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Historic Overview

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1.1 The Early Stages

Polymers are composed of very large molecules, each of which includes a large number of repeating structural units. The oldest and most abundant group of polymers consists of the natural polymers, such as cellulose, proteins, rubbers, and so on. One of these, natural rubber, occurs in the form of a latex, that is defined as the “viscid, milky juice secreted by the laticiferous vessels of several seed-bearing plants, notably *Castillia elastica*,” and so on (Bovey *et al.*, 1955). By far the most important natural latex is that obtained from the rubber tree *Hevea brasiliensis*. This tree, originally from Brazil, as may be deduced from its name, was transplanted to Malaya, Sri Lanka and the East Indies (Hauser, 1930) in 1876, and eventually has made this area the most important source of natural rubber. The latex that is obtained from the tree is usually denoted as “natural latex” and is a colloidal suspension of rubber particles stabilized by protein. The rubber content of the latex is between 32 and 38% by weight, the protein 1 to 2%, different natural sugars about 2% and about 0.5% of inorganic salts (Hauser, 1930). The rubber particles vary largely in size from quite small, circa 50 nm, up to 1–2 micrometres. The rubber latex is coagulated, washed and worked into sheets that form the basis for further industrial use.

In view of the latex origin of natural rubber, it was not surprising that, when the need for a synthetic equivalent arose, the mimicking of natural rubber latex was an obvious starting point. The effort, and great success, of making synthetic rubber by emulsion polymerisation has led to the word “latex” eventually being used to refer to a colloidal suspension of *synthetic* polymers, as prepared by emulsion or suspension polymerisation. Such *synthetic latexes* are to be distinguished from dispersion of polymers prepared by grinding the polymer with water and a dispersing agent. This chapter will treat the early

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stages of the “invention” and production of synthetic latexes by emulsion polymerisation from the beginning and up to the middle of the twentieth century. Several reviews and book chapters on the early developments in emulsion polymerisation have already been written, and have been a natural starting point for this text. One of the first reviews is that of Hohenstein and Mark from 1946 (Hohenstein and Mark, 1946). The following is a direct quotation from their work (reprinted from J. Polymer Sci., by permission):

The earliest observations on polymerisation of olefins and diolefins as far back as 1838 (Mark and Rafft, 1941; Regnault, 1838) refer almost entirely to the pure liquid phase and describe the gradual transition from a liquid monomer to a viscous or solid polymer under the influence of heat, light, or a catalytically active substance. The idea of using a finely divided monomer in an aqueous suspension or emulsion seems to have been first conceived, about 1910, by Hofman and Delbrück (Hofman and Delbrück, 1909, 1912) and Gottlob (Gottlob, 1913). There were two main reasons for the desire to carry out the polymerisation of various simple dienes in the presence of a diluting agent: one, the fact that the use of metallic sodium as catalyst, which was common practice at that time, led to highly heterogeneous materials and posed a rather difficult problem regarding the complete removal of the alkali metal from the final polymer. The more important incentive for the use of an aqueous system, however, were the facts that all native rubbers occur in the form of latexes and that, obviously, polymerisation in the plant takes place under mild conditions in an aqueous phase without the application of elevated temperatures and high pressures, and certainly without the use of such catalysts as metallic sodium or alkali alkyls.

The aim of reproducing the physiological conditions occurring in the plant is mentioned in some of the earlier disclosures (Gottlob, 1913; Hofman and Delbrück, 1909, 1912), and led to the preparation and stabilization of the “emulsions” as described in these patents *not* with the aid of soap or other surface-active agents, but by application of hydrophilic protective colloids such as gelatin, egg albumin, starch, milk, and blood serum. Certain remarks in the text of these patents indicate that these protective colloids not only emulsify the hydrocarbon monomer but may also act as catalysts during the polymerisation. We have carried out a number of polymerisations, following closely the methods given as examples in two of these patents and have substantially confirmed the results of the claims. In these experiments we observed a *very slow, partial* conversion of the monomer (isoprene, dimethylbutadiene) into a polymer latex. The total amount of polymer formed varied between 40% and 80%; the duration of the reaction was in certain cases as much as six weeks. The results, in general very erratic and almost irreproducible, create the impression that the reaction under such conditions could be considered a *suspension polymerisation* catalyzed by the oxygen of the air, which was never specifically excluded in any of the examples. In order to check this conclusion we repeated a few experiments of this type with deaerated monomer and deaerated water under nitrogen and found that under these conditions only *extremely slow* polymerisation can be observed. In some instances conversion was not achieved at all.

It seems, therefore, that the early practice, as disclosed in the above-mentioned patents, is substantially different from what is known today as emulsion polymerisation, and is essentially a suspension polymerisation in which the protective colloids act as suspension stabilizers and which is catalyzed by the presence of small amounts of oxygen.

In 1915 and 1916, Ostromislensky (Ostromislensky, 1915, 1916; Talalay and Magat, 1945) carried out similar experiments with vinyl halides and discussed the advantages of the presence of an inert diluent. However, since there is no mention of the use of soap or other micelle-forming substances in his articles either, it seems that his observations also refer to “uncatalyzed” or photocatalyzed polymerisation in solution and suspension.

It was only in 1927 that the use of *soap* and similar substances (ammonium, sodium, and potassium oleates, sodium butylnaphthalene sulphonate) was disclosed in patents by Dinsmore (Dinsmore, 1927) and Luther and Heuck (Luther and Heuck, 1927). The examples cited in these disclosures approach present practice to a considerable degree; they specify the simultaneous use of emulsifiers and catalyst (water- or monomer-soluble peroxides) and describe conversions and reaction times of the same order of magnitude as reported in more recent scientific articles. It seems, therefore, that the use of catalyzed emulsion polymerisation is about twenty years old (in 1946, Ed. note).

In the years following a large number of additional patents accumulated, with an almost confusing multitude of disclosures and claims (compare references (Hoseh, 1940, 1941; Scheiber, 1943; Talalay and Magat, 1945)). On the other hand, during this same period (1930–1940) only very few articles were published in scientific journals. Dogadkin (1936) and his collaborators (Balandina *et al.*, 1936a, 1936b; Berezan, Dobromyslowa, and Dogadkin, 1936) studied the polymerisation of butadiene in the presence of soap, peroxides, and other catalysts at different temperatures and investigated the kinetics of this reaction. Fikentscher (Fikentscher, 1934), at a meeting of the Verein Deutscher Chemiker in 1938, gave a general description of the course of emulsion polymerisation of dienes and advanced, for the first time, the hypothesis that polymerisation takes place essentially in the aqueous phase and not inside the monomer droplets. In 1939, Gee, Davies, and Melville (Gee, Davies, and Melville, 1939) investigated the polymerisation of butadiene vapour on the surface of water containing a small amount of hydrogen peroxide and came to certain conclusions about the kinetics of this process. While the mechanism of emulsion polymerisation was thus only infrequently and briefly discussed in the scientific literature between 1930 and 1940, much work was carried out during this same period in the research departments of various industrial organizations, as shown by the large number of patents filed and issued in many countries.

One of the authors (H. M.) had an opportunity to discuss the problem of emulsion polymerisation in the period between 1935 and 1938 with Drs. Fikentscher, H. Hopff, and E. Valko in Ludwigshafen am Rhine. At that time they offered several arguments in favour of polymerisation taking place preponderantly in the aqueous phase. Valko even considered it as highly probable that the monomer, solubilised in the micelles of the soap solution, was most favourably exposed to the action of a water-soluble catalyst and, therefore, might be considered as the principal site of the reaction. At a seminar on high polymers in Kansas City in September, 1945, Dr. F. C. Fryling told us that he had, at the same time, independently arrived at very similar conclusions on the basis of his own observations. It appears, therefore, that some of the more recent developments were anticipated to a certain extent in the unpublished work between 1930 and 1940.

