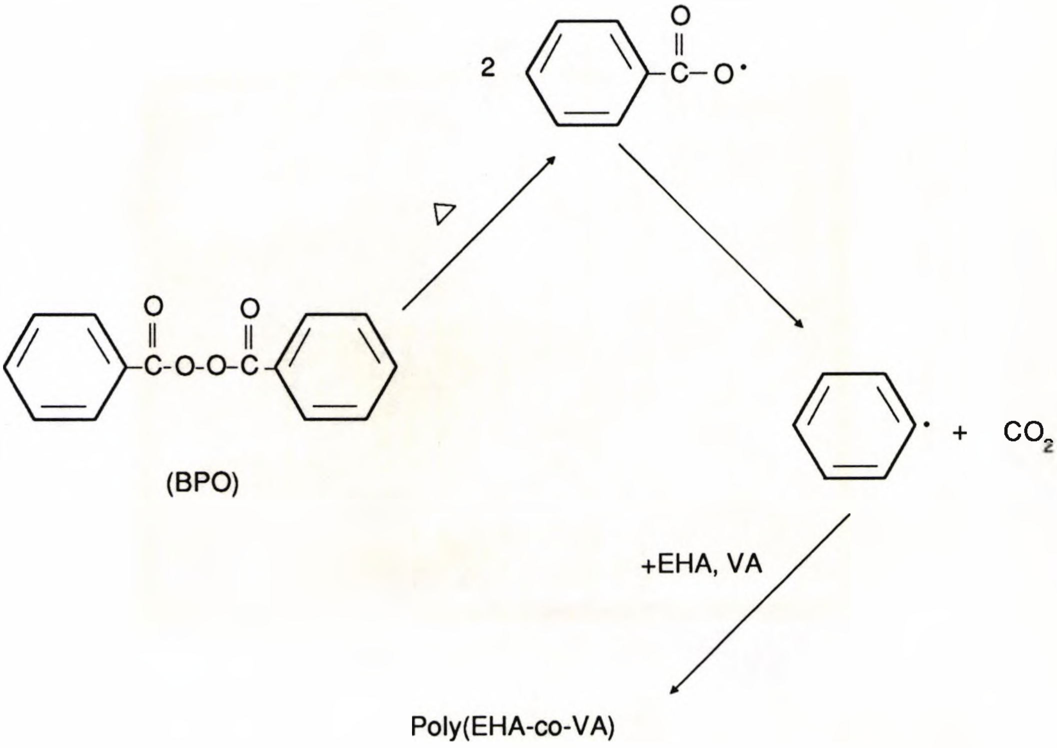
Fig.9.13 SEM Photograph of Polymer Latex Produced by Suspension Copolymerisation of EHA and Acrylic Acid

9.3 Thermal Polymerisation

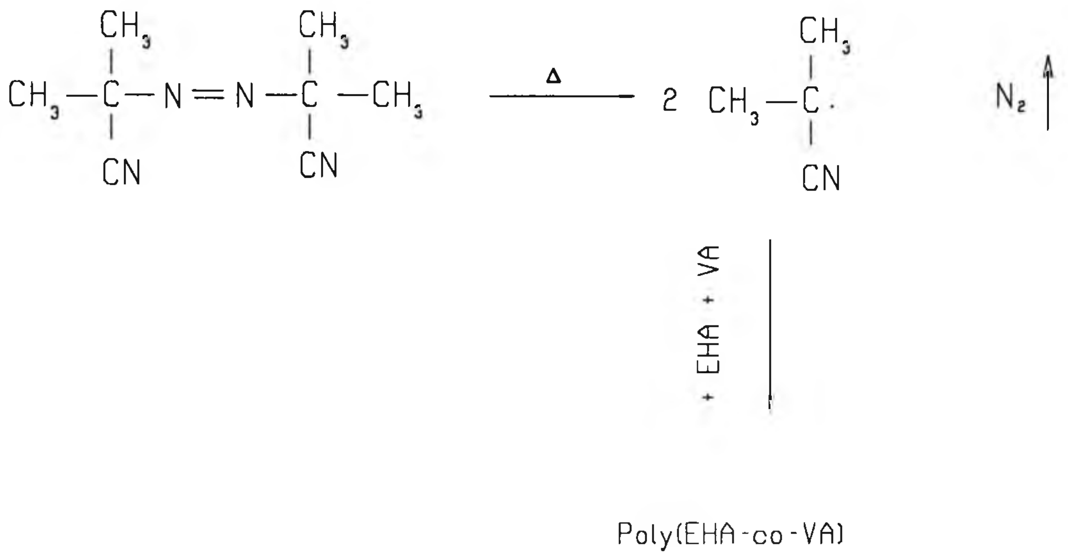
The experimental details for the thermal suspension copolymerisations of EHA and VA using (i) BPO and (ii) AIBN as the initiator have been described in Section §6.5.2. BPO and AIBN are commonly used free-radical initiators which undergo decomposition at elevated temperature (as shown in Schemes 9.2 and 9.3).

9.3.1 BPO as Initiator

The suspension copolymerisation of pre-emulsified EHA/VA in water was initiated by BPO in a conventional batch reactor under mechanical stirring. Using the same polymerisation mixture, comparative polymerisation was

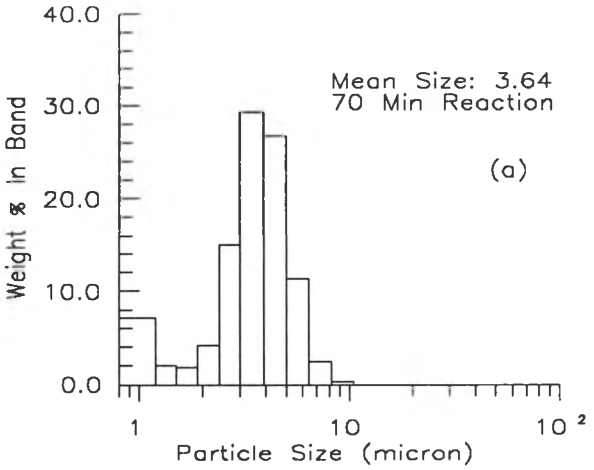


Scheme 9.2 The Initiation of Copolymerisation of EHA and VA by Benzoyl Peroxide



Scheme 9.3 The Initiation of Copolymerisation of EHA and VA by α,α'-Azoisobutyronitrile

carried out in the whistle reactor under continuous homogenisation. Fig.9.14(a-b) represents the particle size distributions of copolymer suspensions produced. In the conventional reactor, a polymerisation product with 58.9% yield and a mean particle size of 3.64 µm was obtained, compared with 41.1% yield and 2.06 µm mean particle size for suspension polymerisation in the whistle reactor. These two comparative experiments show that the continuously applied homogenisation reduced the mean particle size. However, the yield is less for the polymerisation in the whistle reactor. This is probably due to variation of the polymerisation conditions in these two experiments such as nitrogen atmosphere flow rates and amount of oxygen



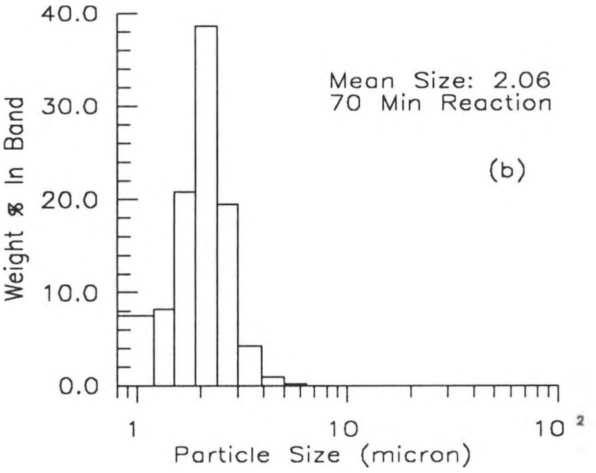
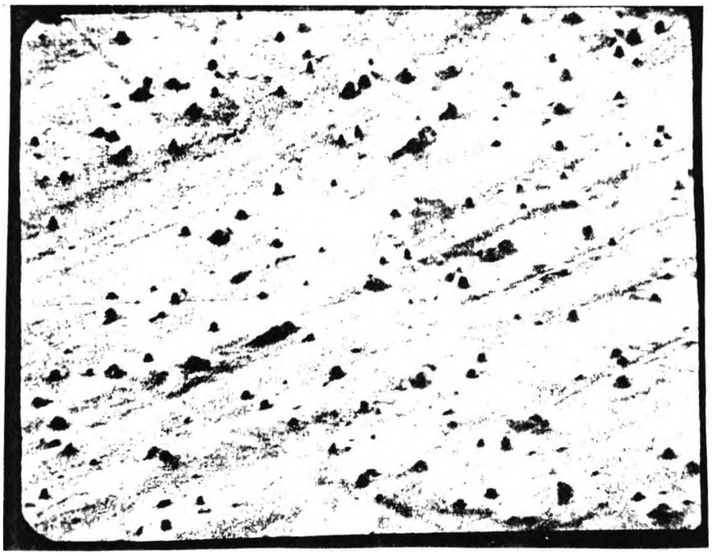


Fig.9.14(a-b) Particle Size Distributions of Polymer Latexes Produced by Suspension Copolymerisation in a) a Conventional Batch Reactor b) the Whistle Reactor

inside the reaction systems. Fig.9.15 and Fig.9.16 are the SEM photographs of the copolymer suspensions obtained.

10 μm

Fig.9.15 SEM Photograph of Polymer Latex Produced
by Suspension Copolymerisation of EHA and VA in a Conventional Batch Reactor



10 μm

Fig.9.16 SEM Photograph of Polymer Latex Produced
by Suspension Copolymerisation of EHA and VA in the Whistle Reactor

9.3.2 AIBN as Initiator

The suspension copolymerisations of EHA/VA in water were initiated by AIBN in the whistle reactor where the mixtures were subjected to continuously applied homogenisation. Fig.9-17(a-b) represents the particle size distributions of copolymer suspensions produced with different levels of

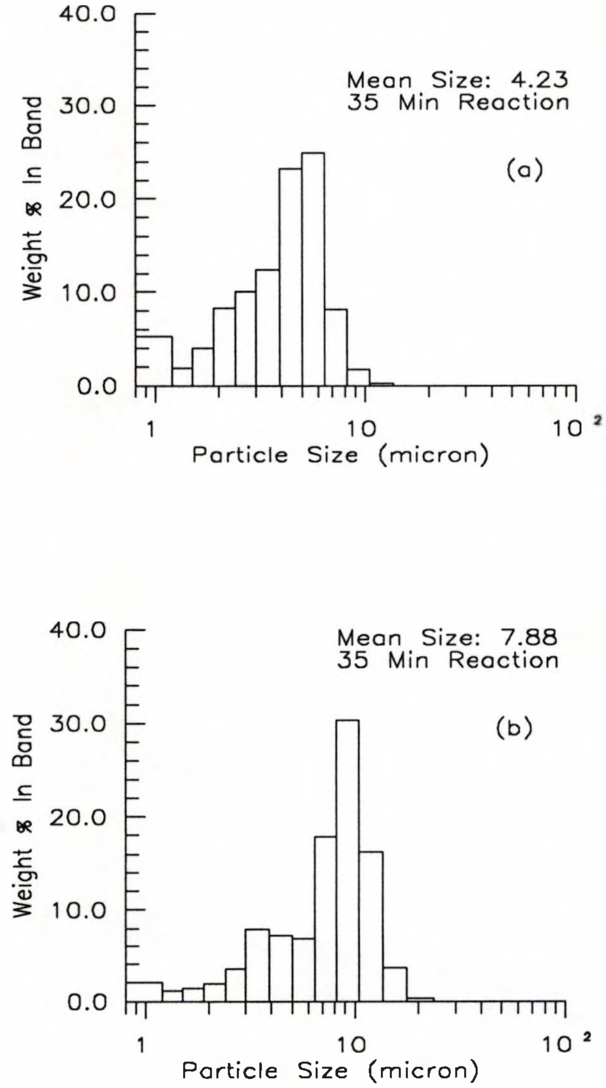


Fig.9.17(a-b) Particle Size Distributions of Polymer
Latexes Produced by Suspension Copolymerisation of EHA and VA:
a) using 3% PVA; b) using 1.5% PVA Based on the Weight of Monomer

PVA in the water phase. Fig.9.18 and Fig.9.19 are the SEMs of the copolymer suspensions obtained. A stable polymer suspension with 92.0% yield and a mean particle size of 4.23 μm was obtained after 35 minutes of reaction when 3% PVA based on the weight of monomer was used. Comparative reaction with 1.5% of PVA based on the weight of monomer mixture as protective colloid gave a copolymer suspension with 71.0% yield and a mean particle size of 7.88 μm, as summarised in Table 9.4. Clearly, a decrease in the level of PVA results in decreased rate of polymerisation and increased mean particle size. High conversion of monomers to polymer was obtained using AIBN as the initiator and it seems that AIBN is more efficient in initiating the suspension copolymerisation of EHA and VA than BPO.

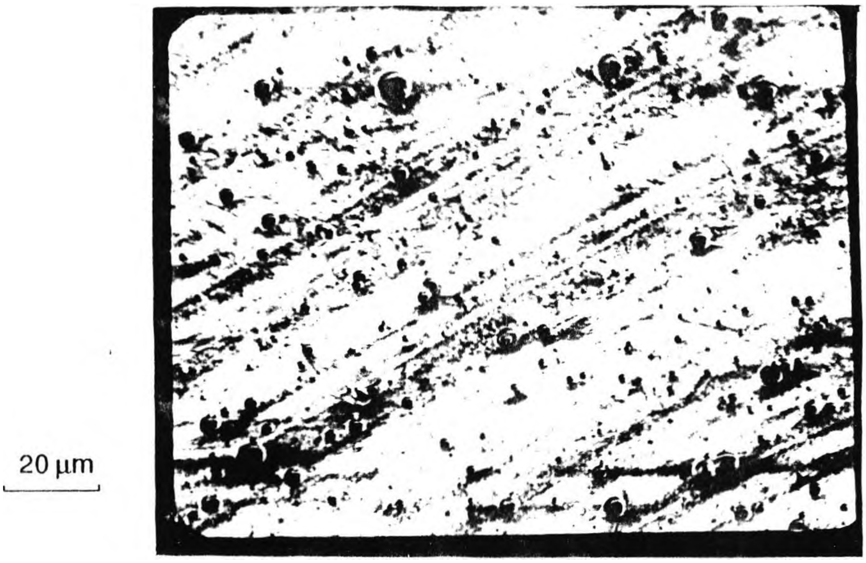


Fig.9.18 SEM Photograph of Polymer Latex Produced
by Suspension Copolymerisation of EHA and VA using 3% PVA
Based on the Weight of Monomer

20 μm

Fig.9.19 SEM Photograph of Polymer Latex Produced by Suspension Copolymerisation of EHA and VA using 1.5% PVA Based on the Weight of Monomer

Table 9.4 Properties of Polymer Suspensions Obtained using Different Levels of PVA

PVA Level (%)	Yield (%)	Mean Particle Size (μm)
3	92	4.23
1.5	71	7.88#

9.4 Summary

The work described in this chapter has shown that:

- Stable polymer latexes can be produced by suspension polymerisation in the whistle reactor.
- For both UV-induced and thermally initiated suspension polymerisation systems in the present work, it seems that the particle nucleation takes place not only in monomer droplets but also in the true aqueous phase.
- The polymer suspensions produced in the whistle reactor with continuous homogenisation have a slightly smaller mean particle size than those produced by suspension polymerisation without continuous homogenisation. This is due to the decreased number of oversized polymer particles as a result of the breakup of particle agglomerates by ultrasonic homogenisation.
- The average molecular weight is lower for the polymer produced with continuous homogenisation. This is most likely due to fast generation of free-radicals in the monomer droplets.
- VA is reluctant to copolymerize with acrylate in the suspension copolymerisation. The shelf life of the polymer suspension is reduced as a result of the incorporation of VA comonomer and this is probably due to the presence of unreacted monomers in the polymer particles.
- AIBN is more efficient in initiating the suspension copolymerisation of EHA and VA than BPO.
- Increasing the level of PVA favours the production of a small particle size polymer suspension.

- In some cases, the mixing of oxygen in the monomer mixture by ultrasonic cavitation may increase the induction period in the thermal suspension polymerisation. However, the rate of UV-induced suspension polymerisation of EHA was increased as a result of the applied ultrasonic homogenisation due to the better exposure of the reactant to the UV-irradiation.