No work in emulsion polymerisation was published in the next three years, except for brief references in the books of Mark and Raft (Mark and Raft, 1941) and of Scheibler (Scheiber, 1943). In 1941, Fryling (Fryling, 1944) described a very useful method for carrying out emulsion polymerisation experiments in 10-gram systems and, together with Harrington (Fryling and Harrington, 1944), investigated the pH of mixtures of aqueous soap solutions and substituted ethylenes, such as acrylonitrile, styrene, etc.; they concluded that the monomer which was solubilized in the McBain layer micelles (McBain, 1942; McBain and Soldate, 1944) was very likely to be the most important site for initiation of polymerisation. Hohenstein, Mark, Siggia, and Vingiello (Hohenstein, 1945; Hohenstein, Siggia, and Mark, 1944a; Hohenstein, Vigniello, and Mark, 1944b) studied the polymerisation of styrene in aqueous solutions without soap and in aqueous emulsions in the presence of soap. At the New York meeting of the American Chemical Society in September, 1944, Vinograd delivered three excellent lectures (Vinograd, Fong, and Sawyer, 1944) on the polymerisation of styrene in aqueous suspension and emulsion. At the same meeting, Frilette (Frilette, 1944) reported on experiments on the polymerisation of styrene in very dilute aqueous systems.

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In 1945, Hohenstein, Siggia, and Mark (Siggia, Hohenstein, and Mark, 1945) published an article on the polymerisation of styrene in agitated soap emulsions, and Hughes, Sawyer, and Vinograd (Hughes, Sawyer, Vinograd, 1945), Harkins (Harkins, 1945a), and Harkins with a number of collaborators (Harkins 1945b) contributed very valuable x-ray data on the McBain micelles (McBain, 1942) before, during, and after polymerisation. In the same year, two very interesting articles appeared, by Kolthoff and Dale (Kolthoff and Dale, 1945) and Price and Adams (Price and Adams, 1945), on the influence of catalyst concentration on the initial rate of polymerisation; and Montroll (Montroll, 1945) developed a general phenomenological theory of processes during which diffusion and chemical reaction cooperate in the formation of large molecules.

A large amount of basic research was carried out on all phases of emulsion polymerisation as part of the government rubber program, most of which has not yet (1946, ed. note) been released for publication. [The paper of Kolthoff and Dale (Kolthoff and Dale, 1945) was part of this program and was published with the permission of the Rubber Reserve Company, Washington, D. C.] One can, therefore, look forward in the not too distant future to many informative articles in this field.

As far as our present knowledge goes, it seems appropriate to distinguish between the following three types of vinyl polymerisation of diluted monomers:

1. Polymerisation in *homogeneous solution* in which the monomer, all species of the polymer molecules, and the initiator (catalyst) are soluble in the diluting liquid (e.g., styrene polymerisation in toluene with benzoyl peroxide). If the solution is sufficiently dilute, such a process begins and ends in a completely homogeneous system with a dilute molecular solution of the monomer at the beginning and a dilute molecular solution of the various species of the polymer at the conclusion of the reaction. A number of recent papers (see original publication) describe studies on olefin polymerisations under such conditions. If the system is not sufficiently dilute, toward the end of the reaction a concentrated polymer solution is obtained containing aggregations and entanglements of the macromolecules which represent a certain deviation from molecularly homogeneous dispersion. A particularly interesting case of solution polymerisation occurs if the monomer is soluble in the liquid, whereas certain species of the polymer, namely, those of higher degrees of polymerisation, are insoluble in it. The polymerisation of styrene, the copolymerisation of vinyl chloride and vinyl acetate in methanol, and the polymerisation of acrylonitrile in water are examples of reactions that start in a molecularly homogeneous phase but continue and end in a system consisting of a swollen gel and a supernatant liquid solution.
2. Polymerisation in heterogeneous suspension, in which the monomer is mechanically dispersed in a liquid, not a solvent for it and for all species of polymer molecules. The initiator is soluble in the monomer. In such cases polymerisation takes place in each monomer globule and converts it gradually into a polymer “bead” or “pearl”; the liquid plays only the role of a carrier, which favours heat transfer and agitation but does not interfere with the reaction as such. The polymerisation of styrene or dichlorostyrene in aqueous dispersion is an example of such a process. It must, however, be noted that the monomer is never completely insoluble in any carrier liquid and, in certain cases, such as bead polymerisation of vinyl acetate in water, is even fairly soluble in it. These reactions are, then, processes in which solution polymerisation and suspension polymerisation occur simultaneously in the different phases of the heterogeneous system—the former in the aqueous, the latter in the monomer, phase. The amount of polymer formed in each phase depends upon the solubility of the monomer in water, and upon the distribution of the catalyst or catalysts in the two phases. If the monomer is only moderately soluble in water, the amount of polymer formed in the aqueous phase is not considerable but its degree of polymerisation is low, because of the small monomer

concentration, and one obtains a polymer containing a noticeable amount of low molecular weight species. In fact, polymers prepared under such conditions occasionally show a molecular weight distribution curve with two distinct peaks, the smaller of which corresponds to the lower molecular weight. This effect is exaggerated if, for some reason, one increases the solubility of the monomer in the aqueous phase by the addition of organic solvents like methanol, alcohol, or acetone. This consideration shows that suspension polymerisation can be a fairly complex process the complete elucidation of which is rather difficult. In the articles which attempt to contribute quantitative results (Hohenstein, 1945; Hohenstein, Vigniello, and Mark, 1944b; Vinograd, Fong, and Sawyer, 1944), monomers and catalysts were selected which are only very slightly soluble in water and probably approach the case of a heterogeneous suspension polymerisation to a fair degree. Another factor which may complicate the elucidation of suspension polymerisation is the use of suspension stabilizers, which may solubilize part of the monomer and, therefore, create an intermediate case between solution and suspension polymerisation.

3. Polymerisation in emulsion, in which the monomer is: (a) *dispersed in monomer droplets* stabilized by an adsorbed layer of soap molecules (Fryling and Harrington, 1944; Vinograd, Fong, and Sawyer, 1944; Kolthoff and Dale, 1945; Price and Adams, 1945; Siggia, Hohenstein, and Mark, 1945); (b) solubilised in the soap micelles (McBain, 1942; McBain and Soldate, 1944; Harkins, 1945a) which exist in an aqueous soap solution of sufficient concentration; and (c) molecularly dissolved in the water. The amount of polymer formed in the droplets, in the micelles, and in solution will depend upon the way in which the monomer and catalyst are distributed in the *three* existing phases: the monomer phase, the soap micelle phase, and the water phase – and possibly also upon the accessibility and reactivity of the monomer in these three phases. In certain aqueous soap emulsions, such as styrene, dichlorostyrene, or isoprene, the amount of molecularly dissolved monomer is small and, therefore, the reaction will occur preponderantly either in the monomer droplets or in the soap micelles. If the polymer formation occurs preponderantly in the micellar phase, one is inclined to speak of a typical *emulsion* polymerisation. If, however, polymerisation takes place to a considerable extent both in the monomer droplets and the soap micelles, the case is intermediate between *suspension* and *emulsion* polymerisation. There also exist emulsion polymerisations (vinyl acetate, acrylonitrile) in which the *monomer* is substantially soluble in water and a reaction which is a superposition of solution, suspension, and emulsion polymerisation is expected.

These brief remarks suffice to show that one must select the system for investigation with care if complications and overlapping between different types of reactions are to be avoided.

This citation tells much about the early start of our understanding of the emulsion polymerisation mechanisms, even though, at that time, a quantitative theory was not yet developed. Basic understanding of the relative importance of the aqueous, organic and micellar phases was also somewhat lacking. These topics will be treated thoroughly throughout this book. At this point, however, the very important, so-called, GR-S recipe for synthetic rubber must be mentioned. Even if the production of synthetic latexes was known in the 1930s, the cost was higher than that of natural rubber. However, the need for large amounts of synthetic rubber arose as a result of World War II, after the Japanese conquests in South East Asia. The secret United States Synthetic Rubber Program (1939–1945) resulted in the famous GR-S rubber recipe, the so-called “Mutual” recipe that was used for the first time by the Firestone and Goodrich companies in 1942 and adopted for large-scale production in early 1943 (Bovey *et al.*, 1955):

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Table 1.1 A typical recipe for a styrene-butadiene latex.