Chapter 10

Emulsion Polymerisation in the Whistle Reactor

10.1 Introduction

Partially hydrolysed polyvinyl acetate, namely polyvinyl alcohol (PVA) is one of the commonly used emulsion stabilisers. For stabilisation of an emulsion system, about 5% of PVA based on the weight of aqueous phase is usually used in emulsion polymerisation. It has been a common practice to use PVA in conjunction with other cationic and anionic emulsifiers for the best stabilisation of the emulsion polymerisation systems. If only PVA, a mild emulsion stabiliser, is present in a polymerisation system, polymer particle agglomeration will become significant especially when polymer particles become sticky or the shearing force due to mixing is not enough, or the PVA concentration is too low. Particle agglomeration can result in the broadening of the particle size distribution and the formation of oversized polymer particles and the gellation of the reaction system in the extreme case. This chapter describes emulsion polymerisations of EHA and emulsion copolymerisations of EHA and VA in the presence of about 1% of PVA based on the weight of aqueous phase, carried out in the whistle reactor under continuous ultrasonic homogenisation. It was hoped that the continuously applied ultrasonic homogenisation would prevent polymer particle agglomeration. Three initiating methods i.e. UV–initiation, thermal initiation and redox–initiation were used for the emulsion polymerisation in the whistle reactor and they are described separately in Section §10.2, Section §10.3 and Section §10.4.

10.2 UV–Induced Emulsion Polymerisation

10.2.1 Introduction

The procedure adopted for the UV–induced emulsion polymerisation was similar to that for the UV–induced suspension polymerisation which has been already discussed in Section §9.2. The difference was that water–soluble Type II photoinitiators are used instead of BME. Typical initiator/co–initiator used in the present work was WB4698/N–methyldiethanolamine which undergoes H–abstraction upon UV–irradiation (see Scheme 10.1).

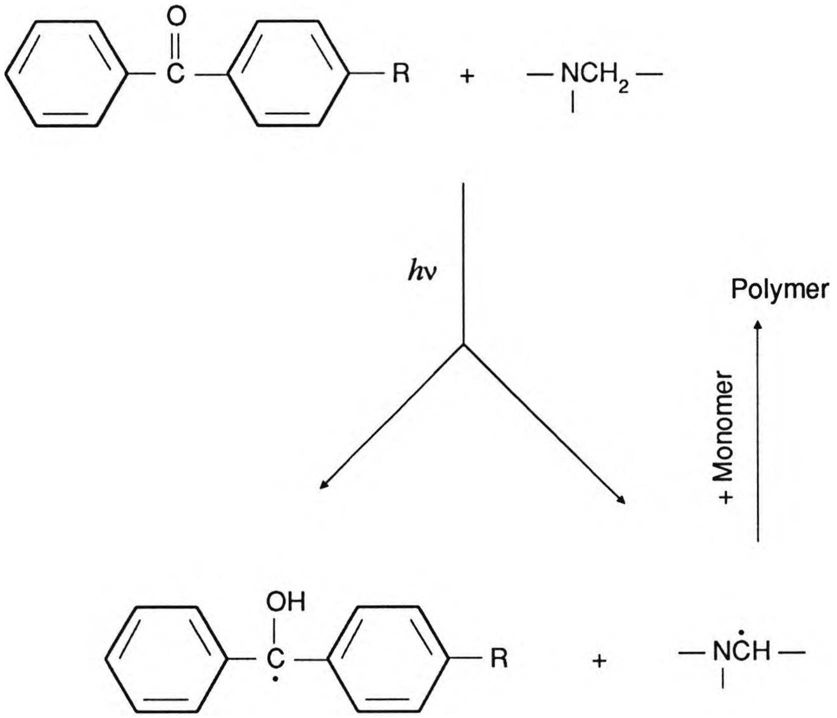
10.2.2 Emulsion Polymerisations of EHA with and without Continuous Homogenisation

The experimental details for the emulsion polymerisations of EHA with and without continuous homogenisation have been described in Section §6.6.1.2 and Section §6.6.1.1, respectively.

Two different methods have been used for the UV–induced emulsion polymerisations of EHA:

- emulsification of the monomer with water through the homogeniser followed by polymerisation of the pre–emulsified EHA without continuously applied ultrasonic homogenisation,

and



R = $CH_2SO_3^-$ for WB4698

R = $CH_2N^+(CH_3)_3$ for BTC

R = $CH_2N^+(CH_3)_2(CH_2)_2OCOCH{=}\,CH_2$ for ABQ

Scheme 10.1 Initiation of Emulsion Polymerisation.

- emulsification of the monomer with water through the homogeniser followed by polymerisation of the monomer emulsion under continuously applied ultrasonic homogenisation.

The properties of the polymer suspension produced with and without continuous homogenisation are compared in Table 10.1.

Table 10.1 Properties of Polymer Emulsions Produced with and without Continuous Homogenisation (see §6.6.1.1 and §6.6.1.2 for details of the reaction systems)

Properties	with Continuous Homogenisation	without Continuous Homogenisation
Solid Content (%)	21.0	10.6
Mean Particle Size (μm)	2.09	8.52
Shelf Life (months)	≈ 6	unstable

10.2.2.1 Rates of Polymerisations

Fig.10.1 shows the plots of conversion against reaction time for the emulsion polymerisations of EHA with and without continuously applied ultrasonic homogenisation. As shown in this figure, 52% conversion was obtained after 40 minutes of UV–irradiation in the emulsion polymerisation under continuous homogenisation, compared with about 12% conversion for the polymerisation without continuously applied ultrasonic homogenisation. Similarly to that of the suspension polymerisations described in Chapter 9, the rate of polymerisation was increased by using continuous ultrasonic homogenisation. It is well known that the rate of emulsion polymerisation is proportional to the concentration of the monomer/polymer (M/P) particles ($[N]$) which serve as the locus for the initiation and chain propagation. It is also well known that the concentration of the M/P particle ($[N]$) in emulsion polymerisation depends on the concentration of emulsifier (or surfactant) and the concentration of initiator. Under continuous circulation through the

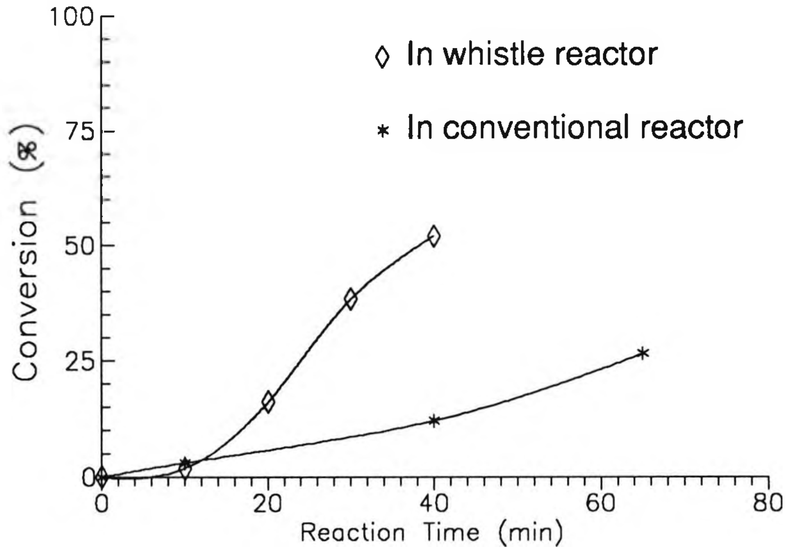


Fig.10.1 Plots of Conversion against Time
in Emulsion Polymerisation of EHA with and without Continuous Homogenisation

homogeniser, the reaction mixture had better exposure to the UV–irradiation. Thus the number of photons absorbed by the initiator per unit time per unit volume was increased. Consequently, more M/P particles are formed when using continuous homogenisation. The continuously applied homogenisation has probably played an important role in preventing particle agglomeration and in maintaining a high concentration of M/P particles. Indeed, the rate of emulsion polymerisation was accelerated as a result of continuously applied ultrasonic homogenisation. Yet there are difficulties in understanding the mechanism by which the rate of polymerisation was increased until the particle size distributions of the polymer emulsions and the molecular weight distributions of the resultant polymers have been examined (see the following section).

10.2.2.2 Changes of Particle Size Distributions During Polymerisation

Fig.10.3(a–e) and Fig.10.2(a–f) show the particle size distributions and mean particle sizes of samples at different reaction times for the emulsion

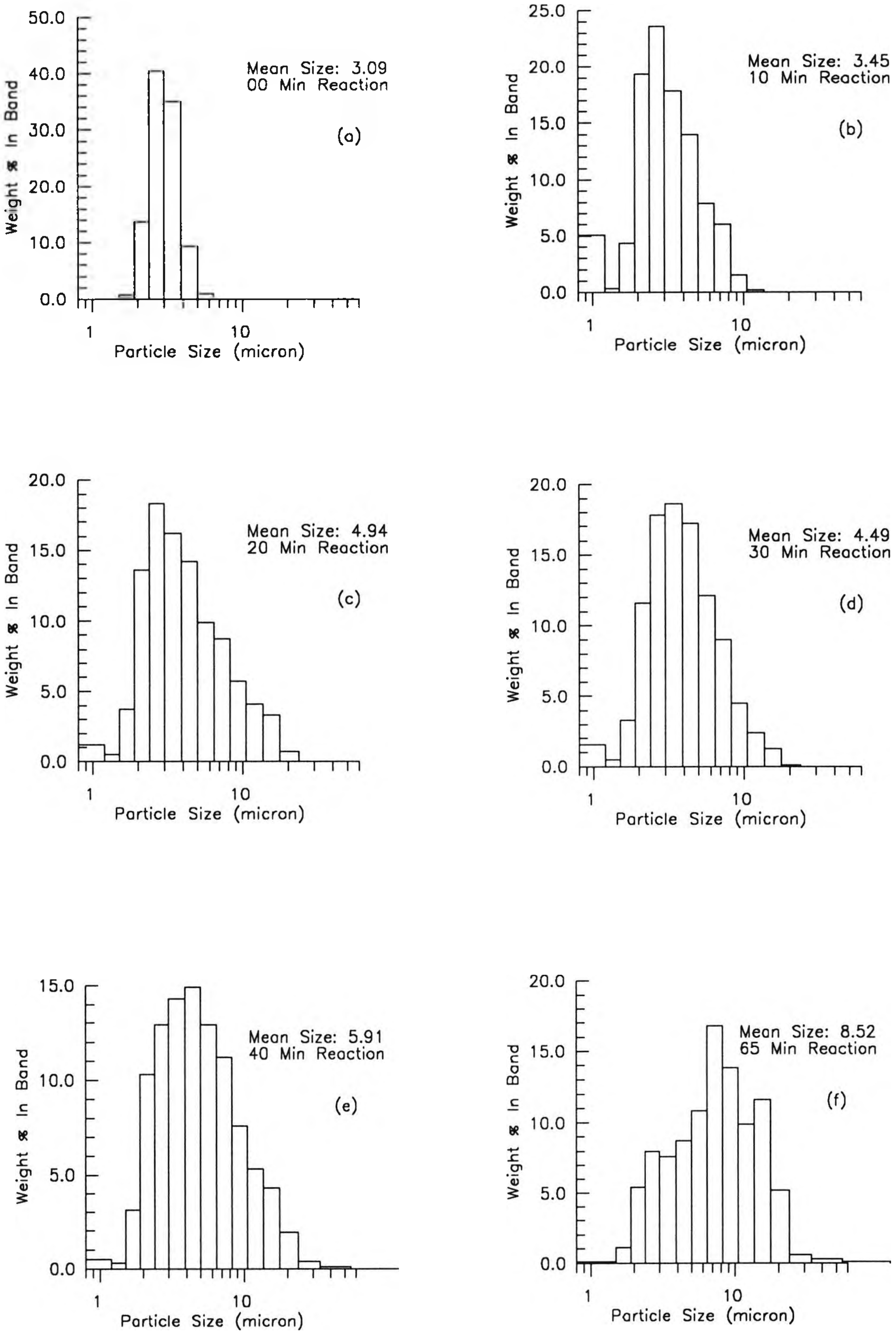


Fig.10.2(a-f) Particle Size Distribution
at Different Reaction Times in Emulsion Polymerisation of Pre-emulsified EHA

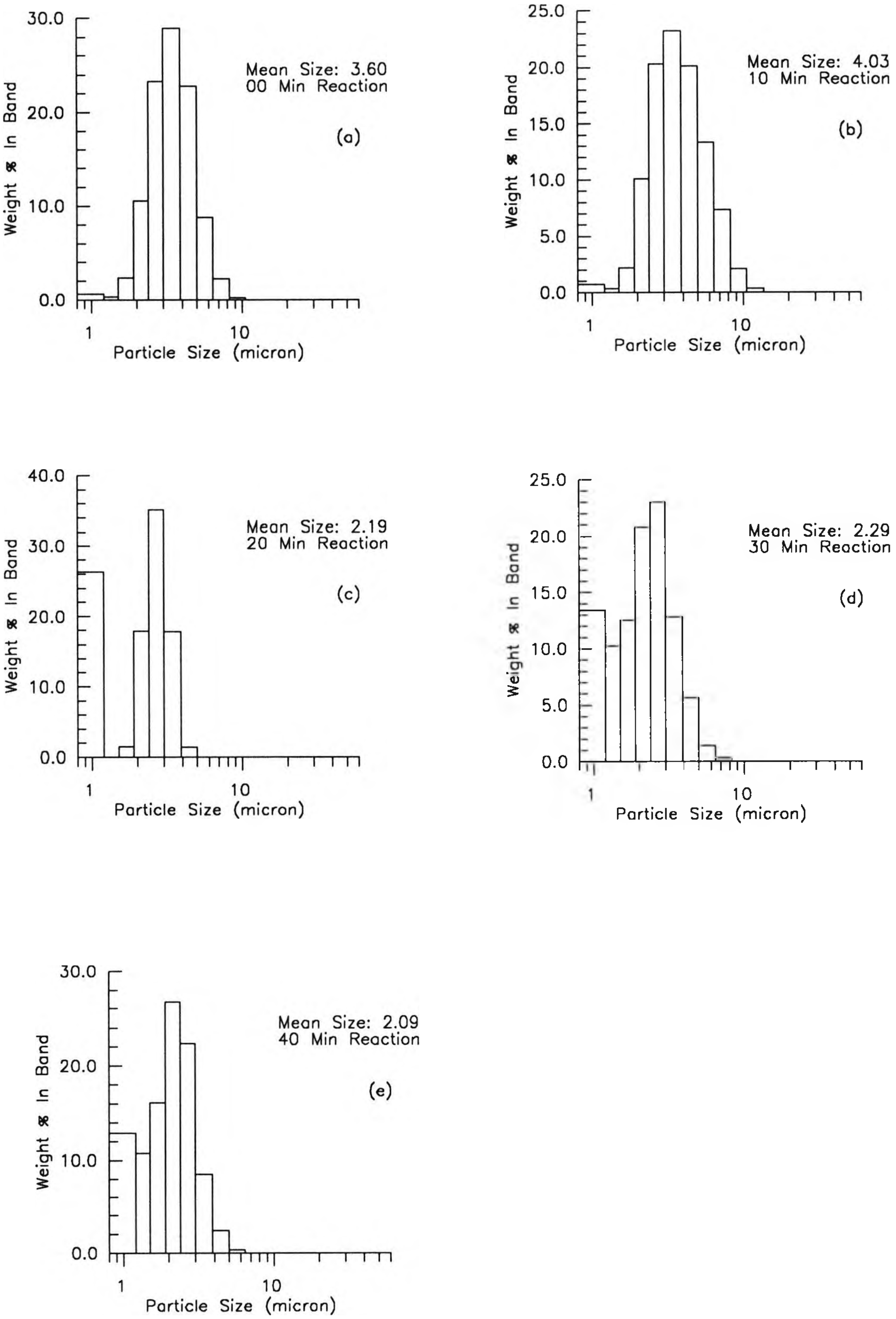


Fig.10.3(a-e) Particle Size Distribution
at Different Reaction Times in Emulsion Polymerisation of EHA under Continuous Homogenisation

polymerisation of EHA with and without continuously applied ultrasonic homogenisation, respectively. Fig10.4 shows the mean particle sizes at different times of polymerisation with and without continuous homogenisation.