Ingredients	Parts by weight
Butadiene	75
Styrene	25
Water	180
Soap	5.0
n-Dodecyl mercaptan	0.50
Potassium persulfate	0.30

The American Chemical Society has declared this program as one of their “historic chemical landmarks”. By 1945, the United States was producing about 920 000 tons per year of synthetic rubber, 85% of which was GR-S rubber. As we see (Table 1.1), the recipe is quite simple, and each ingredient has its specific function. The 3 : 1 ratio (5.8 : 1 molar) of butadiene and styrene gives the polymer its useful physical properties. In addition, butadiene does not homopolymerise readily, and the copolymerisation with styrene gives the process a “normal” rate. The soap controls the nucleation and stabilization of the particles, whereas the potassium persulfate acts as initiator. The traditional soap used was a commercial fatty acid soap containing mainly C₁₆ and C₁₈ soaps, but the effect of different soaps from C₁₀ to C₁₈ was investigated. The role of the mercaptan has been debated, and it has been frequently stated that the mercaptan and persulfate form a redox couple. However, the most accepted role of the mercaptan is as an inhibitor and chain transfer agent: to inhibit the formation of cross-linked, *microgel*, particles during the polymerisation. When the rubber is used in end products, such as car tyres, and so on, it is cross-linked in its final shape, a process that is called vulcanisation. This utilizes the tetra-functionality of the butadiene (two double bonds), but this cross-linking is, naturally, not wanted during the emulsion polymerisation. Adding (amongst others) mercaptan to avoid this cross-linking action thus controls the process. The process is also stopped at 60–80% conversion and the monomers removed by flash distillation. The GR-S rubber recipe has been modified from the “Mutual” recipe over the years. Especially, the lowering of the polymerisation temperature to 5 °C has improved the process by increasing the achievable molecular weight. That again makes it possible to “extend” the polymer by adding inexpensive petroleum oils and rosin derivatives. Because persulfate is too slow as an initiator at such low temperatures, the development of more active (redox) initiator systems was required.

In Germany, production of synthetic rubber had also been developed during the War. These products were named Buna S (a butadiene-styrene copolymer) and Buna N (a butadiene-acrylonitrile copolymer) and these products were patented by the I.G. Farbenindustrie in the 1930s. In 1937 the annual German production of Buna S was 5000 tons. Though these were much more expensive than natural rubber, production was pushed ahead for the very same reasons the American synthetic rubber program was accelerated – the uncertain access to natural rubber under war conditions. After the war, the know-how that had been developed both in Germany and in the US was used in many other industrial emulsion polymerisation systems that began their development both before and after the war. Another example of this is neoprene rubber, poly(chloroprene)

[poly(2-chloro-1,3, butadiene)]. Because neoprene is more resistant to water, oils, heat and solvents than natural rubber, it was ideal for industrial uses, such as telephone wire insulation and gasket and hose material in automobile engines. Neoprene was developed at DuPont's research laboratory for the development of artificial materials; founded in 1928, the laboratory was being led by the famous chemist Wallace Hume Carothers. DuPont started production of this polymer in 1931, but improved both the manufacturing process and the end product throughout the 1930s. Elimination of the disagreeable odour that had plagued earlier varieties of neoprene made it popular in consumer goods like gloves and shoe soles. World War II removed neoprene from the commercial market, however, and although production at the Deepwater plant was stepped up, the military claimed it all. DuPont purchased a government-owned neoprene plant in Louisville, Kentucky, to keep up with increasing demand after the war.

The emulsion polymerisation of PVC was patented by Fikentscher and coworkers at the I.G. Farben already in 1931 (Fikentscher, 1931). PVC is a polymer that has many useful properties, among others very low permeability of small molecules such as air (oxygen) and water. In many examples, the use of water-soluble initiators and a range of emulsifiers including sulfonated organic derivatives, such as the sodium salts of Turkey Red Oil and diisobutyl naphthalene sulfonic acid, were described. This was the birth of the modern PVC emulsion polymerisation process and further development work continued both in Germany and in the US during the 1930s and eventually in the UK in the late 1930s. Because of Germany's lead in this field, the plants there continued with the emulsion process for most applications for a longer period after World War II, whereas in the US and the UK production methods changed from emulsion to suspension polymerisation for all but the plastisols and special applications. Polymerisation of PVC was also started as an emulsion process in Sweden in 1945 by (what became) KemaNord and in Norway in 1950 by Norsk Hydro. This was the origin of the Norwegian work with emulsion polymerisation (and also that of the present author).

We see from the citation above that Mark and Hohenstein mention the monomers styrene, dichlorostyrene, isoprene, vinyl acetate and acrylonitrile. After the invention of emulsion polymerisation, many monomers were investigated, but not all of these were of commercial interest. Further development of emulsion polymerisation of vinyl acetate and the acrylates, especially for paint and binder applications, first speeded up after the War, when more advanced copolymers were developed. This development is described further in Chapter 2.

In academia, these developments were closely paralleled by increasing understanding of the mechanistic and, subsequently, kinetic theories. Among these, the Harkins and Smith–Ewart theories are the most prominent and important. The Harkins theory has already been mentioned in the citation from Hohenstein and Mark above (Hohenstein and Mark, 1946). It appeared in a series of publications between 1945 and 1950 (Harkins, 1945a, 1945b, 1946, 1947, 1950). Harkins' interest was chiefly the role of the surface-active substances in emulsion polymerisation. The Harkins theory is, therefore, a qualitative theory, but it is often looked upon as the starting-point of all “modern” theories of emulsion polymerisation, see Figure 1.1. The essential features of the theory are (Blackley, 1975):

1. The main function of the monomer droplets is to act as a reservoir of monomer.
2. The principal locus of initiation of polymer particles is monomer swollen emulsifier micelles

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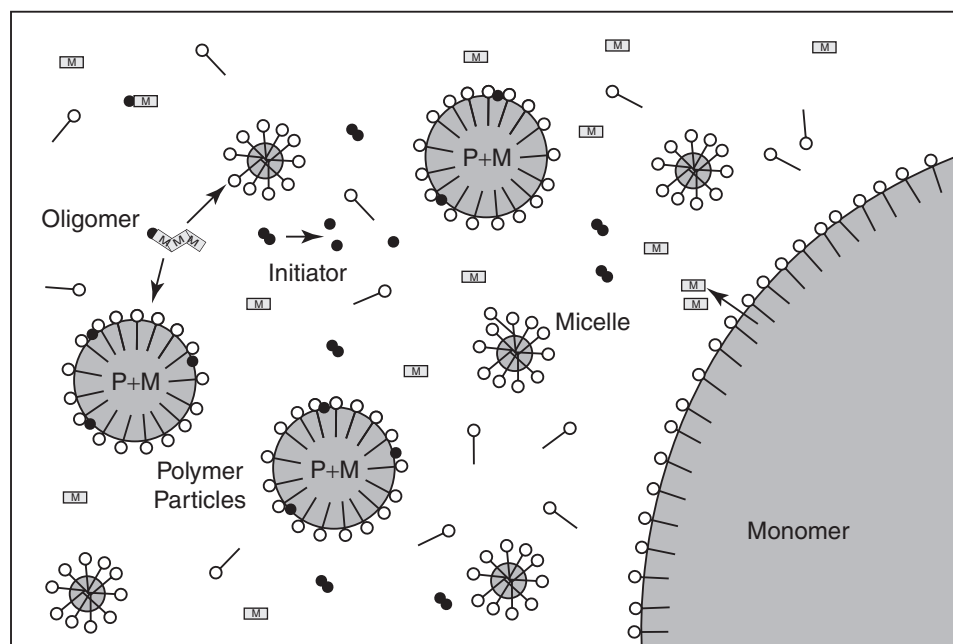


Figure 1.1 Cartoon of an emulsion polymerisation based on the Harkins theory. Ingredients are monomer, surfactant, and initiator. The surfactant forms micelles and the initiator is soluble in water. This “snapshot” is taken during Interval I, when particles are being formed and monomer is present both as free droplets, in aqueous solutions, in micelles and in already formed polymer particles. The surfactant is distributed as dissolved molecules, in micelles, adsorbed on polymer particles and on monomer droplets (to a lesser degree).

3. The main locus of polymerisation is the initiated polymer particles. During polymerisation monomer diffuses through the continuous phase and particles grow by this adsorption and subsequent polymerisation.
4. A small amount of particle nucleation can occur within the true aqueous phase. The significance of this nucleation is considered less and less important as the amount of soap increases.
5. Growth of the polymer particles leads to an increase in surface area. This increase leads to the adsorption of soap from the aqueous phase, which again leads to dissolution of micelles.
6. Nucleation stops when no more micelles are present and the major part of polymerisation takes place in the polymer particles.
7. Continual absorption of monomer into growing polymer–monomer (swollen) particles leads to the disappearance of the monomer droplets as a separate phase. This happens after micellar soap has disappeared, and the system therefore only consists of monomer–swollen polymer particles.

Harkins did not state explicitly how the water soluble initiator would be able to initiate the swollen monomer, and therefore “oil-rich” soap micelles. This detailed mechanism

was somewhat unclear at the time (maybe still is), but it has been assumed that the initial polymerisation takes place within the aqueous phase. How these polymers (oligomers) would be able to go into the micelles was not discussed. Harkins based his theory both on earlier opinions, as described above, and on experimental evidence. Building on the Harkins theory, the Smith–Ewart theory, which appeared in 1948, was the major leap forward in emulsion polymerisation. This is described further in Section 1.2.2 below.

1.2 The Second Half of the Twentieth Century

Following the pioneering work on synthetic rubber, and also other earlier patents such as that for neoprene and PVC, several new industrial processes were developed utilizing emulsion polymerisation. In the second half of the twentieth century emulsion polymerisation was developed to high sophistication, both experimentally and theoretically. It has indeed reached such a level of sophistication that it is called by many a “ripe” technology. This means that the major problems, both experimental and theoretical, have been solved and that current activities are concerned with reaping the profits and refining both products and theories. However, new developments are still possible, and theories are maybe not as solidified as may be imagined. In this section, the stages leading up to the present situation will be considered.

1.2.1 Product Development

As a part of the interest in more advanced applications of emulsion polymers, many have investigated the different ingredients in the polymerisation. In the beginning, different emulsifiers and different initiators were being developed. The GR-S recipe was, as mentioned, eventually modified with different soaps and with redox initiator systems in order to make it possible to run the process at lower temperatures. Earlier, other emulsifier systems, especially natural resins, had been tested. In the second part of the century, non-ionic emulsifiers were becoming more important. Among the most popular of these were the “Triton” and similar emulsifiers. These are nonyl- or octyl-phenols modified by ethylene oxide to give poly(ethylene glycol)-based emulsifiers. (Because of their toxicity these are now replaced by fatty alcohol-based polymers). It was shown early that these were not efficient for particle nucleation (see below), but excellent as emulsion stabilizers. They therefore became very popular as co-emulsifiers in addition to sulfates, sulfonates, and similar. In the same class come surface-active polymers, *protective colloids*. Many types of these have been developed, and they are used extensively in industrial production, either during polymerisation, or as post-additives to improve storage stability and other properties. There have also been efforts to develop surface-active initiators (“ini-surfs”) and copolymerisable emulsifiers (“surf-mers”). The idea behind this is to anchor the stabilizing groups better to the particle surface in order to improve stability. Many research groups have been working on this during the last quarter of the twentieth century, but successful commercial products are not abundant. The reason is probably that the combination of functionalities makes the emulsion polymerisation process more difficult to control and have several unexpected side effects. For instance will surface active initiators and/or monomers influence the nucleation process and make this more difficult to control.

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A post-war outgrowth of the synthetic rubber work found tremendous interest in the US for styrene butadiene rubber (SBR) dispersions for their utility in water-based latex paint. The first SBR was sold into architectural coatings application in 1948. Consumer desire for easy clean-up and new roller technology combined to make a rapid market shift. Sales of SBR latex increased extremely quickly, with 33% of solvent-based interior paints replaced by latex paint within four years of its introduction in 1947. Other polymers during the 1950s and 60s gradually replaced SBR. The deficiencies of SBR that account for this shift include colour stability and chalking. Styrene acrylics were introduced in 1953 to address some of these issues; current styrene acrylics are often sold as “modified acrylics” even though they may contain as much as 50% by weight styrene. The technology that is incorporated into acrylic gloss paints is based on over 40 years history of research and development by the world’s major polymer manufacturers. The first 100% acrylic emulsion polymer developed for use as a paint binder was introduced by the Rohm and Haas Company in 1953. This company had its early business in the production and sales of Plexiglas (PMMA homopolymer), and the introduction of emulsion polymers based on PMMA (and other comonomers) was therefore a natural development. During the last 50 years these polymers have been developed into a much diversified class of binders for all kinds of applications, including inks, industrial and maintenance finishes, floor polishes, cement modifiers, roof mastics and adhesives.

In a similar way other polymers, like PVC and poly(vinyl acetate) (PVAc) homo- and copolymers have been developed further into the wide range of products seen today. PVAc-based polymers are also used in paint binders, as well as in the very popular carpenter’s glue. As paint binders, they compete with acrylates, but are less hydrolytically stable and, therefore, not as durable in moist environments and less scrub resistant. They are, however, often used in less expensive paints because of their lower cost. PVAc homopolymer emulsions began to be used in paints before the war, with one British company founded in 1939 for PVAc manufacture. After the war, development of vinyl acetate-based resins continued in Western Europe. The high T_g of PVAc homopolymer made the use of plasticizer necessary. The superior colourfastness and yellowing resistance of vinyl acetate-based resins helped drive the market in Europe away from SBR. Copolymers of vinyl acetate with acrylates, versatate, and ethylene reduced the necessity for plasticizer and enhanced performance in terms of alkali resistance, scrub, and so on. In both acrylics and PVAc-based products, development has been much concentrated on finding copolymer compositions with good application properties at the same time as giving a stable polymer latex and a controllable process. Surfactants and other additives have played a major role in this development. One example is the introduction of amino functionality in latex paints in order to improve wet adhesion properties.

In academia, as well as in some companies, new advanced types of emulsion polymer particles have been developed during the last quarter of the twentieth century. Among these are, for instance, core-and-shell particles for paint and binder applications. In order to obtain a continuous film in a dry paint, film-forming agents in the form of high boiling glycols or hydrocarbons (volatile organic compounds, VOCs) are often added. These are, however, not so environmentally friendly and also unwanted for technical reasons. Poly(acrylate) copolymers have, therefore, been developed with a soft shell polymer on top of a hard core. The technical requirements for producing and controlling such a particle structure have been

the object of many scientific papers (Sundberg *et al.*, 1990; Lee and Rudin, 1992, González-Ortiz and Asua, 1996a, 1996b, 1996c), but a predictive theory for the structure–property relationship of this type of emulsion polymer is still missing, probably because of its extremely complex nature. This has not, however, hindered industrial products based on this type of latex. Another similar product is the hollow latex particles, produced by the Rohm and Haas company (Kowalski, Vogel, and Blankenship, 1981). These are based on core-and-shell particles in which the core is an originally water-swollen polymer that is later collapsed into a void. The application of these particles is for pigment substitutes and other additives. The same company also has developed very advanced multi-lobe particles by means of multistage addition of co-monomers with subsequent phase separation into separate, but still connected spheres. They show that this type of latex gives the product especially useful rheological properties.

Core-and-shell composite particles based on inorganic cores with a polymer shell have also been investigated by several researchers, but do not seem to have reached industrial products. The reason for this is probably the high cost and possibly limited benefits of this type of latex compared to existing products. A similar type of product is composite particles based on pre-emulsified polymers, like epoxies or polyesters (alkyds), with a subsequent addition of new monomers and polymerisation. This technique is partly connected to the process of “mini-emulsion” polymerisation described in the next section. A type of core-and-shell particle or at least multi-phase particle may be obtained in this type of process. However, industrial applications of this type of product are not yet found on a large scale. Applications of polymer particles, mainly made by emulsion polymerisation, in the biomedical field were concentrated initially in the areas of blood flow determination and *in vitro* immunoassays. Microspheres have been employed for the determination of myocardial, cerebral and other blood flow and perfusion rates. Polymer particles and latexes in particular have been extensively used in immunoassays, starting in 1956 with the development of the Latex Agglutination Test (Singer and Plotz, 1956). Later a significant number of additional applications of polymer particles in the biomedical field emerged. These applications exploit advances in polymer chemistry in combination with new developments in the field of biotechnology. Some of these applications are solid-phase immunoassays, labelling and identification of lymphocytes, extracorporeal and haemoperfusion systems, and drug delivery systems. Magnetic microspheres have also been introduced by several companies for cell separation and other therapeutic as well as diagnostic applications. This technology has obtained enormous popularity since around 1990 (see also Chapter 10).