Small M/P particles below 1.2 μm appeared at the beginning of polymerisation both with and without continuous homogenisation, indicating that there are particle nucleations in the aqueous phase i.e homogeneous particle nucleation.

For emulsion polymerisation without continuously applied ultrasonic homogenisation, the overall mean particle size increased from 3.09 μm to 3.45 μm during the first 10 minutes of reaction, in spite of small polymer particles formation at the beginning of the polymerisation. After 20 minutes of polymerisation, the mean particle size further increased to 4.94 μm (see Fig.10.2a–c). Particle agglomeration was responsible for the increase in mean particle size.

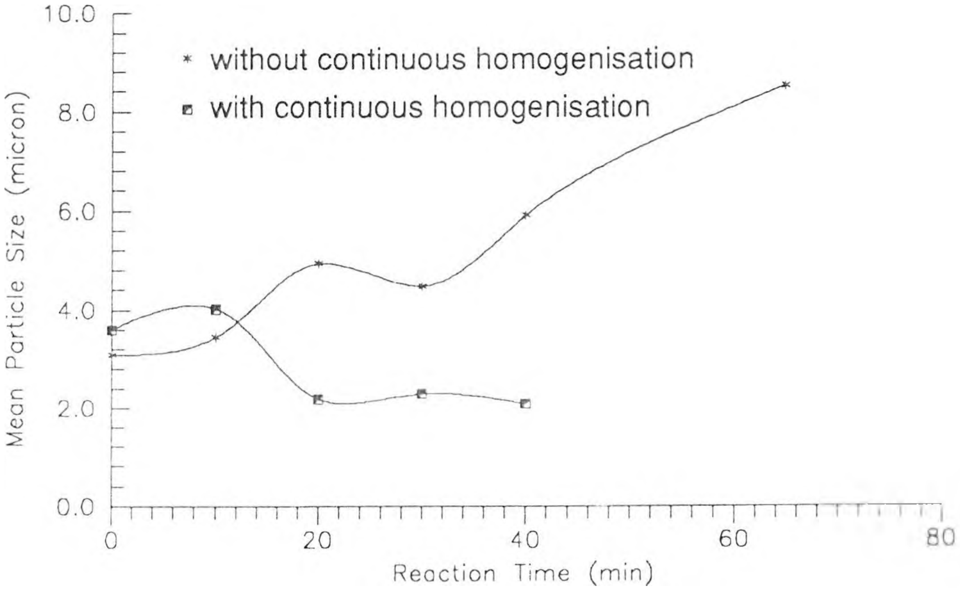


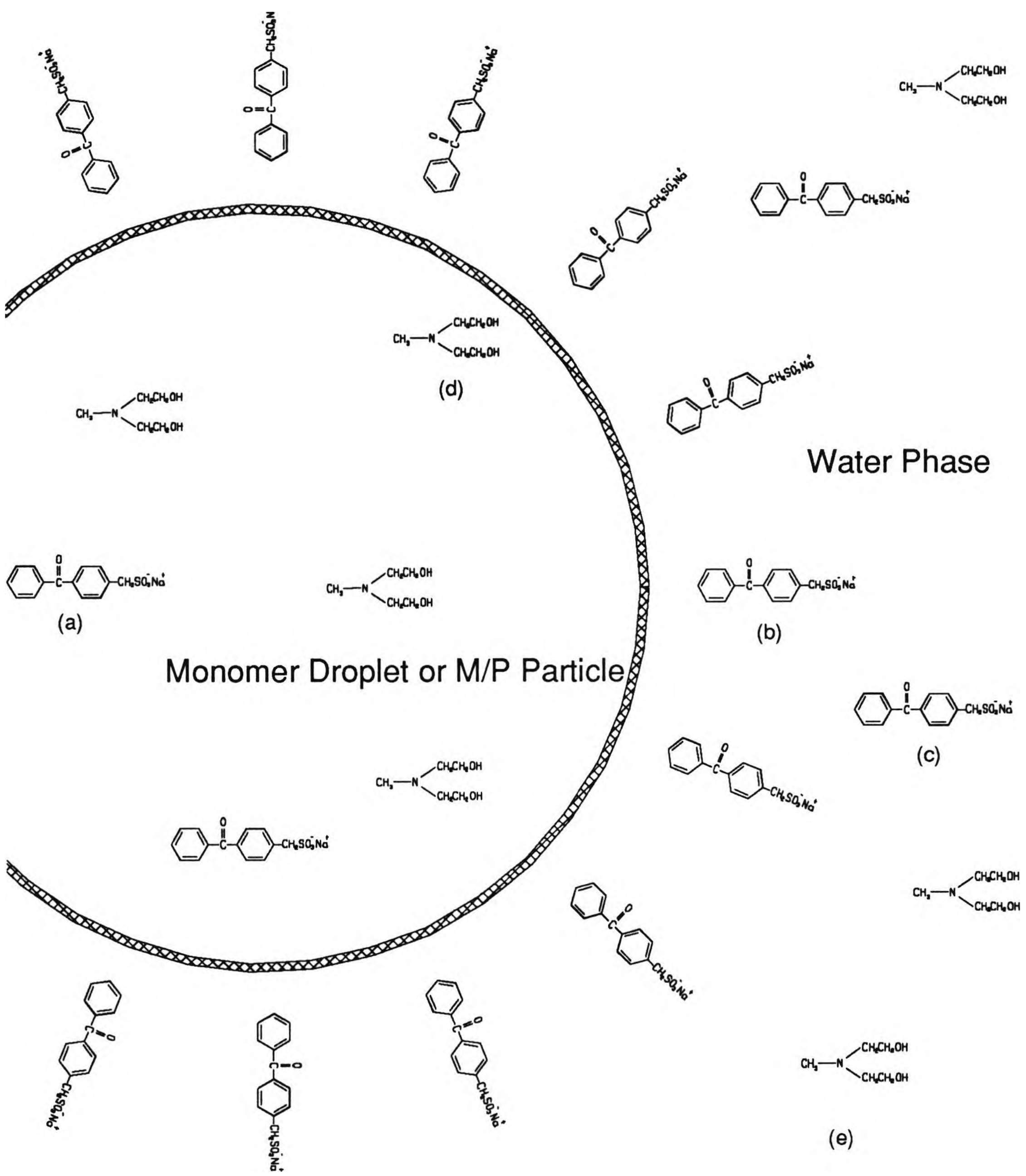
Fig.10.4 Plot of Particle Size against Reaction Time
in Emulsion Polymerisation of EHA with and without Continuous Homogenisation

Small M/P particles can capture free radicals more efficiently than large monomer droplets and large M/P particles. Therefore, polymerisation in small M/P particles is faster than in large ones, and the fast consumption of monomer in small M/P particles will lead to the diffusion of monomer into the small M/P particles. The diffusion of monomer from large M/P particles resulted in a decrease in the sizes of these large M/P particles, and this allows for the decrease of the mean particle size from 4.94 μm to 4.49 μm at 30 minutes of polymerisation. The mean particle size increased to 8.52 μm during further polymerisation (see Fig.10.2d–e). This is clearly a result of the agglomeration of the polymer particles which are viscous and sticky at this stage of polymerisation. The particle agglomeration during polymerisation led to a decreased concentration of the M/P particles. Because the concentration of the M/P particles ([*N*]) is low, the rate of polymerisation is thus reduced (see Section §10.2.2.1).

For the emulsion polymerisation with continuously applied ultrasonic homogenisation, small particles were also formed at low conversion. However, unlike the emulsion polymerisation without continuously applied ultrasonic homogenisation, most of these newly formed small M/P particles remained stable, as can be seen from Fig.10.3(a–c). Although there was a slight increase in the mean particle size during the first 10 minutes of polymerisation, the mean particle size decreased steadily to 2.09 μm at 40 minutes of polymerisation. With continuous ultrasonic homogenisation, the final latex product has a much smaller mean particle size, 2.09 μm, compared with 8.52 μm of the latex produced without continuous ultrasonic homogenisation. Therefore, it is assumed that break–up of large particles occurs to give small ones and the agglomeration of particles during polymerisation is discouraged by the continuous ultrasonic homogenisation. The high concentration of M/P particles ([*N*]) achieved during polymerisation is responsible for the increased rate of polymerisation (see Section §10.2.2.1).

It is noted that the particles of the final polymer emulsion produced under continuous homogenisation show a bimodel distribution, with one group of particles below 1 μm and another group above 1 μm. One may assume that, similarly to the suspension polymerisation systems described in Chapter 9, there are also two polymerisation processes (i.e. emulsion polymerisation in homogeneously nucleated particles and suspension polymerisation in monomer droplets) proceeding simultaneously in this emulsion polymerisation system. The small particle were presumably formed by the growing homogeneously nucleated primary particles. It is true that the agglomeration of the small particles will result in large particles, however it seems that most of the large particles were formed by direct polymerisation within the monomer droplets. Thus it is assumed that some active α–aminoalkyl free–radicals were generated directly within the monomer droplets and M/P particles. This can occur if the WB4698 molecules were adsorbed on the monomer droplets and on the M/P particles; hence H–abstractions can take place on the interfaces between the particles and the aqueous phase (see Fig.10.5). Moreover, active α–aminoalkyl free–radicals may also be generated directly within the monomer droplets and M/P particles by H–abstractions between the co-initiator amine and WB4698 molecules dissolved in the monomer droplets. As a result, M/P particles could form by droplet nucleation followed by suspension polymerisation in these droplets.

Fig.10.6(a–b), shows the scanning electron microphotographs of the polymer latexes produced by emulsion polymerisations with and without continuous ultrasonic homogenisation.



a (b) + d $\xrightarrow{h\nu}$ Free-Radicals in Monomer Droplet or in M/P Particles

b(c) + d $\xrightarrow{h\nu}$ Free-Radicals in Water Phase

Fig.10.5. Generation of α-Aminoalkyl radicals

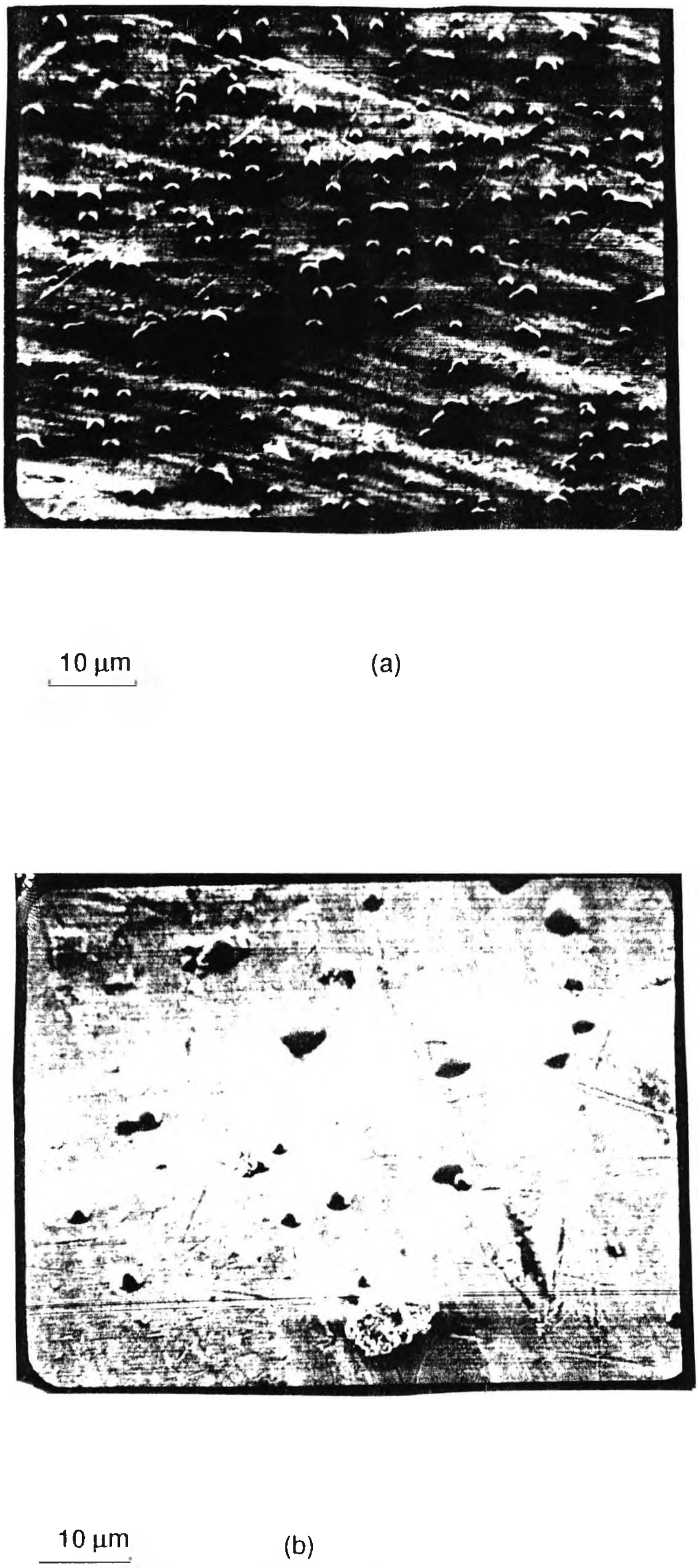


Fig.10.6(a-b) SEM Photographs of Polymer Latexes
Produced by Emulsion Polymerisation of EHA (a) with Continuous Homogenisation;
(b) without Continuous Homogenisation

10.2.2.3 Molecular Weight Distributions

Fig.10.7 illustrates the molecular weight distributions of poly(2–ethylhexyl acrylates) produced by emulsion polymerisations with and without continuous homogenisation. As can be seen from this figure, the molecular weight distributions of polymers produced by emulsion polymerisations with and without continuous homogenisation are similar, and both have a few characteristic peaks. Notably, there is a fraction of polymer with relatively low molecular weight near $5\times10^{5}$and a fraction of polymer with relatively high molecular weight near 5×10^{6}. As has been discussed in Section §10.2.2.2, some active α–aminoalkyl free–radicals could have generated directly within the monomer droplets and M/P particles. As a result, M/P particles could form by

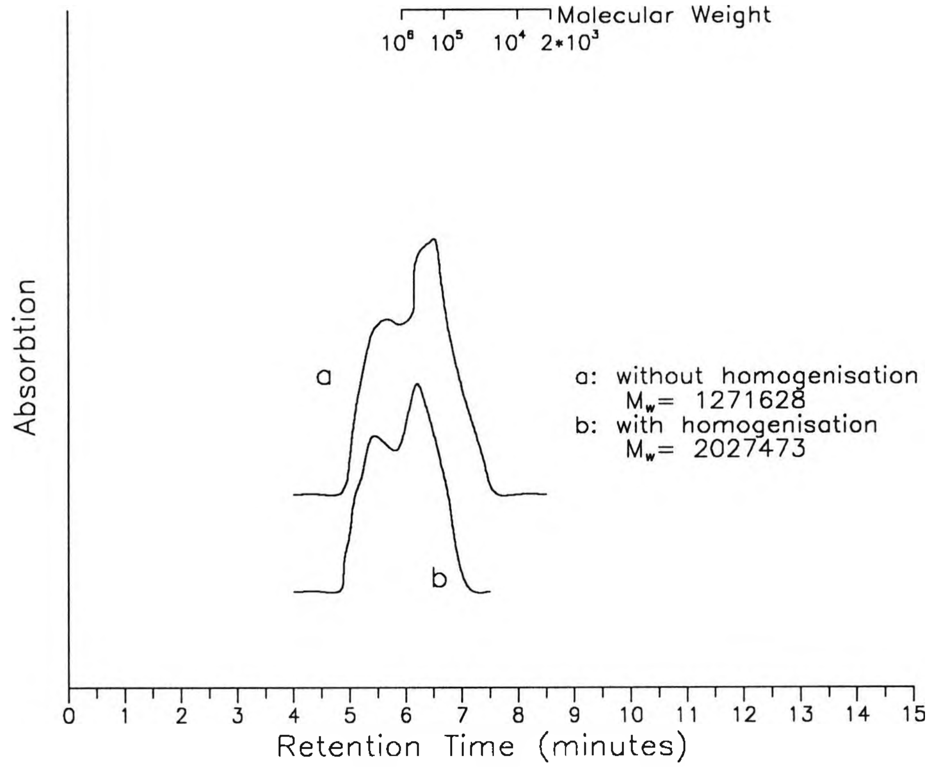


Fig.10.7 GPC Traces of Poly(2-ethylhexyl acrylate)s
Produced by Emulsion Polymerisation of EHA (a) without Continuous Homogenisation;
(b) with Continuous Homogenisation

droplet nucleation, followed by suspension polymerisation in these droplets. The fraction of polymer with relatively low molecular weight could have been formed by the suspension polymerisation processes, and the fraction of high molecular weight fraction could have been formed mainly by the true emulsion polymerisation processes.