1.2.2 Kinetic Theory

Definitely the most important theory in emulsion polymerisation is the Smith–Ewart theory. This theory was first published in 1948 (Smith and Ewart, 1948) and since then has been the subject of continuing discussion and refinement. The theory is based on the Harkins mechanisms and then tries to predict the rate of reaction and its dependence upon the concentrations of the main components of the system. The rate of reaction is considered to be equal to the total rate of polymerisation in the nucleated soap micelles, which then have been converted to polymer particles. There is no polymerisation in the aqueous phase or in

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the monomer drops. The total rate can then be set equal to the rate in each polymer particle, multiplied by the number of particles:

$$R_p = -\frac{d[M]}{dt} = k_p[M]_p \bar{n} \frac{N}{N_A} \quad (1.1)$$

Here $[M]$ is the total amount of monomer in the system, k_p is the propagation rate constant, $[M]_p$ is the concentration of monomer in the latex particles, \bar{n} the average number of radicals in the particles, N the total number of particles, and N_A is Avogadro's number.

The quantitative theory is therefore centred on predicting (i) the number of particles nucleated and (ii) the rate of polymerisation in each particle. The Smith–Ewart theory operates in the three *intervals* of the polymerisation process, and defines three *cases* for the kinetics. The intervals correspond to the three stages in the Harkins theory: *Interval I* is the nucleation stage where micelles are present and the particle number increases; *Interval II* corresponds to the stage when the particle number is constant and free monomer drops are also present, and *Interval III* is the last part of the polymerisation when the monomer drops have disappeared. Smith and Ewart developed an expression for the particle number created by nucleation in the soap micelles that is still considered essentially correct, within its limits (meaning that monomers, surfactants and generally conditions can be found when the S–E theory is *not* correct and that our understanding today is more detailed). The expression for the particle number, N , is

$$N = k(\rho_i/\mu)^{2/5}(a_s[S])^{3/5} \quad (1.2)$$

Here ρ_i is the rate of initiation, μ is the volumetric growth rate, $\mu = dv/dt$, a_s is the specific surface area of the emulsifier (“soap”) and $[S]$ is the concentration of emulsifier (also denoted as $[E]$). The constant k has a value between 0.37 in the *lower limit* and 0.53 in the *upper limit*. The two *limits* are obtained by deriving the particle number under slightly different suppositions: In the *upper limit* the rate of nucleation is constant and equal to the rate of radical generation, ρ_i , up to the point where there are no micelles left. This means that the particles implicitly are not assumed to absorb any radicals during the nucleation period, or that at least this rate is negligible. This may or may not be true, as discussed later (Chapter 3). On the other hand, in the *lower limit* the particles adsorb radicals at a rate according to their surface area. This, naturally, leads to a lower particle number, but the two limits, surprisingly enough, only differ by the constant k and are otherwise equal! The mathematics involved in deriving these equations is quite straightforward in the case of the upper limit, but somewhat more involved in the case of the lower limit. Smith and Ewart did this derivation very elegantly and later work, both analytical and numerical has shown Equation 1.2 to be a limiting case of a more general solution for the particle number.

The second part of the Smith–Ewart theory concentrates on calculating the average number of radicals per particle. As long as the monomer concentration in particles is constant, as may often be the case in *Interval II*, this number then yields the rate of polymerisation. Smith and Ewart did this by means of a recursion equation that is valid for the situation prevailing after particle formation is finished,

$$\begin{aligned} \rho_A N_{n-1}/N + (n+1)(k_s a_s [S]/v) N_{n+1} + (n+2)(n+1)(k_t^*/v) N_{n+2} \\ = \rho_A N_n/N + n(k_s a_s [S]/v) N_n + n(n-1)(k_t^*/v) N_n \end{aligned} \quad (1.3)$$

where ρ_A is the total rate of radical absorption or entry in the particles (in molecules per unit volume), k_s is the rate “constant” for desorption or exit of radicals from the particles, a_s the specific surface area and k_t^* the termination constant in latex particles. The particle number N_n denotes the number of particles with n -occupancy of radicals. Smith and Ewart then discussed three *limiting cases*: Case 1: $\bar{n} \ll 0.5$, Case II: $\bar{n} = 0.5$, and Case 3: $\bar{n} \gg 0.5$. Case 2 is that which has later been most generally known as the Smith–Ewart theory and is the only case that has been given a complete treatment by Smith and Ewart. The solution for this case is also obvious from simple consideration of the situation in a randomly selected particle. The condition for this case is

$$k_s a_s [S] / v \ll \rho_A / N \ll k_t^* / v \quad (1.4)$$

This means that the rate of adsorption of radicals in polymer particles is much larger than the rate of desorption (so the latter can be neglected) and much lower than the rate of termination. The kinetic conditions may, for this case, be easily deduced by regarding the adsorption and termination processes in a single particle. When a radical enters a “dead” particle ($n = 0$), it becomes a “living” particle ($n = 1$), and polymerisation proceeds with the present monomer. This situation is maintained until another radical enters ($n = 2$). Because the rate of termination is high, the two radicals terminate immediately, and the particle is again “dead”. Due to the random nature of the adsorption process (diffusion), the particle is switched on and off at random intervals, but as a time average each of the two states are present half of the time, or the half is present all the time, that is, $\bar{n} = 0.5$. This number has become more or less synonymous with the Smith–Ewart theory, but is only a special case.

The two other cases occur when the left side (Case 1) or the right side (Case 3) of Equation 1.4 are not fulfilled, giving negative or positive deviations from the 0.5 value. Smith and Ewart did not treat these cases completely, re-absorption of radicals was only included for the case when termination in the particles is dominating (their *Case 1B*) and particles with more than one radical (Case 3) were only considered when desorption is negligible. Also they did not give the full solution of the recursion equation (1.3). This was not solved until 1957 by Stockmayer (Stockmayer, 1957). If desorption is neglected, the solution is

$$\bar{n} = \frac{I_0(a)}{I_1(a)} \quad (1.5)$$

where I_0 and I_1 are Bessel functions of the first kind, and

$$a = \sqrt{8\alpha}, \quad \alpha = \frac{\rho_A}{N k_t^* / v} \quad (1.6)$$

Stockmayer also presented solutions for the case that takes into account desorption of radicals. This solution, however, is wrong for the most important range in desorption rates. But Stockmayer’s solution(s) led the way for the possibility of exact mathematical solution of emulsion polymerisation kinetics at a time when digital computers were not yet very important in chemical computations. The general solution when desorption is taken into account was presented by O’Toole (O’Toole, 1965). He applied a modified form of the

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Smith–Ewart recursion equation that gave the solution

$$\bar{n} = \frac{a}{4} \frac{I_m(a)}{I_{m-1}(a)} \quad (1.7)$$

where the dimensionless parameter m is given by $m = k_d/(k_t^*/v)$, that is the ratio between the desorption and termination rates. Here, the Smith–Ewart desorption “constant” $k_s S/v$ has been replaced by k_d , signifying that the desorption rate must not necessarily be proportional to the particle surface area. In addition, desorption also normally would only happen to monomer (or other small) radicals produced by chain transfer; k_d will, therefore, also include the chain transfer constant. We see that when desorption is zero, $m = 0$, and O’Toole’s solution is equivalent to Stockmayer’s. O’Toole used radical occupancy probabilities in the modified recursion equation, and was thus able to compute the probability distribution functions that have importance for computing the molecular weight distribution. However, neither Stockmayer nor O’Toole took into consideration the fate of the desorbed radicals. This was the main objection of Ugelstad and coworkers (Ugelstad, Mørk, and Aasen, 1967; Ugelstad and Mørk, 1970) when presenting their theory in 1967. Their main incentive was that the kinetics of PVC emulsion polymerisation did not fit the Smith–Ewart theory. First, they found a very low value of $\bar{n} < 0.5$ and secondly, the Smith–Ewart Case 1 kinetics did not fit either. Ugelstad’s argument was that ρ_A and ρ_i cannot be treated as *independent* parameters as in both Stockmayer’s and O’Toole’s solutions, but that they are connected by processes in the continuous (water) phase. The desorbed radicals may be re-absorbed, either before or after having polymerised to some degree in the continuous phase, or they may terminate there. Ugelstad therefore introduced an additional equation for taking these processes into account in a simplified fashion:

$$\rho_A = \rho_i + \sum k_d N_n n - 2k_{tw}^* [R\cdot]_w^{*2} \quad (1.8)$$

Here, k_{tw}^* is the termination constant and $[R\cdot]_w^*$ is the radical concentration in the water phase. This equation is brought into dimensionless form by dividing by Nk_t^*/v and by realizing that $\bar{n} = (\sum nN)/N$, so that resultant equation is

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \quad (1.9)$$

This treatment only introduced one additional dimensionless parameter, Y , which is a measure of the degree of water phase termination. $Y = 0$ therefore represents the case when all desorbed radicals are re-absorbed. The disadvantage of this treatment is that a general solution cannot be made without the use of numerical methods, that is, computers. Aasen also simplified O’Toole’s Bessel function expression for \bar{n} to a simple converging continued fraction (Ugelstad, Mørk, and Aasen, 1967) that can be solved simultaneously with Equation 1.9. This equation is

$$\bar{n} = \frac{\alpha}{m + \frac{2\alpha}{1 + m + \frac{2\alpha}{2 + m + \frac{2\alpha}{3 + m + \dots}}}} \quad (1.10)$$

If $m = 0$ and α is small ($\ll 1$), this equation is seen to give the famous $\bar{n} = 0.5$. For a given system the rate of initiation and thus ρ_i , and correspondingly α' , is an independent

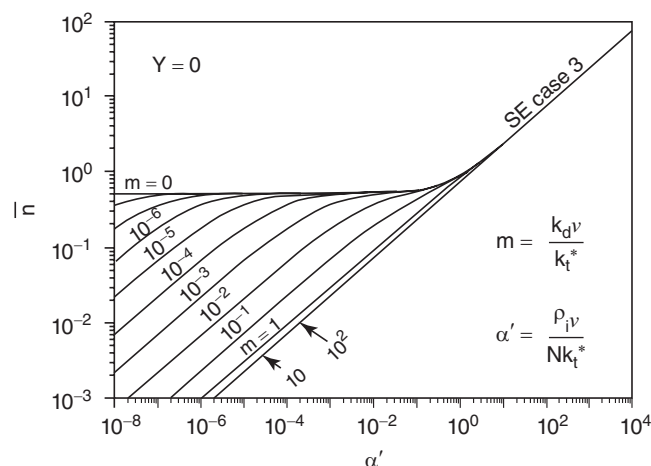


Figure 1.2 Average number of radicals per particle, \bar{n} , calculated from the theory of Ugelstad and coworkers. \bar{n} is given as a function of the dimensionless parameters α' and m when there is no termination in the aqueous phase ($Y = 0$). Case 2 of the Smith–Ewart theory, $\bar{n} = 0.5$, is described by the horizontal line where $m = 0$.

variable; and Equations 1.9 and 1.10 can be solved by successive approximations to give \bar{n} . These equations give the famous curves for \bar{n} as a function of α' , as shown in Figure 1.2 for the most simple case when $Y = 0$.

Solutions for other values of Y are given by Ugelstad and Hansen (Ugelstad and Hansen, 1976) in their 1976 review of emulsion polymerisation. In this way, the complete solution to the steady-state Smith–Ewart based theory is available. Ugelstad and coworkers (Ugelstad *et al.*, 1969; Ugelstad and Mørk, 1970) found the theory to fit the emulsion polymerisation kinetics of PVC to a very high precision and later found this also to be the case for bulk polymerisation of the same monomer because of PVC's low solubility in its monomer. One important factor in these calculations was the particle size dependence of the desorption constant. The surface area/volume dependence assumed by Smith and Ewart was discussed by Nomura, Harada and coworkers in 1971 (Nomura *et al.*, 1971; Harada *et al.*, 1972). They concluded that the desorption constant should be proportional to the particle radius/volume, that is, inversely proportional to the square of the particle size. This dependence was used successfully by Ugelstad and coworkers in their calculations.

Around the same time as Ugelstad and coworkers introduced their theoretical and experimental results, Gardon also published in a series of papers (Gardon, 1968, 1970a, 1970b) a re-examination and recalculation of the Smith–Ewart theory. Some of the results that were obtained were more special solutions of the more general solutions developed by Stockmayer–O'Toole and Ugelstad and some assumptions have later been disputed. One of these assumptions is that the rate of adsorption of radicals in micelles and particles is proportional to their surface area. This is the same assumption that was made by Smith and Ewart, and was derived by Gardon from geometric considerations assuming the radicals move in straight lines to collide with the surface. For that reason this model is also called

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the *collision model*. However, this has been shown to be correct for only a limited range of conditions, especially because Gardon did not take the concentration gradient necessary for mutual diffusion into consideration, the so-called *diffusion model* that gives proportionality with the particle radius rather than with its surface area. Also Gardon did not include desorption and re-absorption of radicals. Much of Gardon's semi-analytical computations has later been made needless by numerical computer technology. It may be said then that the Gardon theory has not been applied very much in the later years.

During the last quarter of the twentieth century several groups have been occupied with the kinetic theory of emulsion polymerisation, bringing it to still higher degrees of sophistication by investigating different details that had not earlier been considered. Among the most well-known of these groups are Nomura and coworkers in Japan and Gilbert, Napper and coworkers in Australia. One of their main contributions has been the independent measurements and estimation of many of the rate constants involved in initiation, propagation and termination, in addition to producing advanced models with computer simulation. Among these are non-steady state reaction kinetics, and the development of particle size and molecular weight distributions. In order to have a realistic model that can be used for prediction and/or process control it is necessary to have good independent estimates for the constants in order to avoid what is popularly referred to as "curve fitting". Through a series of publications they have investigated many aspects of these problems. Also Asua and his coworkers in Spain have contributed to more detailed descriptions of the mechanisms. Among other contributions, primarily in process control and reaction engineering, they have published a more detailed description of the desorption mechanism, taking also the reactions in the aqueous phase into consideration (Asua, Sudol, and El-Aasser, 1989). They have also published work on general parameter estimation (De la Cal, Adams, and Asua, 1990a; De la Cal *et al.*, 1990b). More thorough descriptions of the more recent work are given in Chapter 3.

The first part of the Smith–Ewart theory, the nucleation part (Interval I) was not in the beginning debated to the same degree as the rate of polymerisation. This may be because people found that observations agreed with the theory, or maybe rather that they did not. Observations have not always agreed with the exponents 0.4 and 0.6 predicted by the theory in Equation 1.2 nor with the absolute particle number, but this has been found to be very dependent on the specific system studied. Experiments with more water-soluble monomers, such as those by Priest (Priest, 1952) and Patsiga (Patsiga, Litt, Stannett, 1960) with vinyl acetate and Giskehaug (Giskehaug, 1965) with PVC did not fit this theory. In the beginning there were some researchers who performed modifications and recalculations of the Smith–Ewart theory (Gardon, 1968; Parts, Moore, and Watterson, 1965; Harada *et al.*, 1972), and found that some of the details of the theory had to be modified. Parts *et al.* (Parts, Moore, Watterson, 1965) proposed, for instance, that in order to explain the experimental particle numbers, the absorption efficiency of radicals in micelles is lower than in particles. The particle numbers (or more correctly, particle sizes) calculated by Gardon were found to describe some experimental results for styrene and methyl methacrylate fairly well, whereas other data on particle numbers were 2–3 times lower than predicted. Another feature of the Smith–Ewart theory is that the reaction rate at the end of Interval I is expected to be higher than the steady-state value of 0.5, but there is little evidence for such a maximum in rate. There was, therefore, need for a more detailed description of the conditions during Interval I. Objections to Harkins and subsequently the SE theory also appeared for other