The relation between kinetic chain length (X_n) and the rate of propagation (R_p) and the rate of polymer molecule formation (R_f) is (Lin, S.A. et al 1982):

$$X_n = \frac{R_p}{R_f} \quad \text{i.e. } X_n \propto R_p$$

The weight average molecular weight (M_w) is higher for the polymer produced with continuous homogenisation. As discussed previously in Section §10.2.2.1 and Section §10.2.2.2, under continuous homogenisation, the concentration of M/P particles $[N]$ is much higher than that of polymerisation without continuous homogenisation. As a result, the rate of chain propagation (R_p) is increased and so is the kinetic chain length (X_n) and the weight average molecular weight (M_w) when using continuous homogenisation.

Under the experimental conditions, the molecular weight of the polymer produced was not reduced through degradation by the applied ultrasonic homogenisation. This supports the conclusion drawn in Section §9.2.2.3 that the low molecular weight obtained in suspension polymerisation of EHA when using continuous homogenisation is unlikely to be due to ultrasonic degradation but is partially due to the high rate of suspension polymerisation under continuous homogenisation.

10.2.3 Emulsion Polymerisation of EHA Using Different Co–initiator Amines

10.2.3.1 Introduction

The experimental details for the emulsion polymerisations of EHA with different co–initiator amines have been described in Section §6.6.1.3.

The photoinitiator used i.e. WB4698 is water–soluble. The co–initiator amines can be soluble in water, soluble in monomer, or soluble in both water and monomer. The photoinitiation of the polymerisation requires firstly the formation of a α–aminoalkyl radicals by H–abstraction between the WB4698 molecule and the co–initiator amine molecule (R_2NCH_2R'), and secondly the addition reaction of the α–aminoalkyl radical ($R_2N\dot{C}HR'$) to a monomer molecule (M).

i.e. $$WB4698 + R_2NCH_2R' \longrightarrow R_2N\dot{C}HR'$$

and $$R_2N\dot{C}HR' + M \longrightarrow R_2NCHR'\dot{M}$$

Accordingly, the rate of initiation (R_i) is determined by the rate coefficients of the reactions between the triplet state of WB4698 and the amine and between the α–aminoalkyl radical and the monomer molecule. To explore the effect of the chemical structure of the co–initiator amine on the emulsion polymerisation of EHA, a series of amines with different structures was used for the emulsion polymerisation of EHA in the whistle reactor.

Table 10.2 shows the yields and mean particle sizes of the polymer latexes and the weight average molecular weights of the polymers produced by emulsion polymerisation of EHA using different amines.

Table 10.2 Properties of Polymers and Polymer Latexes Produced by Emulsion Polymerisations using Different Co–initiator Amines

Amines	Reaction Time (minutes)	Yield (%)	Mean Particle Size (μm)	Weight Average Molecular Weight
N–methyldiethanolamine	60	78.0	3.64	1459746
N,N–dimethylethanolamine	60	88.4	3.57	700213
triethanolamine	60	80.7	5.80	538623
triethylamine	60	83.0	3.47	140225
N–n–butyldiethanolamine	60	85.1	2.36	610101
N,N–bis(2–hydroxyethyl)–p–toluidine	80	5.0	unstable	
N–tert–butyldiethanolamine	80	62.3	2.87	1093570
2–diethylaminoethyl acrylate	80	18.0	unstable	
2–(2–diethylamino–ethoxyl)–ethanol	50	49.8	2.36	558343

10.2.3.2 Rate of Polymerisation

As shown in Table 10.2, low yield unstable polymer emulsions were obtained when using N,N–bis(2–hydroxyethyl)–p–toluidine or 2–diethylaminoethyl acrylate as co–initiators. N,N–Bis(2–hydroxyethyl)–p–toluidine has an aromatic group. It is not certain if the aromatic group affected the performance of the amine as co–initiator. However, it is true that N,N–bis(2–hydroxyethyl)–p–toluidine has the highest molecular mass within the amines used. Moreover, it has only 4 α–hydrogens available for H–abstraction. This may be partially responsible for the low rate of polymerisation. 2–Diethylaminoethyl acrylate can copolymerize during reaction. The H–abstraction with the WB4698 molecule may be delayed due to decreased mobility of the 2–diethylaminoethyl acrylate when copolymerized with EHA. It is evident that both 2–diethylaminoethyl acrylate and N,N–bis(2–hydroxyethyl)–p–toluidine are very poor co–initiators for the emulsion polymerisation of EHA.

Like N,N–bis(2–hydroxyethyl)–p–toluidine, N–tert–butyldiethanolamine also has only 4 α–hydrogens available for H–abstraction. Only about 60% conversion was obtained after 80 minutes of irradiation using N–tert–butyldiethanolamine as co–initiator compared with about 80% conversion after 60 minutes of irradiation when using other amines as the co–initiators.

Apart from N,N–bis(2–hydroxyethyl)–p–toluidine and 2–diethylaminoethyl acrylate, other amines are more satisfactory co–initiators. High yield stable emulsions were obtained using these amines. Also it seems that there is little effect on the rate of emulsion polymerisation due to the water solubilities of the co–initiator amines. The rate of emulsion polymerisation, however, probably depends only on the concentration of the M/P particles.

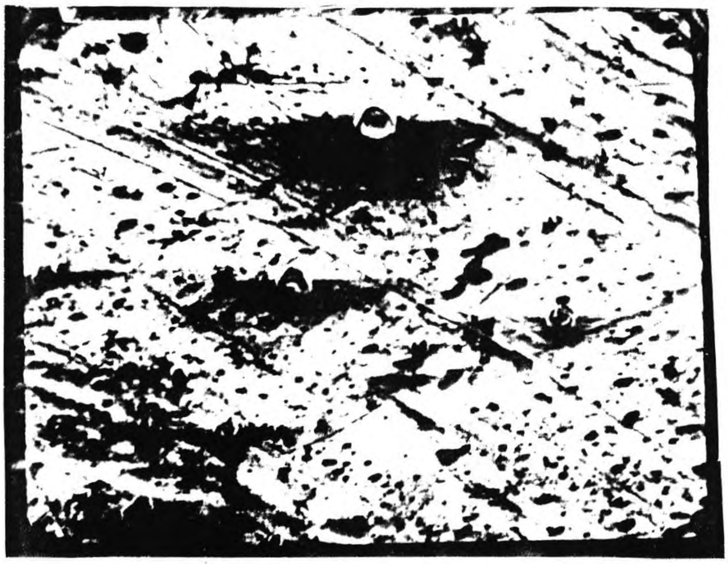
10.2.3.3 Mean Particle Sizes of the Polymer Latexes

The mean particle sizes of the polymer emulsions produced are shown in Table 10.2. Different mean particle sizes were obtained with different co–initiator amines. The largest mean particle size is 5.80 µm for the polymer emulsion produced using triethanolamine as co–initiator. The smallest is 2.36 µm for the polymer emulsions produced using N–n–butyldiethanolamine or 2–(2–diethylamino–ethoxyl)–ethanol as the co–initiators. According to the results in Table 10.2, there is no direct correlation between the percentage yields and the final mean particle sizes of these polymer emulsions. The percentage yield depends on the rate of emulsion polymerisation which in turn, depends on the concentration of the M/P particles formed at the early stage of polymerisation. The final mean particle size of the polymer emulsion depends on the concentration of the M/P particles formed at the early stage of the polymerisation, and the subsequent particle agglomerations during polymerisation. Thus a bigger mean particle size is obtained with the polymerisation in which the particle agglomeration is significant.

Triethanolamine is a poor co–initiator for emulsion polymerisation of EHA, as the emulsion produced contains large particles and this results in poor storage stability. It seems that N–n–butyldiethanolamine is the best co–initiator within the amines used, because both high yield and small final mean particle size are obtained when it is used as the co–initiator. As additional information, Fig.10.8–Fig.10.14 show the SEM photographs of the polymer latexes produced emulsion polymerisations of EHA using different co–initiator amines.

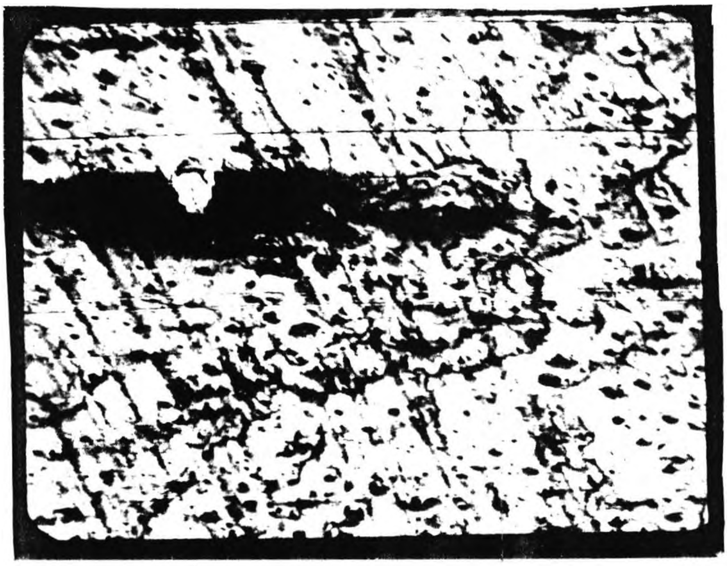
20 μm

Fig.10.8 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using N-methyldiethanolamine as the Co-initiator



20 µm

Fig.10.9 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using N,N-dimethylethanolamine as the Co-initiator

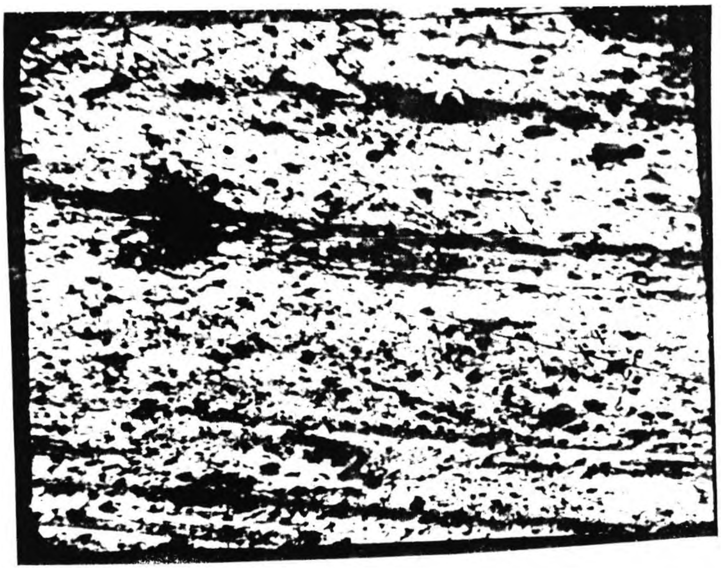


20 µm

Fig.10.10 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using Triethanolamine as the Co-initiator

20 µm

Fig.10.11 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using Triethylamine as the Co-initiator



20 µm

Fig.10.12 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using N-n-butyldiethanolamine as the Co-initiator

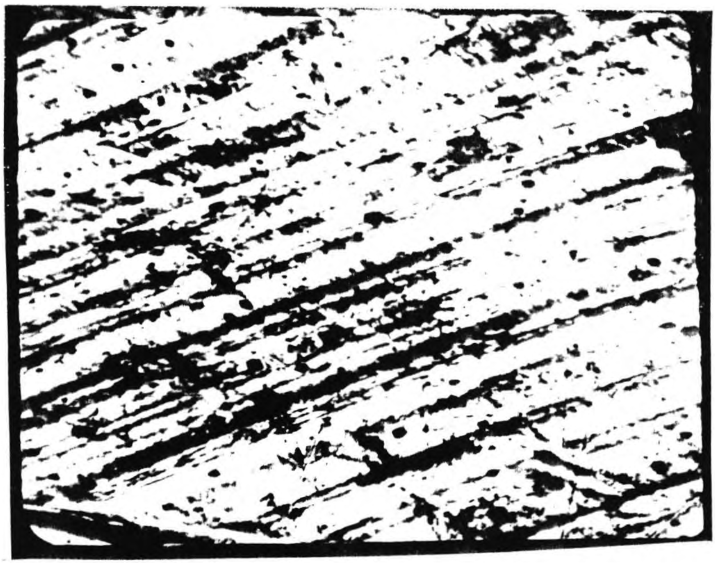


Fig.10.13 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using N-tert-butyldiethanolamine as the Co-initiator

Fig.10.14 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using 2-(2-diethylamino-ethoxyl)-ethanol as the Co-initiator

10.2.3.4 Molecular Weight Distributions

Fig.10.15 illustrates the molecular weight distributions of the polymers produced with different co–initiator amines. Again, the major feature of some of the GPC traces in Fig.10.15 is that there is a fraction of low molecular weight polymer and a fraction of high molecular weight polymer. As has been discussed in Section §10.2.2.3, the fraction of polymer with relatively low molecular weight could have been formed by the suspension polymerisation processes, and the fraction of high molecular weight fraction could have been formed mainly by the true emulsion polymerisation processes. The percentages of the high molecular weight and low molecular weight polymers may be related to the percentage of the partition of the co–initiator amine in the aqueous phase and the monomer droplets. As an extreme example, triethylamine is almost exclusively dissolved in the monomer droplets; as a result most of the free–radicals might have generated in the monomer droplets, and the polymerisation could not be a true emulsion polymerisation but a true suspension polymerisation. Indeed only one peak was observed in its GPC trace which gave a relatively low average molecular weight.

The weight average molecular weights are summarised in Table 10.2. According to this table, polymers with different average molecular weights were obtained with co–initiators of different structure. In an α–aminoalkyl radical, the alkyl groups (CH_2 , CH_3) contribute to its oil–solubility, whereas N and O in the molecule can form H–bonding with water molecules and thus contribute to its water solubility. Thus the water solubility or the degree of solvation of an α–aminoalkyl radical in water is proportional to $\frac{\text{total number of N and O in the radical}}{\text{number of C in the radical}}$. The α–aminoalkyl radicals generated in the aqueous phase are solvated by the surrounding water molecules. If the activation energy for the reaction between the unsolvated α–aminoalkyl radical and a monomer molecule is E_a , and the energy of the α–aminoalkyl radical is lowered by an amount ΔH_s when it is solvated (Nonhebel,D.C. &

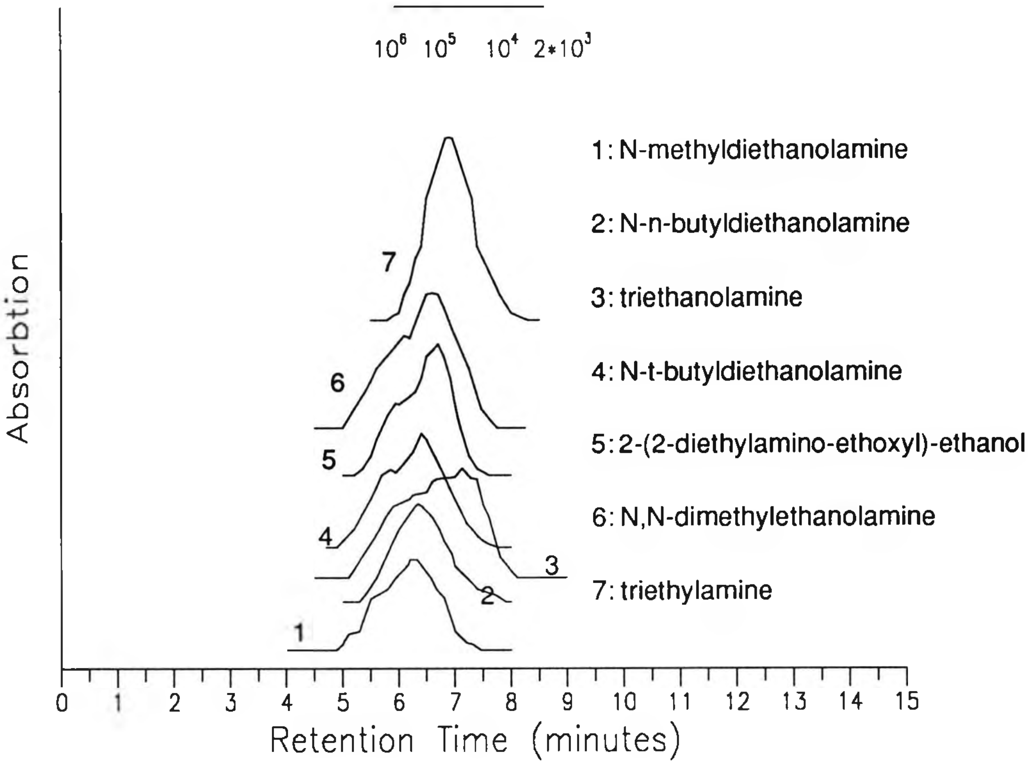


Fig.10.15 GPC Traces of Polymers
Produced by Emulsion Polymerisation of EHA with Different Co–initiator Amines