reasons: Particles can be formed and stabilized even in systems with no micelles (below the critical micelle concentration, CMC) and even in systems completely without emulsifier. Roe (Roe, 1968), in a well-known article, showed experimental evidence that in a mixture of ionic (sodium dodecyl sulfate, SDS) and non-ionic emulsifiers the particle number is not dependent on the total number of micelles, but rather only on the number of SDS micelles. That means that the non-ionic micelles do not participate in particle formation, at least not to the same degree as the ionic. Roe then went forward and re-derived the Smith–Ewart expression for the particle number, Equation 1.2, on a pure non-micellar basis. The quantity S was then redefined to be the total surface area of emulsifier available for particle stabilization, but apart from that, all parameters and conditions were the same. Roe proposed to use “some sort of adsorption isotherm” to better describe the role of the emulsifier, but did not propose any quantitative equations for such isotherms. Roe’s considerations could, therefore, explain some of the controversies of the Harkins theory, but still many questions were left, because a detailed description of the process of so-called homogenous nucleation was not given.

The derivation of a separate theory for homogenous nucleation was started by Fitch and coworkers (Fitch, Prenosil, and Sprick 1969; Fitch and Tsai, 1971) who worked with methyl methacrylate. They based their qualitative description on that of Priest (Priest, 1952) where a growing (oligomeric) radical in the aqueous phase can self-nucleate when reaching a certain chain length, the so-called critical chain length. Fitch and coworkers both determined this chain length for MMA and derived an expression for the particle number. This expression was based on the finding that the rate of polymerisation of MMA in Interval I could be described by homogenous polymerisation in the aqueous phase during the whole nucleation period for initiator concentrations below 10^{-3} M. In their model they used non-steady state homogenous kinetics. They also based the rate of adsorption in particles on Gardon’s collision model. They found that the expression they derived gave a good prediction of the particle number when high amounts of emulsifier were used. In many systems, however, it has been shown that the collision model is incorrect, and Fitch and Shih (Fitch and Shih, 1975) found later that the diffusion model was more correct for seeded nucleation experiments (it was shown later by the present author, however, that both models may be correct, depending on the conditions). The work on the theory for homogenous nucleation was continued at that time (1975) by Hansen and Ugelstad (Hansen and Ugelstad, 1978, 1979a, 1979b, 1979c) based on Fitch and Tsai’s ideas. They derived an expression for the rate of adsorption of radicals in micelles and particles that can take into consideration both reversible diffusion and electrostatic repulsion. By means of this expression the low capture efficiency of micelles that was postulated by Parts and coworkers (Parts, Moore, and Watterson, 1965) could be explained, as well as many other special cases, such as the possible validity of both the diffusion and collision theories under different conditions. They also developed an expression for the particle number in the case where all nucleated particles are stable and found this to fit well the observed data for styrene. They solved their model by numerical integrations by means of digital computers that were beginning at that time to become useful for advanced simulations. They also formulated expressions to calculate the so-called limited coagulation in order to explain the much lower particle numbers formed in systems with low or zero emulsifier concentration. Because of the computational requirements of their model, however, they were not at that time able to follow this model to any equilibrium situation. Fitch later named this combined

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model the HUFT (Hansen, Ugelstad, Fitch, and Tsai) model, which acronym has obtained some popularity. Hansen has in later publications (Hansen and Ugelstad, 1982, Hansen, 1992a, 1992b) described the consequences of the model in more detail.

Fitch and coworkers (Fitch and Watson, 1979a; Fitch *et al.*, 1984) later investigated the limited coagulation process. They performed coagulation experiments with MMA, using photo-initiation of homogeneous solutions and light scattering detection. Fitch and Watson used flash initiation and investigated the subsequent coagulation process. They clearly showed that coagulation takes place below the CMC and they could calculate the stability ratio as a function of surfactant (SDS) concentration. The Australian group, Feeney, Lichti, Gilbert and Napper (FLGN) initiated and continued work on particle nucleation during the 1980s. Especially, they have contributed with new experimental work, and this has been followed up partly by new theoretical ideas. Traditionally the comparison between theory and experiment with respect to particle nucleation is done by comparing (final) particle numbers and/or the rate of polymerisation. FLGN argue that several other parameters provide additional and more sensitive information about the nucleation mechanism. Such parameters are the particle size distribution, molecular weight distribution (also in the aqueous phase), and the rate parameters for absorption (entry) and desorption (exit). By measuring the rate constants explicitly, they were aiming to avoid the “curve fitting” dilemmas that are inherently present in the theoretical calculations cited above. They measured the particle size distribution as a function of time (Lichti, Gilbert, and Napper, 1983; Feeney, Napper, and Gilbert, 1984), and from the observation that these distributions are positively skewed, they concluded that the particle formation rate must be an increasing (or at least not decreasing) function of time, and that this may only be explained by a limited coagulation mechanism (they named this *coagulative nucleation*). That such a mechanism is active below the CMC comes as no big surprise, while it seems contradictory to other experimental and theoretical work that this should also be a governing mechanism above the CMC, especially for monomers such as styrene that adsorbs surfactants well, and emulsifiers such as SDS that form gaseous/liquid expanded layers when used alone and, therefore, have very fast adsorption/desorption kinetics. The theories of Gilbert and coworkers are further described in Chapter 3.

More recently, Tauer (Tauer and Kühn, 1995, 1997; Tauer and Deckwer, 1998) proposed an alternative framework for modelling particle nucleation in an emulsion on the basis of a combination of classical nucleation theory and the Flory–Huggins theory of polymer solutions. The basic assumption is that water borne oligomers form stable nuclei under critical conditions. The only adjustable model parameter is the activation energy of nucleation. The model allows calculation of the chain length of the nucleating oligomers, the number of chains forming one nucleus, the diameter of the nucleus, the total number of nuclei formed and the rate of nucleation. Based on the kinetic constants and model parameters, numerical results characterizing particle nucleation were calculated for the polymerisation of styrene, methyl methacrylate, and vinyl acetate as model systems. Still, this model has not been thoroughly tested, and several objections may also be raised to its validity. It will remain to be seen to what degree this model will be adopted in the future. There is, however, another aspect of nucleation and kinetics that was discovered in the early 1970s: the role of the monomer droplets was reconsidered. This is described in the next section.

Interval III of the Smith–Ewart theory has maybe not been the object of the same attention as Intervals I and II. This stage, when monomer drops have disappeared, is more like a

suspension or bulk polymerisation, and some of the special features of emulsion polymerisation are not so essential. However, the compartmentalization effect on the kinetics is still present, and this interval also has its own special problems when the monomer concentration and the termination constant decrease. The Smith–Ewart theory, the Stockmayer–O’Toole solution and the work of Ugelstad and coworkers mentioned above describes the kinetics in this interval as well, as long as the monomer concentration and the termination constant are accounted for. The connection between these two and their effect on the rate, and also possibly on nucleation, has been the source of separate research work. The so-called gel effect was investigated already by Gerrens in 1956 (Gerrens, 1956). He showed that the rate increase due to this effect varies with the particle size of the latex; the strongest increase is obtained with the largest particle sizes. This is a natural consequence of the rate of termination being the lowest for high particle volumes and thus the possibility for \bar{n} to increase beyond 0.5 is most probable for these. Comprehensive treatments of this interval were done by Nomura and coworkers (Nomura *et al.*, 1971, Nomura *et al.*, 1975) and Friis and coworkers (Friis and Hamielec, 1973a; Friis and Nyhagen, 1973b, Friis and Hamielec, 1974a; Friis *et al.*, 1974b) in the early 1970s. Friis and Hamielec made use of kinetic results from bulk polymerisation from which they found k_t as a function of conversion. By modelling k_t versus conversion by a mathematical expression, it was possible to calculate the rate in Interval III by computer simulation. This methodology has also been the way in later work by others, where different mathematical expressions have been proposed for the termination constant.