Walton,J.C., 1974), then activation energy for the reaction between the α–aminoalkyl radical and a monomer molecule is increased to $E_b = E_a + \Delta H_s$. Hence the rate of reaction (R_i) decreases. As has been discussed in Section §10.2.2.3, the relation between kinetic chain length (X_n) and the rate of propagation (R_p) and the rate of polymer molecule formation (R_f) is:

$$X_n = \frac{R_p}{R_f} \quad \text{i.e. } X_n \propto R_p$$

In the case when there is no chain transfer reaction, $R_f = R_i$ hence $X_n \propto \frac{1}{R_i}$ i.e. $M_w \propto \frac{1}{R_i}$. This means that solvation of the α–amino radical increases the molecular weight. In Table 10.3, the degree of solvation of the α–aminoalkyl radicals in water, represented by $\frac{\text{total number of N and O in the radical}}{\text{number of C in the radical}}$ is correlated with the weight average molecular weights of the polymers produced. It generally follows the rule that higher average molecular weight is produced with α–aminoalkyl radicals of higher degree of solvation in water. However, N–tert–butyldiethanolamine and triethanolamine are the exceptions. It should be noted that N–tert–butyldiethanolamine has only 4 α–hydrogens available for H–abstraction. As a result, the concentration of the α–aminoalkyl radicals in the aqueous phase is low. This will result in a reduced rate of initiation and an increased weight average molecular weight. For triethanolamine, it is most likely that the low molecular weight obtained is due to the very low concentration of M/P particles [*N*] (see §10.2.2.1), i.e. large mean particle size in the polymerisation system.

Table 10.3 Weight Average Molecular Weights of Polymers Produced by Emulsion Polymerisations using Co–Initiator Amines with Different Degree of Solvation in Water Phase

Amines	Yield (%)	Degree of Solvation	Weight Average Molecular Weight
triethylamine	83.0	$\frac{1}{6}$	1.40×10^5
2–(2–diethylamino–ethoxyl)–ethanol	49.8	$\frac{3}{8}$	5.58×10^5
N–n–butyldiethanolamine	85.1	$\frac{3}{8}$	6.10×10^5
N–tert–butyldiethanolamine	62.3	$\frac{3}{8}$	1.09×10^6
N,N–dimethylethanolamine	88.4	$\frac{1}{2}$	7.00×10^5
N–methyldiethanolamine	78.0	$\frac{3}{5}$	1.46×10^6
triethanolamine	80.7	$\frac{2}{3}$	5.39×10^5

10.2.4 Emulsion Polymerisations Using BTC as the Initiator

The experimental details for the emulsion polymerisations using BTC as the initiator are given in Section §6.6.14.

Fig.10.16 shows the plots of conversion against reaction time for the emulsion polymerisations of EHA using WB4698 and BTC as the initiators respectively. In both polymerisations, N–methyldiethanolamine was used as the co–initiator. It clearly shows that the rate of polymerisation is higher when using BTC as the initiator compared with WB4698. However, the resultant polymer emulsion produced using BTC as the initiator phase–separated in a week after polymerisation, unlike the polymer emulsion produced using WB4698 as the initiator which was still stable after six months from polymerisation.

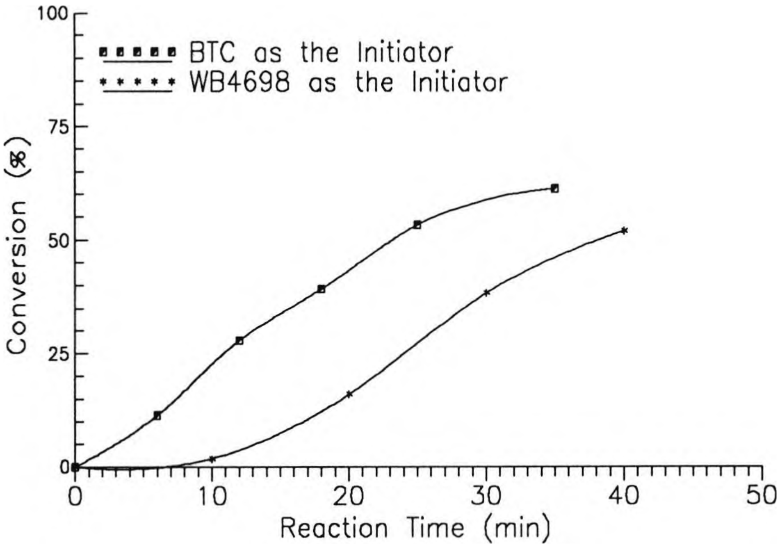


Fig.10.16 Conversion/Time of EHA Emulsion Polymerisation

Fig.10.17 shows the plots of conversion against reaction time for the emulsion polymerisations of EHA using BTC as the initiator and N–methyldiethanolamine, N,N–dimethylethanolamine as the co–initiators respectively. It can be seen that N,N–dimethylethanolamine is a more effective co–initiator than N–methyldiethanolamine for the emulsion polymerisation of EHA. This is also true for the emulsion polymerisation of EHA using WB4698 as the initiator (see Fig.10.18). The polymer emulsion produced by emulsion polymerisation using BTC as the initiator and N,N–dimethylethanolamine as the co–initiator is also unstable and phase–separated after a few days of storage.

10.2.5 Emulsion Polymerisations of EHA in the Presence of a Nonionic Surfactant

The experimental details for the emulsion polymerisation of EHA in the presence of Igepal CO–990, a nonionic surfactant have been described in Section §6.6.1.5.

10.2.5.1 Rate of Polymerisation

Fig.10.19 shows the plots of conversion against reaction time for the emulsion polymerisations of EHA in the presence of Igepal CO–990 and PVA respectively. It shows that the rate of polymerisation of EHA is higher when using the surfactant. The surfactant used is more efficient in stabilising the M/P particles and in preventing polymer particles from agglomeration. As a result, the concentration of M/P particles was increased and hence the rate of initiation and rate of polymerisation.

Fig.10.20 shows the plots of conversion against reaction time for the emulsion polymerisation of EHA in the presence of Igepal CO–990 using WB4698 and ABQ as the initiators, respectively. It shows that WB4698 is more efficient than ABQ in initiating the emulsion polymerisation of EHA.

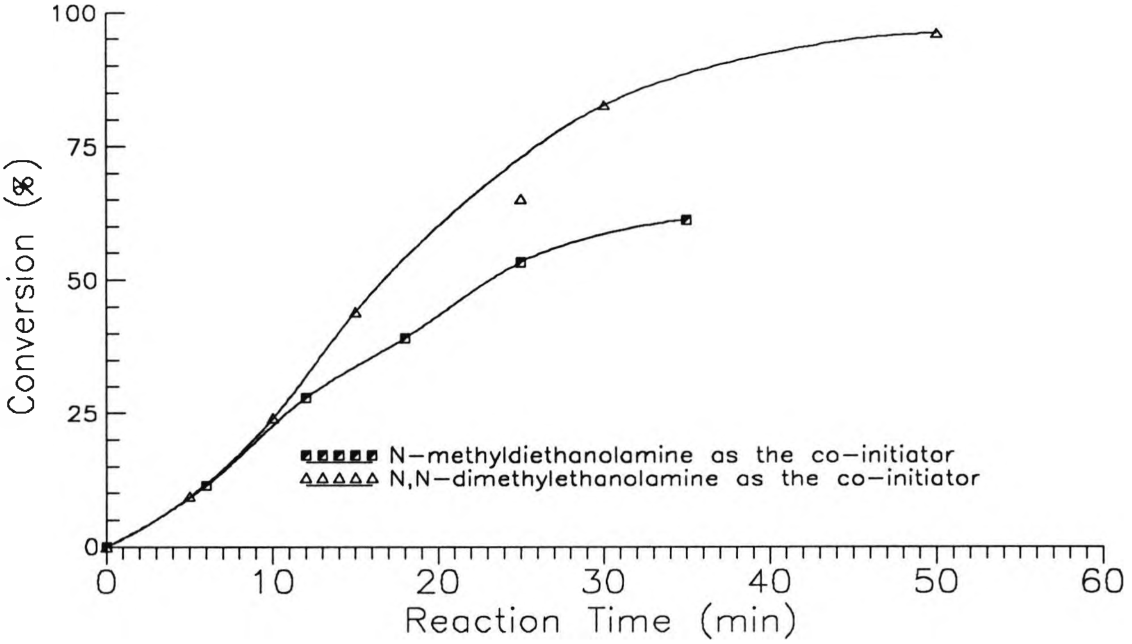


Fig.10.17 Conversion/Time of EHA Emulsion Polymerisation

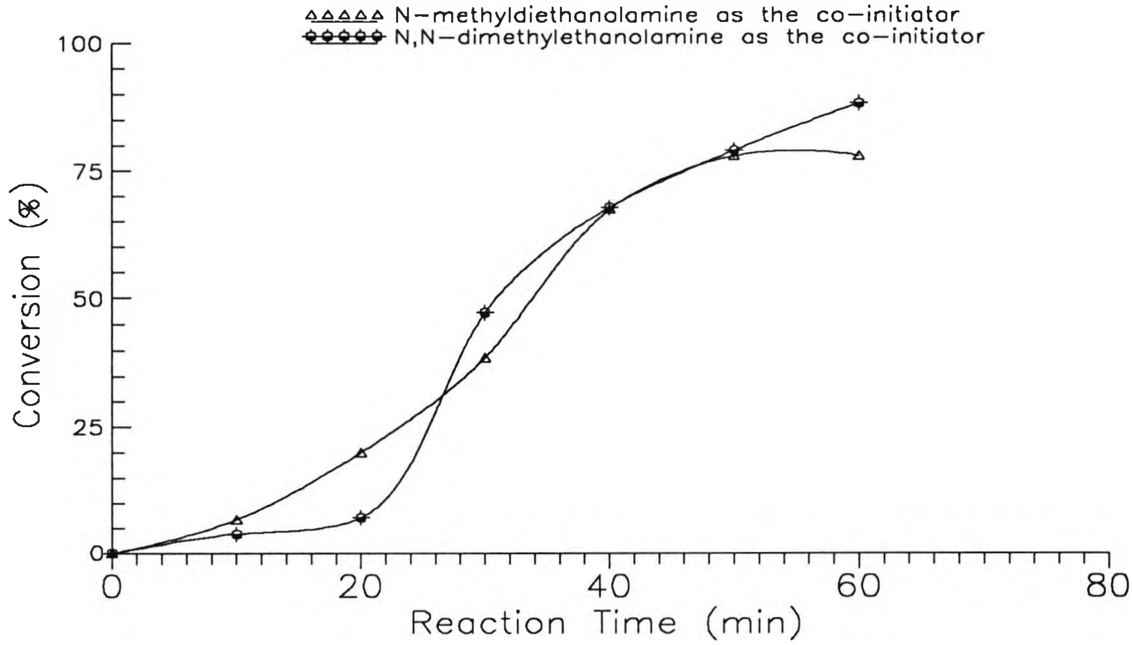


Fig.10.18 Conversion/Time of EHA Emulsion Polymerisation

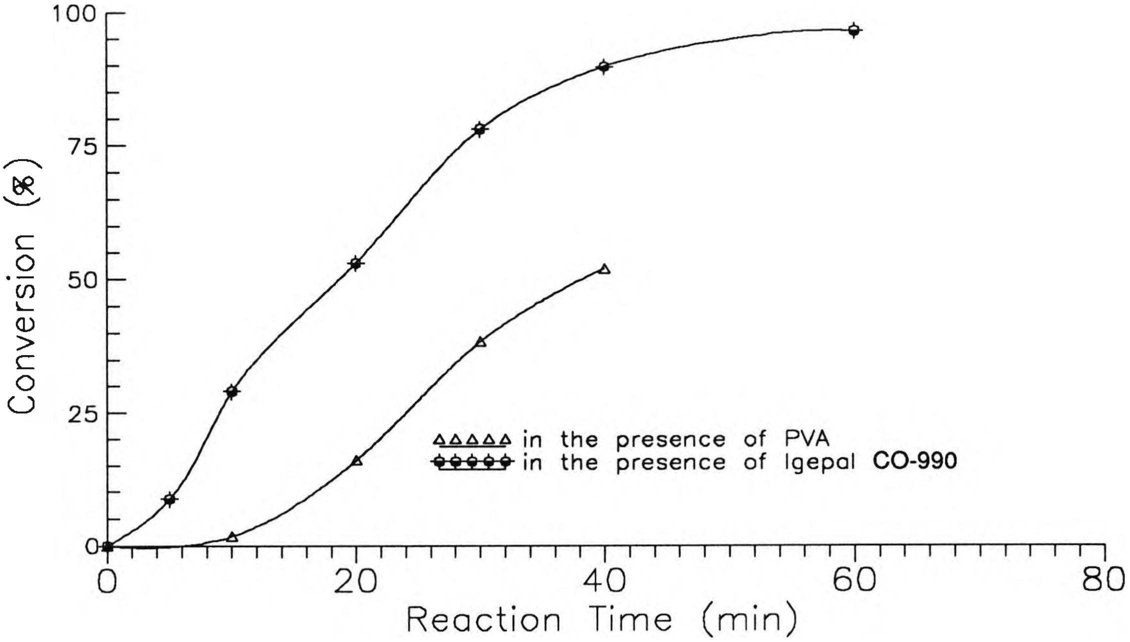


Fig.10.19 Conversion/Time of EHA Emulsion Polymerisation

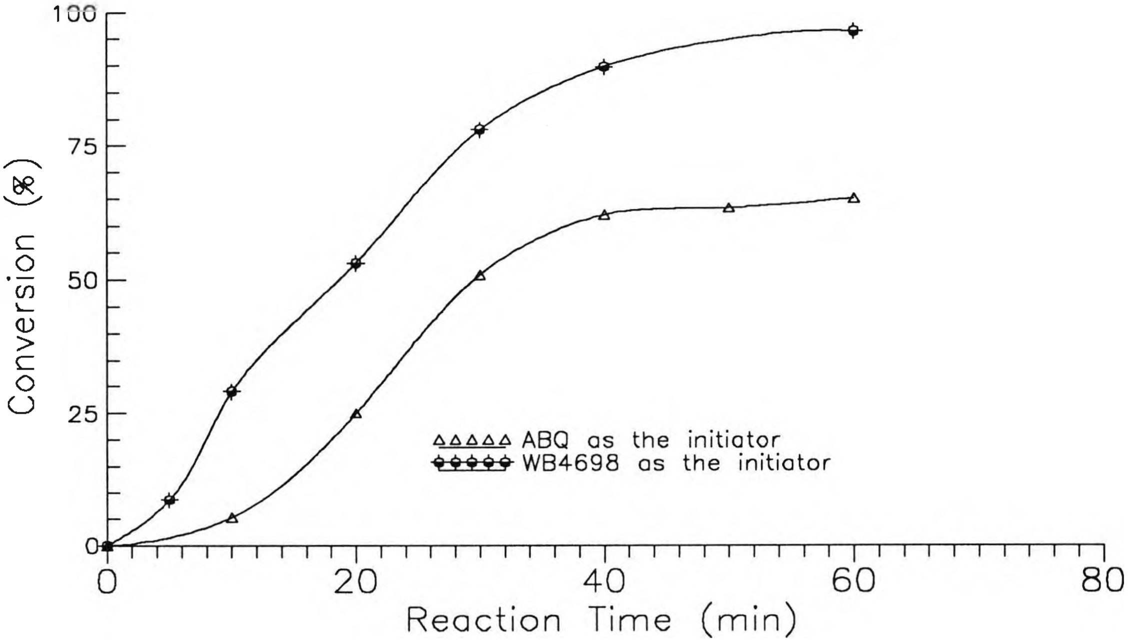


Fig.10.20 Conversion/Time of EHA Emulsion Polymerisation

One difference between the two photoinitiators is that WB4698 is not polymerizable, but ABQ is polymerizable. It is certainly reasonable to suppose that the polymerisation of ABQ will reduced its mobility and hence reduce the rate of bimolecular H–abstraction. As a result, the rate of free–radical generation was reduced. This could account for the poor initiation efficiency of ABQ.

10.2.5.2 Particle Size Distributions

Fig.10.21(a–b) illustrates the particle size distributions of the polymer emulsions produced by the emulsion polymerisation of EHA in the presence of Igepal CO–990 using WB4698 and ABQ as the initiators. A small mean particle size of 1.26 μm was obtained when using WB4698 as the initiator. This means that the concentration of M/P particles is higher when using WB4698 as the initiator. The concentration of M/P particles $[N]$ is dependent on the concentrations of surfactant $[E]$ and the initiator $[I]$ (Lin, S. A. et. al. 1982). In such a UV–induced polymerisation system, $[N]$ also depends on the initiation efficiency of the photoinitiator f, i.e. $[N] \propto [E]\cdot[I]\cdot f$. The decreased initiation efficiency of ABQ is responsible for the reduced concentration of M/P particles and hence the decreased rate of polymerisation.

It is certain that the surfactant used provided effective stabilisation of the M/P particles against agglomeration. A polymer emulsion with small mean particle size was obtained when Igepal CO–990 was used to replace PVA. In the presence of Igepal CO–990, the mean particle size of the polymer emulsion was 1.26 μm compared with 2.09 μm when using PVA (see Section §10.2.2.2).

10.2.5.3 Molecular Weight Distributions

Fig.10.22 represents the molecular weight distributions of the poly(2–ethylhexyl acrylate) produced in the presence of Igepal CO–990 and PVA, respectively. The polymer produced in the presence of PVA had a higher

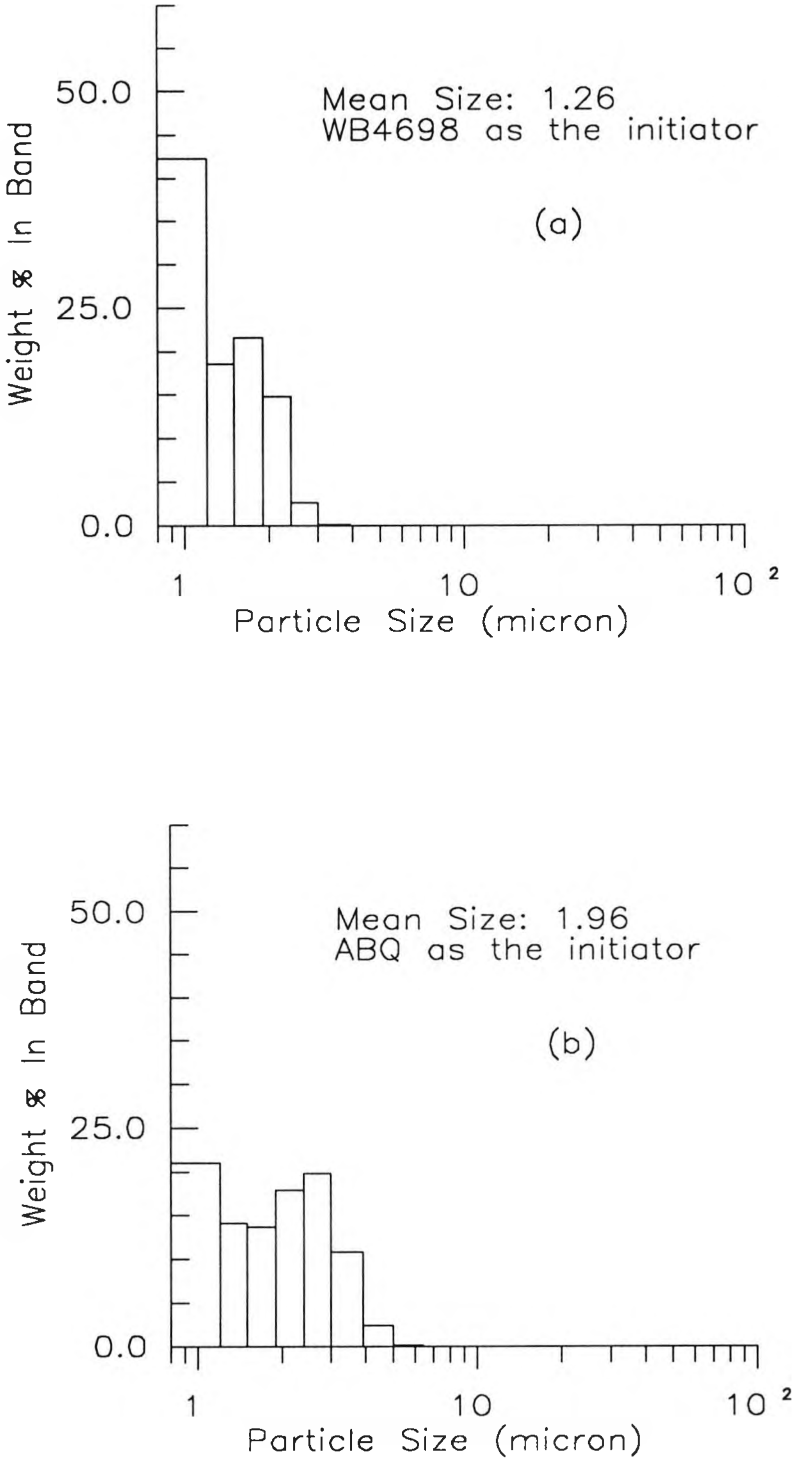


Fig.10.21(a-b) Particle Size Distributions of EHA
Polymer Emulsions

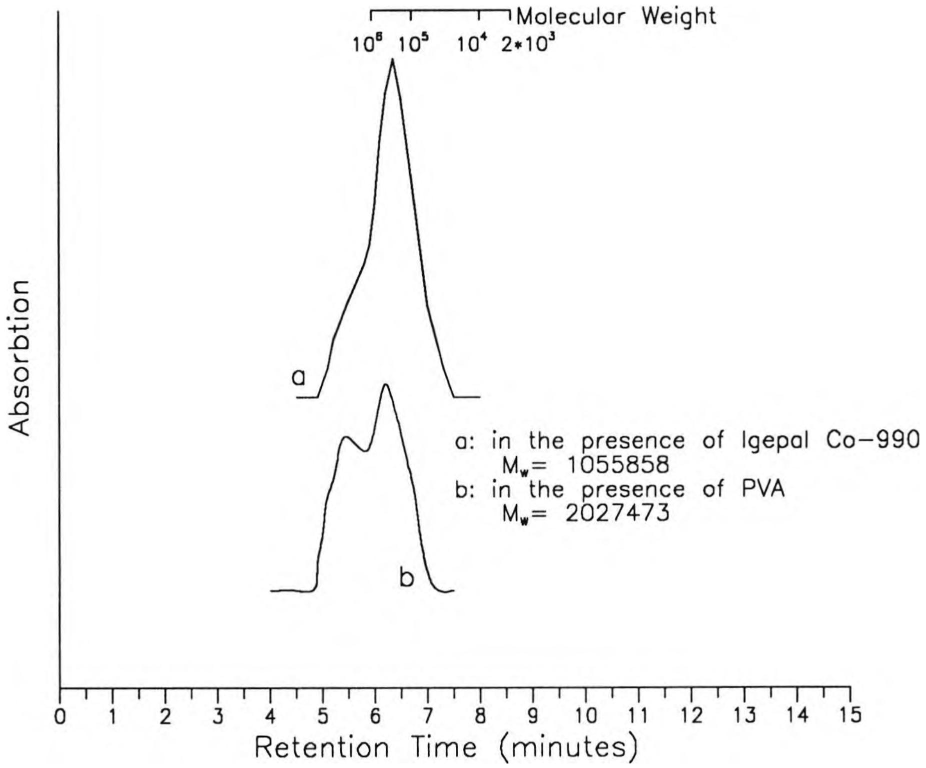


Fig.10.22 GPC Traces of Poly(2-ethylhexyl acrylate)s

average molecular weight than that obtained in the presence of Igepal CO–990. As has been discussed in Section §10.2.5.1 and Section §10.2.5.2, the rate of polymerisation, as well as the concentration of M/P particles, is higher for the emulsion polymerisation in the presence of Igepal CO–990 than in the presence of PVA. This would have increased the molecular weight of the polymer produced. However it is clearly shown by the GPC traces in Fig.10.21 that the molecular weight is small when using Igepal CO–990. As has been discussed previously in Section §10.2.3.4 the molecular weight (M_w) depends on the rate of propagation (R_p) and the rate of initiation (R_i), and

$M_w \propto \frac{R_p}{R_i}$. Thus the low molecular weight obtained in the presence of Igepal CO–990 may be related to the fast rate of initiation for this emulsion polymerisation. To initiate polymerisation, the free–radicals must diffuse from the aqueous phase to the M/P particles. If an M/P particle is enveloped with a layer of high molecular weight PVA, the rate of diffusion of free–radicals to the M/P particle may be significantly delayed. This could account for the increased molecular weight produced in the presence of PVA.

10.2.6 Emulsion Copolymerisations of EHA and VA

The experimental details for the UV–induced emulsion copolymerisations of EHA and VA have been described in Section §6.6.1.6.

With WB4698 as initiator, an 80% yield was obtained in 120 minutes of UV–irradiation compared with 58.6% in 180 minutes with ABQ as the initiator. This again shows that WB4698 is more effective than ABQ in the initiation of EHA emulsion polymerisation. Like the UV–induced suspension polymerisations (see Section §9.2.3), the rate of emulsion polymerisation and the shelf life of the resultant polymer emulsion is reduced when VA is used as the comonomer.

10.3 Thermal Polymerisation

10.3.1 Introduction

In the above sections, the emulsion polymerisations in the whistle reactor initiated by UV–irradiation have been described. In Section §10.2.2, the UV–induced emulsion polymerisations were carried out in the whistle reactor with and without continuously applied homogenisation. A high rate and small mean particle size were obtained when using continuous homogenisation. In this section, attention is drawn to the emulsion polymerisations in the whistle reactor under the initiation of thermal free–radical initiators. Thermal emulsion polymerisations were carried out using one of the following three methods:

- polymerisation in a stirred batch reactor without pre–emulsification of the monomer/water mixture.
- emulsification of the monomer with water through the homogeniser followed by polymerisation of the pre–emulsified EHA without continuously applied ultrasonic homogenisation, and
- emulsification of the monomer with water through the homogeniser followed by polymerisation of the monomer emulsion under continuously applied ultrasonic homogenisation.

The resultant polymer emulsions were characterised and the results will be discussed in the following sections.

10.3.2 Homopolymerisations of EHA

The experimental details of homopolymerisations of EHA in emulsions under thermal initiation have been described in Section §6.6.2.1, Section §6.6.2.2 and Section §6.6.2.3. The results of the polymerisations using three different procedures are compared in Table 10.4. Clearly, under the initiation by ammonium persulphate, emulsion polymerisation of unemulsified EHA by merely mechanical stirring in the batch reactor failed to produce a stable polymer emulsion. With pre–emulsification of the reaction mixture, the reaction system remained stable and a polymer emulsion with 13.87 μm mean particle size was produced, although it is not long term stable and phase–separated after a few days. The application of continuous ultrasonic homogenisation during the course of polymerisation enabled some reduction of the mean particle size and longer shelf life of the resultant polymer emulsion. As can been seen from Table 10.4, the mean particle size increased during continuous homogenisation, indicating the increased tendency of particle agglomeration at the high conversion. However, it is evident from the comparison between the polymerisations with and without continuous homogenisation that the continuously applied homogenisation partly prevented the particle agglomeration during polymerisation.

Table 10.4 Results of Emulsion Polymerisations of EHA using Different Procedures

Procedure Used for Polymerisation		Time of Reaction (min)	Properties of Resultant Latexes	
monomer emulsification	continuous homogenisation during reaction		mean particle size (μm)	shelf life
No	No	15		unstable
Yes	No	30	13.87	3 days
Yes	Yes	10	4.57	4 weeks
		20	4.56	
		30	5.70	
		40	5.39	
		55	9.28	

10.3.3 Copolymerisations of EHA and VA

The experimental details for the emulsion copolymerisations of EHA and VA under thermal initiation have been described in Section §6.6.2.4, Section §6.6.2.5 and Section §6.6.2.6. A derivative of azoisobutyronitrile, 4,4–azobis(4–cyanovaleric acid) i.e. AICA was used as the water soluble initiator. The results of copolymerisations using different procedures are shown in Table 10.5. Unlike the polymerisation using ammonium persulphate as the initiator, the reaction system remained stable even when no pre-emulsification or continuous homogenisation was used. However, without monomer pre-emulsification, the resultant polymer emulsion has a large mean particle size and phase-separated soon after polymerisation. In comparison, although some particle agglomerates formed, stable copolymer emulsions with smaller mean particle size were obtained when the reaction mixtures were pre-emulsified even at a reduced level of protective colloid PVA. With continuously applied ultrasonic homogenisation, the mean particle sizes were further reduced, resulting in even more stable copolymer emulsions. Again it may be concluded that the continuously applied homogenisation partly prevented the particle agglomeration during polymerisation.

As shown in Table 10.5, when the amount of PVA was reduced to 4.5 g, the mean particle size was increased for both polymerisations with and without continuous homogenisation.

Table 10.5 Results of Thermal Emulsion Polymerisations and Copolymerisations of EHA and VA

Procedure Used for Polymerisation		Weight of PVA used (g)	Time of Reaction (min)	Properties of Resultant Latexes	
monomer emulsification	continuous homogenisation during reaction			mean particle size (μm)	Conversion (%)
No	No	9.0	35	16	83.3
Yes	No	9.0	35	4.87	84.1
		4.5	35	7.55	68.2
Yes	Yes	9.0	35	3.25	93.2
		4.5	35	4.56	76.0
		9.0*	20	3.16	71.4

* in the presence of 0.3 g chain transfer agent (1-dodecanthoil)

The copolymers produced under the initiation of AICA were of too high molecular weight to be useful as pressure–sensitive adhesives. When dissolved in THF, there were significant amounts of gel which after filtration enabled analysis by GPC to be undertaken.

In Section §6.6.2.7, the copolymerisation was described when it was carried out in the presence of a chain transfer agent, 1–dodecanthiol. There is little difference between the particle sizes obtained with and without the chain transfer agent. However, a low weight average molecular weight of 2.38×10^5 (see Fig.10.23 for the GPC trace) was obtained. The results of the copolymerisation are also listed in Table 10.5.

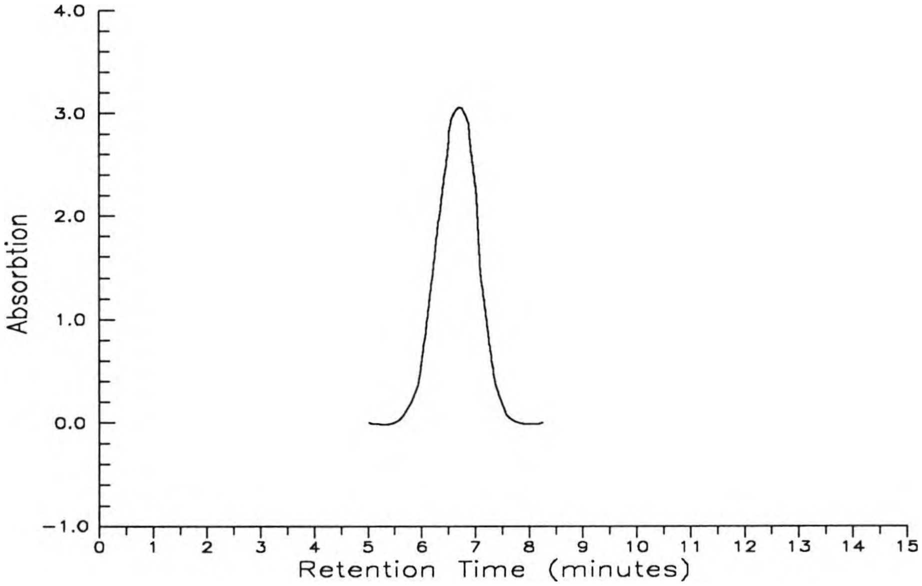


Fig.10.23 GPC Trace of Poly(2-ethylhexyl acrylate)
Produced by Emulsion Polymerisation in the Presence of a Chain Transfer Agent:
1–dodecanthiol

As additional information, the SEM photographs of the resultant copolymer emulsions are shown in Fig.10.24–Fig.10.28.

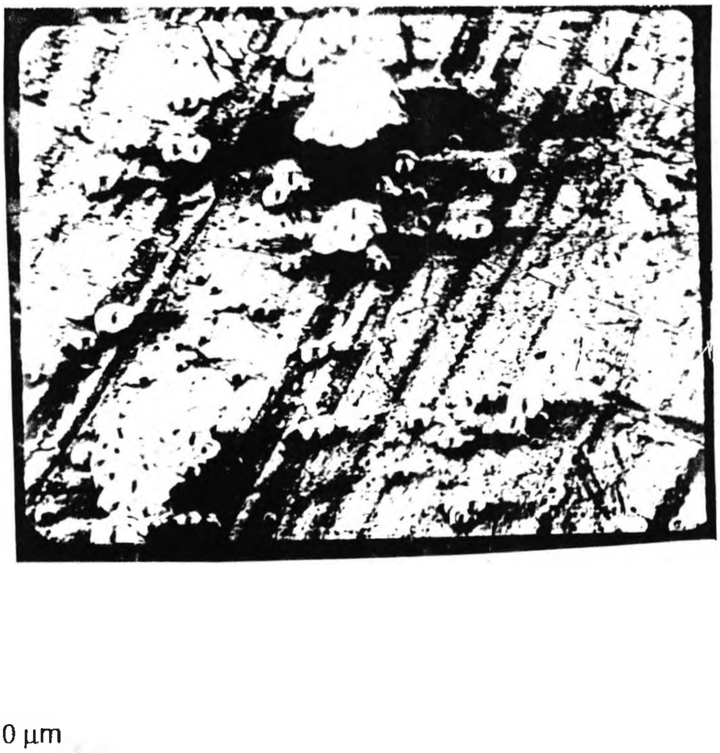


Fig.10.24 SEM Photograph of Polymer Latex Produced by Emulsion Copolymerisation of Pre-emulsified EHA/VA using AICA as the Initiator and 9 g of PVA as the Protective Colloid

20 µm

Fig.10.25 SEM Photograph of Polymer Latex Produced by Emulsion Copolymerisation of Pre-emulsified EHA/VA using AICA as the Initiator and 4.5 g of PVA as the Protective Colloid

20 µm

Fig.10.26 SEM Photograph of Polymer Latex Produced by Emulsion Copolymerisation of EHA and VA using AICA as the Initiator and 9 g of PVA as the Protective Colloid under Continuous Homogenisation

20 μm

Fig.10.27 SEM Photograph of Polymer Latex Produced by Emulsion Copolymerisation of EHA and VA using AICA as the Initiator and 4.5 g of PVA as the Protective Colloid under Continuous Homogenisation

20 μm

Fig.10.28 SEM Photograph of Polymer Latex Produced by Emulsion Copolymerisation of EHA and VA using AICA as the Initiator and 9 g of PVA as the Protective Colloid and in the Presence of 1-Dodecanthiol under Continuous

10.4 Redox–induced Emulsion Polymerisation

10.4.1 Introduction

The experimental details for the redox–induced emulsion polymerisations of EHA have been described in Section §6.6.3. Like emulsion polymerisation under thermal initiation, the redox–induced emulsion polymerisations were also carried out using one of the following three methods:

- polymerisation in a stirred batch reactor without pre–emulsification of the monomer/water mixture.
- emulsification of the monomer with water through the homogeniser followed by polymerisation of the pre–emulsified EHA without continuously applied ultrasonic homogenisation, and
- emulsification of the monomer with water through the homogeniser followed by polymerisation of the monomer emulsion under continuously applied ultrasonic homogenisation.

10.4.2 Polymerisations of EHA

The experimental details for the redox–induced emulsion polymerisations of EHA have been described in Section §6.6.3.1, Section §6.6.3.2 and Section §6.6.3.3. The results of polymerisations using different procedures (see Section §10.4.1) are shown in Table 10.6. Similarly to the thermal emulsion polymerisations, the polymer emulsion produced phase–separated soon after polymerisation when no monomer pre–emulsification or continuous homogenisation was used. In comparison, a stable polymer emulsion was obtained with monomer pre–emulsification. With continuously applied ultrasonic homogenisation, the mean particle size was further reduced, resulting in even more stable polymer emulsion. Again the conclusion may be drawn that the continuously applied homogenisation partly prevented the particle agglomeration during polymerisation. As additional information, the SEM photographs of the resultant copolymer emulsions are shown in Fig.10.29–Fig.10.32.

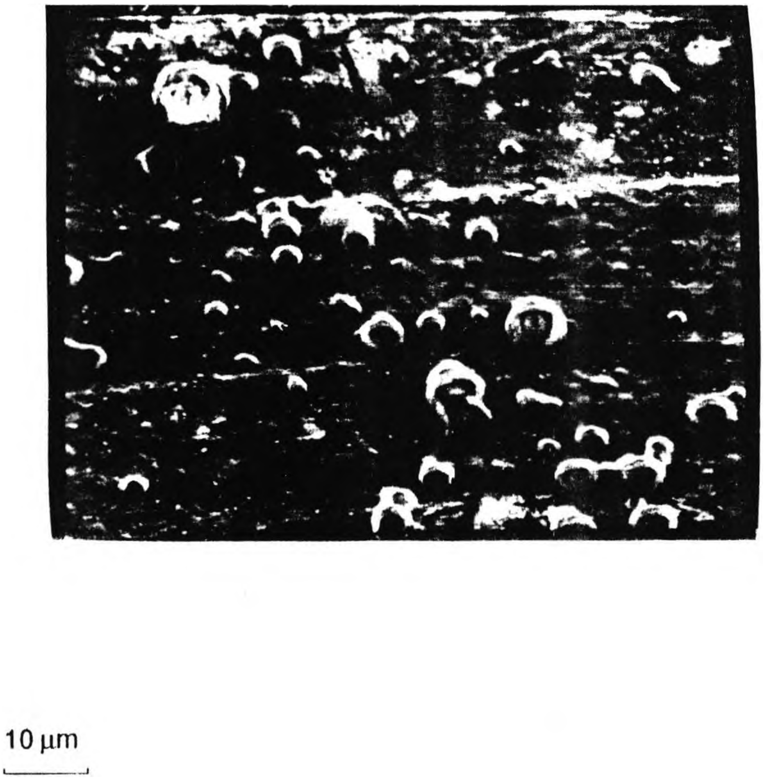
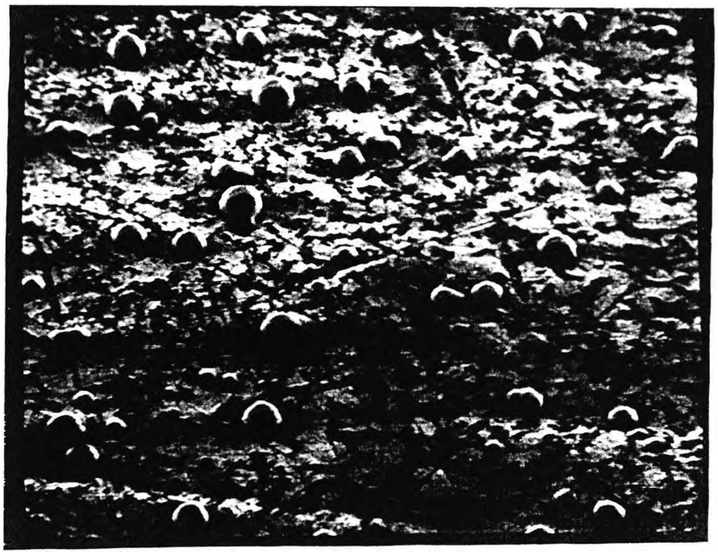


Fig.10.29 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of Pre-emulsified EHA using Ammonium Persulphate/Sodium Persulphate as the Initiator and 4.0 g of PVA as the Protective Colloid

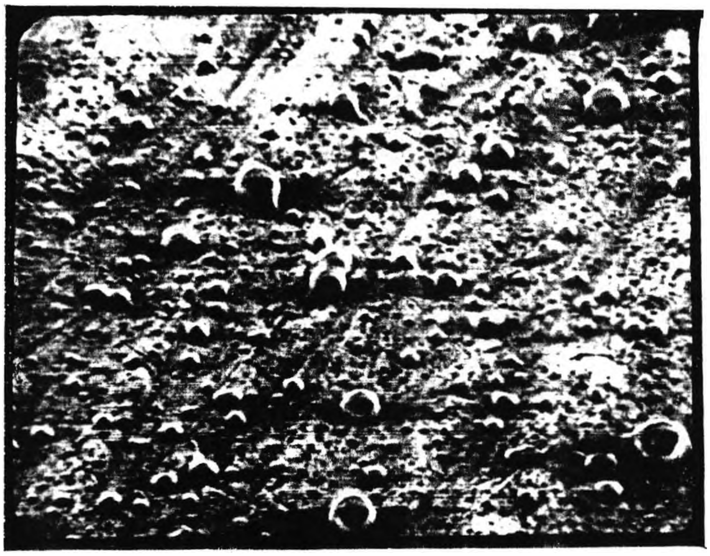
10 µm

Fig.10.30 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of Pre-emulsified EHA using Ammonium Persulphate/Sodium Persulphate as the Initiator and 1.5 g of PVA as the Protective Colloid



10 µm

Fig.10.31 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA Produced using Ammonium Persulphate/Sodium Persulphate as the Initiator and 4.0 g of PVA as the Protective Colloid under Continuous Homogenisation



10 μm

Fig.10.32 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using Ammonium Persulphate/Sodium Persulphate as the Initiator and 1.5 g of PVA as the Protective Colloid under Continuous Homogenisation

10.4.3 Effect of PVA Concentration

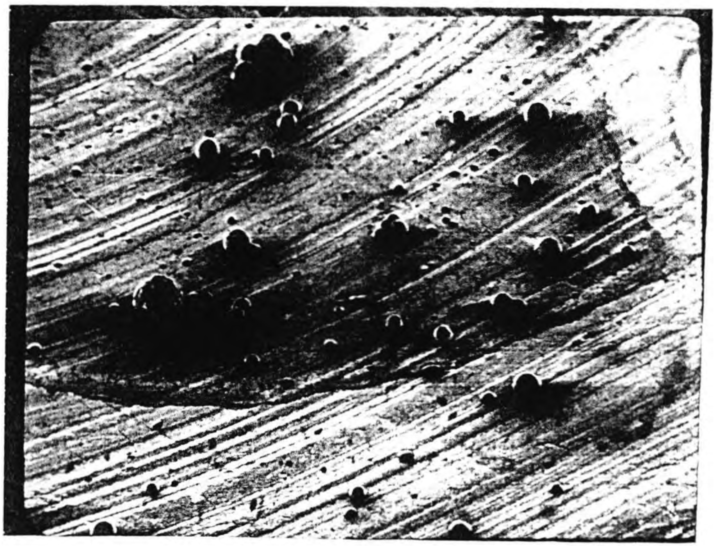
In Section §6.6.3.4, descriptions are given of emulsion polymerisations carried out using different amounts of PVA in the aqueous phase. The results of emulsion polymerisations using different amount of PVA are also shown in Table 10.6. Clearly, higher conversion and small mean particle size can be obtained with higher PVA concentration. Also, the tendency for polymer particle agglomeration was reduced when a high PVA concentration was used.

Table 10.6 Results of Redox-Induced Emulsion Polymerisations of EHA

Procedure Used for Polymerisation		Weight of PVA used (g)	Properties of Resultant Latexes		
monomer emulsification	continuous homogenisation during reaction		mean particle size (μm)	Conversion (%)	Stability
No	No	4.0		81.0	unstable after polymerisation
Yes	No	4.0	5.42	91.0	stable after polymerisation
		1.5		83.5	unstable after polymerisation
Yes	Yes	8.0		very high	stable after 4 months
		4.0	3.51	96.0	stable after 4 months
		2.0		45.3	unstable after 4 months
		1.5	10*	68.0	unstable after 4 months
		0.5		32.0	unstable after 1 week

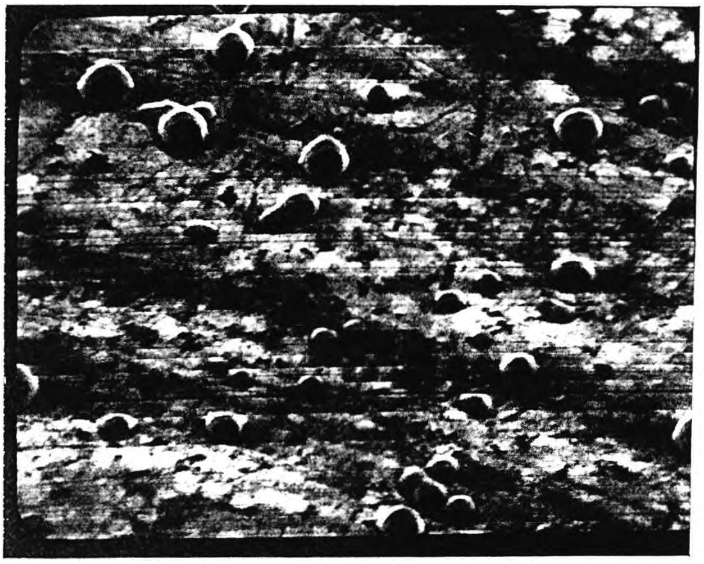
*estimated from SEM photograph

The SEM photographs of the resultant polymer emulsions are shown in Fig.10.33–Fig.10.35.



40 µm

Fig.10.33 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using Ammonium Persulphate/Sodium Persulphate as the Initiator and 0.5 g of PVA as the Protective Colloid under Continuous Homogenisation



10 µm

Fig.10.34 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using Ammonium Persulphate/Sodium Persulphate as the Initiator and 2.0 g of PVA as the Protective Colloid under Continuous Homogenisation

10 μm

Fig.10.35 SEM Photograph of Polymer Latex Produced by Emulsion Polymerisation of EHA using Ammonium Persulphate/Sodium Persulphate as the Initiator and 8.0 g of PVA as the Protective Colloid under Continuous Homogenisation

10.5 Summary

The work described in this chapter can be summarised as follow:

- The rate of UV–induced emulsion polymerisation was increased when using continuous ultrasonic homogenisation, possibly due to the better exposure of the reaction mixture to the UV–irradiation. No effects of ultrasonic homogenisation on the rate of thermally initiated emulsion polymerisations and redox-induced emulsion polymerisations were observed.
- Continuously applied homogenisation has played an important role in preventing particle agglomeration and in maintaining a high concentration

of M/P particles during emulsion polymerisations. With continuous homogenisation, the final latex product has a smaller mean particle size than that produced without continuous ultrasonic homogenisation. This is true for both UV-induced, thermally-induced and redox-induced emulsion polymerisations.

- The polymer particles of the final emulsion produced under continuous homogenisation show a bimodel particle size distribution. The small particle were presumably formed by the growth of homogeneously nucleated primary particles, and most of the large particles were probably formed by direct polymerisations within the monomer droplets. The adsorption of WB4698 molecules on the oil/water interfaces and the partition of the co–initiator amine in the aqueous phase and in the monomer phase might be responsible for the bimodel molecular weight distribution during UV–induced emulsion polymerisations.

- In the cases where there is partition of the co–initiator amines, bimodel molecular weight distributions were observed in the UV–induced emulsion polymerisations.

- When using Igepal CO–990 (a nonionic surfactant) as the emulsifier, the rate of emulsion polymerisation was increased. Moreover, a small mean particle size was obtained. It is evident that Igepal CO–990 is more efficient than PVA in stabilising the M/P particles.

- The molecular weight of the polymer produced in the presence of Igepal CO–990 is lower than that produced in the presence of PVA. The effect of the emulsifier system on the molecular weight of the polymer produced may be too complicated to be easily understood.

Chapter 11

Poly(2–ethylhexyl acrylate) Suspensions and Emulsions as Pressure–Sensitive Adhesives (PSAs)

11.1 Introduction

Poly(2–ethylhexyl acrylate) suspensions and emulsions have been prepared in the whistle reactor (see Chapters 9 and 10). Some aspects of pressure–sensitive adhesives (PSAs) have been described in Chapter 3. In this chapter, adhesive properties of the poly(2–ethylhexyl acrylate) suspensions and emulsions produced in the whistle reactor are characterised and compared with that of solvent–based systems which have already been described in Chapter 7.

It has long been accepted that the best pressure–sensitive performance is achievable by solvent–based PSA systems, and still solvent–based PSAs are common in PSA manufacturing. However, aqueous–based PSAs are becoming increasingly used because they possess many advantages (see Chapter 3). The advantages of the aqueous–based PSA are obtained at the expense of the good tack and good humidity resistance. This is particularly true if a significant amount of emulsifier is present in the system. It has been the target of the present work to eliminate emulsifiers in the preparation of polymer suspensions and emulsions (polymer suspensions and emulsions are here commonly referred to as polymer latexes). It has been successful in producing polymer latexes in the whistle reactor without the use of emulsifiers. However, it has not been possible to eliminate the protective colloid (PVA) in order to obtain stable polymer latexes. Thus the PVA present in the polymer latexes may also decrease their adhesive performance.

11.2 Peel Adhesion

The peel adhesion tests of polymer latexes have been described in §6.7.5. The peel adhesion test results are summarised in Table 11.1. The peel adhesions of polymer latexes prepared are all below 500 g/0.5 inch. In comparison, the maximum peel adhesion for the solvent–based systems are 810 g/0.5 inch [see Table 6.4 for the peel adhesion testing results of poly(2–ethylhexyl acrylates) prepared by solution polymerisations]. Polymer latex No.3 has a weight average molecular weight of 610101 which is similar to that of the poly(2–ethylhexyl acrylate) prepared by solution polymerisation in a batch reactor (weight average molecular weight 512964). However, this polymer latex does not possess equivalent values of peel adhesion for the solvent-based systems, and neither do the other polymer latexes in Table 11.1. Thus it may be the case that the peel adhesion depends both on the molecular weight distribution and the average molecular weight. Latexes No.1and No.2 have relatively high polydispersities $\left(\frac{M_w}{M_n}\right)$ and low peel adhesions compared with latexes No.3 and No.4. Moreover, during the preparation of the polymer samples for GPC measurements, it was noticed that there are significant amounts of insoluble gels (which may be polymers with branching or polymers with very high molecular weight) in polymer latexes No.1 and No.2. However, only a small amount of insoluble gels was present in polymer latex

No.3, and no insoluble gels were found in polymer latex No.4. Thus the low peel adhesions for latexes No.1 and No.2 may due to the presence of insoluble high molecular weight polymers and polymer gels. The insoluble high molecular weight polymers and polymer gels increase the cohesive strength of the polymer but decrease the wetting ability of the polymer on the substrate, and this results in poor peel adhesion.

Table 11.1 Peel and Tack Adhesions and Molecular Weights of Polymer Latexes Prepared Using Different Initiator/Coinitiator/Emulsifier/Protective Colloid Combinations

Latex No.	Initiator/ Coinitiator	Emulsifier/ Protective Colloid	Weight Average Molecular Weight	$\frac{M_w}{M_n}$	Tack (g)	Peel Strength (g/½inch)
1	BME	PVA	245000*	14*	negligible	negligible
2	BME	PVA	125684*	14.2*	209	138
3	WB4698 /BDEA	PVA	610101	3.7	1123	405
4	WB4698 /MDEA	Igepal Co-990	1055858	8.0	1977	225
5	ABQ /MDEA	Igepal Co-990	---------	---	1909	250
6	AICA	PVA	---------	---	182	negligible
7	AICA	PVA	238511	---	469	50

* These values may not be accurate because of the exclusion of high molecular weight polymer fractions and polymer gels.

Latex No.6 was prepared by the copolymerisations of EHA and VA. As can be seen from Table 11.1, the adhesive properties of this latex is not satisfactory. The poor adhesive properties might be a result of high molecular weight of the copolymer. Using the same polymerisation procedure as that for the preparation of latex No.6, latex No.7 was produced in the presence of a chain transfer agent i.e. 1—dodecanthiol. As shown in Table 11.1, the resultant latex No.7 has a low average molecular weight and it has better adhesive properties than latex No.6.

11.3 Tack

In order to further explore the effects of the insoluble high molecular weight polymer fractions and polymer gels on the pressure-sensitive properties, the polymer latexes were characterised by tack test. The detailed testing procedure has been described in §6.7.4. The test results are also summarised in Table 11.1. Again, low tack values were obtained for latexes No.1 and No.2. The presence of polymer gels and extremely high molecular weight polymer fractions increased the rigidities of the polymers and thus resulted in poor wetting on the substrates. From Table 11.1, it can be seen that the best pressure-sensitive tack was obtained for polymer latex No.4 because of the absence of insoluble polymer gels.

11.4 Advantages and Disadvantages of the Aqueous–based Systems and the Solvent–based Systems

The polymer latexes produced in the whistle reactor can be used as pressure–sensitive adhesives. Polymer latexes No.3, No.4 and No.5 in Table 11.1, for example, showed fairly good pressure–sensitive properties. Unsatisfactory pressure-sensitive properties were found for other polymer latexes which probably need regulation of the average molecular weights and molecular weight distributions, and perhaps, most importantly, the elimination of the insoluble polymer gels. The procedure for the preparation of pressure–sensitive adhesives using the whistle reactor is simple compared with conventional emulsion polymerisation, yet it possesses all the advantages of emulsion-based pressure–sensitive adhesives. However, as can been seen from the characterisation results of the polymer latexes and the solvent–based systems, the pressure–sensitive properties obtained for the polymer latexes are not as good as the solvent–based ones. To improve the performance of the polymer latexes as pressure–sensitive adhesives, further work is necessary to eliminate the use of PVA.

11.5 Summary

- The polymer latexes produced in the whistle reactor can be used as alternatives for the solvent–based ones, but need further improvement.
- The average molecular weight and molecular weight distribution are both important in determining the pressure-sensitive properties. One effective way for the reduction of molecular weight is to using a chain transfer agent i.e. 1-dodecanthiol.
- The presence of insoluble high molecular weight polymer fractions and polymer gels are detrimental for the desired pressure–sensitive properties.
- The presence of insoluble gels and high molecular weight polymer fractions in the polymer latexes enables the accurate determination of the weight average molecular weights.
- Further work on the study of the insoluble gel formation during suspension and emulsion polymerisation seems to be necessary.

Chapter 12

Conclusions

(i) Solution Polymerisation

The PSAs prepared by solution polymerisation possess very good adhesive properties.

(ii) Monomer Emulsification

The stability of the pre–emulsified monomer emulsion depends on three factors:

The operating condition of the ultrasonic homogenizer

The composition of the monomer/water mixture to be emulsified, in particular the concentration of the protective colloid i.e. PVA used. There is a limit for the concentration of PVA below which the monomer emulsion becomes very unstable and phase–separates soon after homogenisation. The concentration of the PVA used during suspension or emulsion polymerisations should be above this limit. Monomer pre–emulsification proves to be important in preventing polymer particle agglomeration during the foregoing suspension or emulsion polymerisation processes. In most cases where PVA was used as the protective colloid, the polymerisation systems became unstable during polymerisation without monomer pre–emulsification.

(iii) Polymerisations in the Whistle Reactor

Stable polymer latexes can be produced by emulsion and suspension polymerisations in the whistle reactor.

It seems that the particle nucleation of the suspension polymerisation systems in the present work takes place not only in monomer droplets but also in the true aqueous phase. On the other hand,in UV–induced emulsion polymerisations, the partition of the co–initiator amine in the aqueous phase and in the monomer phase may result in the particle nucleation in both the monomer droplets and the true aqueous phase.

Continuously applied homogenisation has played an important role in preventing particle agglomeration and in maintaining a high concentration of M/P particles during both suspension and emulsion polymerisations. The polymer suspensions produced in the whistle reactor with continuous homogenisation have a slightly smaller mean particle size than those produced by suspension polymerisation without continuous homogenisation. This is due to the decreased number of oversized polymer particles as a result of breakup of particle agglomerates by ultrasonic homogenisation. The latex produced by emulsion polymerisation under continuous homogenisation has a smaller mean particle size than that produced without continuous ultrasonic homogenisation. This is true for UV–induced, thermally–induced and redox–induced emulsion polymerisations.

The polymer latexes produced in the whistle reactor can be used as alternatives for the solvent–based ones, but need further improvement. The presence of insoluble high molecular weight polymer fraction and polymer gels are detrimental for the desired pressure–sensitive properties. The presence of insoluble gels and high molecular weight polymer fractions in the polymer latexes enables the accurate determination of the weight average molecular weights. It was attempted to reduce the molecular weight of the polymer by using a chain transfer agent i.e. 1-dodecanthiol. The adhesive properties were improved to some extent but were still not satisfactory. Further work on the study of the insoluble gel formation during suspension and emulsion polymerisation seems to be necessary.

Appendix I

Algorithm for the Calculation of MRR

The most popular mathematical model for the description of copolymerisation kinetics is the well known Mayo-Lewis equation:

$$\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]} \qquad (1)$$

In the present work a new method for calculating monomer reactivity ratios based on the integrated Mayo-Lewis equation has been derived as follow:

By introducing $J = \frac{[M_1]}{[M_2]}$, $\frac{d\,[M_1]}{d\,[M_2]} = \frac{[M_2]\,dJ}{d\,[M_2]} + J$, equation (1) can be reformed to,

$$\frac{[M_2]\,dJ}{d\,[M_2]} + J = \frac{r_1 J + 1}{\frac{r_2}{J} + 1} \qquad (2)$$

i.e.

$$\frac{d\,[M_2]}{[M_2]} = \frac{\frac{r_2}{J} + 1}{r_1 J + 1 - r_2 - J}\,dJ \qquad (3)$$

Integration of equation (3) from time 0 to time t gives,

$$Y = \left(\frac{X}{Z}\right)^{\frac{k_2}{k_1} - 1} \times \left(\frac{Z + k_1}{X + k_1}\right)^{\frac{k_2}{k_1} - 1 - k_2} \qquad (4)$$

where $Y = \frac{[M_2^t]}{[M_2^0]}$, $X = \frac{[M_1^t]}{[M_2^t]}$, $Z = \frac{[M_1^0]}{[M_2^0]}$, $k_1 = \frac{1 - r_2}{r_1 - 1}$, $k_2 = \frac{1}{r_1 - 1}$.

Equation (4) can be further transformed to equation (5),

$$k_2 = \frac{P + N - Q}{\frac{N - Q}{k_1} + Q} \qquad (5)$$

where $P = \ln Y$, $Q = \ln\left(\frac{X + k_1}{Z + k_1}\right)$, $N = \ln\left(\frac{X}{Z}\right)$.

For a given value of k_1, the value of k_2 can be readily calculated from equation (5). An almost straight line of k_1—k_2 will be derived from each experiment. The intersection point of the k_1—k_2 lines from several experiments can be determined by a computer programme using a least-square minimisation of $\Delta k_2 = \left(\frac{\sum_{i=1}^{i=n} (k_{2i} - \bar{k}_2)^2}{n}\right)^{1/2}$. The values of k_1 and k_2 at this intersection point are taken as the corresponding values for the monomer reactivity ratios $r_1 = 1 + \frac{1}{k_2}$, $r_2 = 1 - k_1 (r_1 - 1)$ to be determined. The standard deviation of r_1 and r_2 can be estimated by,

$$\Delta k_1 = \left(\frac{dk_1}{dk_2}\right)\Delta k_2$$

$$\Delta r_1 = \left|\frac{\Delta k_2}{k_2^2}\right|$$

$$\Delta r_2 = \left|\Delta r_1\, k_1\right| \pm \left|\Delta k_1 (r_1 - 1)\right|$$

Appendix II

Basic Programme for Calculating Reactivity Ratios

```
10  DIM W1(4), W2(4), C(4), F1(4), M10(4), M1(4), M2(4), K2(4), K1(100)
20  DIM Y(4), X(4), Z(4), P(4), Q(4), N(4)
30  REM this programme calculates reactivity ratios
40  REM based on the total conversion and average copolymer composition
50  REM M10 and M20 are the initial molar concentrations of monomer1 and monomer2
60  REM F1 is the molar percentage of monomer1 in copolymer
70  REM CW is the monomer total conversion in weight
80  REM MW1, MW2 are molar masses of monomer1 and monomer2
90  REM W1 and W2 are weights of monomer1 and monomer2 in feed
100 INPUT MW1, MW2
110 FOR J=1 TO 4
120 READ W1(J), W2(J), C(J), F1(J)
130 C(J)=C(J)*(W1(J)+W2(J))/((W1(J)/MW1+W2(J)/MW2)*((1-F1(J))*MW2+F1(J)*MW1))
140 NEXT J
150 K1(0)=0.13
160 FOR K=1 TO 100
170 S=0
180 K1(K)=K1(K-1)+0.001
190 PRINT "K1=";K1(K)
200 FOR I=1 TO 4
```

```
210  M10(I)=W1(I)/MW1
220  M20(I)=W2(I)/MW2
230  M1(I)=M10(I)-F1(I)*C(I)*(M10(I)+M20(I))
240  M2(I)=M20(I)-(1-F1(I)*C(I)*(M10(I)+M20(I))
250  Y(I)=M2(I)/M20(I)
260  X(I)=M1(I)/M2(I)
270  Z(I)=M10(I)/M20(I)
280  P(I)=LOG(Y(I))
290  Q(I)=LOG((X(I)+K1(K))/(Z(I)+K1(K))
300  0N(I)=LOG(X(I)/(Z(I))
310  K(I)=(P(I)+N(I)-Q(I))/((N(I)-Q(I))/K1(K)+Q(I))
320  S=S+K2(I)
330  PRINT "              K2=";K2(I)
340  NEXT I
350  S=S/4
360  B=0
370  FOR U=1 TO 4
380  B=B+(S-K2(U))*(S-K2(U))
390  NEXT U
400  B=SQR(B/4)
410  PRINT "                B=";B
420  NEXT K
430  DATA 150, 50, 0.704, 0.8405, 110, 90, 0.605, 0.7122, 80, 120, 0.456,
     0.6181
440  DATA 60, 140, 0.3385, 0.5758
450  END
```

Appendix III

Specification of Minisonic 4005

Working Dimensions (Case Size):

Height	50 cm
Width	50 cm
Length	106 cm

Capacity Of Glass Vessels:

3 litres each

Nominal Throughput:

2 litres/min

Operating Pressure:

160 - 180 PSIG

Power Supply:

220/240V Single Phase 50 Hz

Motor Rating:

HP (0.375 kw) at 1425 RPM

Shipping Weight :

1701 b (76 kg)

Manufacturer:

Lucas Dawe Ultrasonics Limited,
Concord Road,
West Avenue,
London W3 0SD
Telephone :01 992 6751

Appendix IV

Algorithm for the Mean Particle Size Estimation

The mean particle sizes are calculated using the following equation:

$$S_m = \frac{\sum_{i=1}^{i=n} \left\{ \frac{W_{i-1}\,(S_i + S_{i-1})}{2} \right\}}{\sum_{i=1}^{i=n} \left\{ W_{i-1} \right\}}$$

S_i : the upper band size
S_{i-1} : the lower band size
W_{i-1} : weight in band
S_m : mean particle size

Appendix V

Basic Programme for Calculating the Mean Particle Size

```
10  MODE3
20  REM this programme calculates the average particle size
30  DIM SU(20),SL(20),VL(20),VU(20),VA(20),W(20)
40  INPUT "What is the weight below 1.2 micron ?", WEIGHT(0)
50  SIZE(0) = 0
60  A=0
70  B=0
80  FOR I=1 to 15
90  READ SIZE(I):INPUT"Weight in band",WEIGHT(I)
100 SA(I)=(SIZE(I)+SIZE(I-1))/2
110 A=A+WEIGHT(I-1)*SA(I)
120 B=B+WEIGHT(I-1)
130 NEXT I
140 SM=A/B
150 PRINT "          MEAN SIZE: "; SM
160 DATA 1.2, 1.5, 1.9, 2.4, 3.0, 3.9, 5.0, 6.4, 8.2, 10.5, 13.6, 17.7, 23.7,
    33.7, 54.9
170 END
```

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