1.2.3 Emulsion Polymerisation in Monomer Droplets

As mentioned in Section 1.2.2 the Harkins theory states that no, or at least very little, polymerisation takes place in the monomer droplets. This is essentially correct, and the reason is that the *number* of monomer droplets compared to the particles nucleated from micelles is many orders of magnitude lower. This does not mean that the monomer droplets are not initiated, however, and in many processes a few extra large particles may be observed. Also, monomer suspension polymerisation is often the source of reactor fouling. Many believe these large particles are the left-over of the monomer drops that are probably all initiated, but contribute very little to the over-all conversion because of the peculiar compartmentalization kinetics. It might be thought then, that if the monomer drops could be made smaller and thus more numerous, they might be more important in the nucleation process. This has indeed been shown to be the case.

In the late 1960s Ugelstad and coworkers were investigating an industrial PVC emulsion process that used a fatty alcohol in addition to the ordinary emulsifier in order to obtain especially large polymer particles. These large particles have advantages when used in some PVC paste products. The thought behind the process was that the fatty alcohol was causing limited flocculation of the latex and thus larger particles. The problem was, however, that the process, and especially particle size, was difficult to control. Unknown factors sometimes caused the particles to become very small, like an ordinary emulsion polymer, but it proved very difficult to discover which factors exactly were causing the problem. Every imaginable analysis was done on the ingredients, but there was no clue! It had been observed that the use of the fatty alcohol produced a much “better” monomer emulsion, but this was not connected to anything special. It was not until 1972 that Ugelstad, at that time

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on sabbatical at Lehigh University, proposed that the reason for the large particles could be initiation in the monomer droplets, because these were much smaller in these systems. Experiments done more or less simultaneously in Norway and the US confirmed this theory (Ugelstad, El-Aasser, and Vanderhoff, 1973; Ugelstad, Hansen, and Lange, 1974). The fine monomer emulsion has two effects: first it increases the number of monomer drops to an extent where they become comparable to (but still larger than) ordinary latex particles, secondly the greatly increased surface area causes adsorption of most of the emulsifier and leaves little left in the aqueous phase for “ordinary” nucleation. It was also shown that the reason for the reproducibility problems was the instability of the monomer emulsion (Hansen, Baumann Ofstad, and Ugelstad, 1974). The initial emulsion is produced by spontaneous emulsification by a diffusion process into small fatty alcohol/emulsifier aggregates (drops), but the emulsion is destabilized with time by Ostwald ripening because the fatty alcohol is slightly water-soluble. When the monomer emulsion is destabilized, the emulsifier concentration in the aqueous phase increases and will cause more “ordinary” nucleation, especially if the concentration exceeds the critical micellar concentration.

The conditions for droplet and ordinary nucleation were later investigated in more detail, using styrene as the monomer (Hansen and Ugelstad, 1979c). In these experiments, the monomer emulsions were produced by homogenizing the monomer with a high pressure homogeniser, rather than using a fatty alcohol and spontaneous emulsification. In order to stabilize the emulsion against Ostwald ripening, a water-insoluble substance (hexadecane) was used instead of the fatty alcohol. The advantage of using hexadecane or other paraffins is that the emulsion is much more stable because of the much lower water solubility, and the emulsifier concentration can be controlled more independently of the drop size. Another advantage is that other polymers, such as polyesters, polyamines, and so on, can also be included in the emulsified drops, and subsequently copolymerised with added monomers. It is also possible to add monomers to a homogenized emulsion of hexadecane or other substances so the monomer will swell the preformed emulsion like in a seeded emulsion polymerisation. This process was named “Method #2” by Ugelstad and was patented in 1978. The process of emulsification of the monomer and subsequently droplet initiation has been called the “mini-emulsion” process by El-Aasser and has been the object of thorough investigation and numerous publications from the Lehigh group. Lately, it has also been taken up by others.

In this emulsion polymerisation process a water soluble initiator was originally used, giving the process its characteristic kinetic properties. Dependent on the type of monomer and on the drop size, all types of kinetic behaviour may be observed, but usually the drops are rather large ($>1\ \mu\text{m}$), and SE Case 3 kinetics is often observed. Especially if SE Case 2 kinetics is present ($\bar{n} = 0.5$), but even in the case where $\bar{n} \gg 0.5$, there will be a narrowing of the particle size distribution for most monomers (Hansen and Ugelstad, 1979c), and this is thus a characteristic feature of the mini-emulsion process. However, oil-soluble initiators may also be used in this process, and the process might then rather be named “minisuspension” (or maybe “microsuspension”). Method #2 was shortly after further developed by Ugelstad and coworkers into Method #3, which has later been better known as the Ugelstad Process. This is the so-called two-step swelling process based on polymer seed particles. The intention is to get the seed particles to take up much more monomer than they would otherwise do, because of the limited free energy of mixing of monomer and polymer (mostly entropy driven). In the first step the seed particles are “activated” (swollen)

by a relatively low molecular weight water-insoluble substance (for instance hexadecane) by adding a water-soluble solvent (acetone, methanol, etc.). Afterwards the solvent is removed, effectively trapping the water-insoluble substance in the seed particles. These are now able to take up much more monomer (up to ca 1000 times their volume) because of the increased entropy of mixing in the particles. By using “ordinary” monodisperse seed particles (diameter < 1 µm), much larger monodisperse particles can be produced in one polymerisation process. By repeating the process, extremely large monodisperse particles can be produced (> 100 µm). These particles have, by some, been given the name “Ugelstad particles” or “Ugelstad beads”. The process has been reputed to produce large, monodisperse particles, but in itself it has nothing to do with monodispersity. It is not an emulsion polymerisation process either, because oil-soluble initiators have to be used to avoid new particle nucleation, so it is rather a peculiar suspension polymerisation. The particles have been given several additional properties, like macroporosity, magnetism, different surface coatings and so on, and have become very successful products, especially in the biomedical field. Because of this several groups have developed similar emulsion polymers, based on a variety of modifications of the process.

1.2.4 Industrial Process Control and Simulation

From the earlier days, an objective (the major objective?) of making theories of particle nucleation and growth was to use these for process development, prediction, and finally process control. With the advent of modern digital computer technology, modelling for process control was becoming more realistic. This is a relatively new technology, and has emerged during the last part of the twentieth century. Many companies that do emulsion polymerisation now have developed their own technology in this field that by its nature is regarded as confidential. The public scientific exchange of new developments, and especially clever computer control procedures and modelling, are therefore limited. Another source of separation of the industrial processes from the scientific community working in emulsion polymerisation kinetics is the difference in objectives. Kinetic models do, to a large extent, only predict the molecular level properties and not the macroscopic properties that are important for the users (“customers”) – the so-called end-use properties.

The traditional emulsion polymerisation processes were run in batch reactors and even today, the majority of products are still produced in batch reactors. This is due to both the nature of the nucleation process, that cannot easily be controlled in continuous reactors without some sort of seeding to avoid oscillatory behaviour in particle size and/or molecular weight, and to such factors as co-monomer composition (in copolymerisation processes), fouling, temperature control, sensor technology, and so on. Models for emulsion polymerisation reactors have been published by several researchers. The simplest reactors to model are batch reactors that closely resemble lab reactors. One important design criterion for industrial reactors that differ from lab reactors is temperature control. When the reactor increases in size, the decreased surface/volume ratio of the vessel makes heat transfer an increasing problem, especially because the reaction rate, for reasons of economy, should be as high as possible. Hamielec (Hamielec and MacGregor, 1982) concludes that “the results from simple calculations indicate that for reactor volumes greater than 5000 gal additional cooling capacity would likely be required to achieve commercial production rates”.

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A model for a continuous stirred tank reactors (CSTR) was first presented by Gershberg and Longfield (Gerschberg and Longfield, 1961) in 1961. It is based on the SE Case 2 model, and has been further described and elaborated by Poehlein (Poehlein, 1981). A pioneering modelling framework was presented by Min and Ray (Min and Ray, 1974, 1976a, 1976b, 1978) in 1974–1978. After the work of Min and Ray others have concentrated on practical solutions of the model, testing different numerical techniques and comparing predictions to experimental data for specific polymerisation systems. The main challenge is to do appropriate model simplifications while at the same time producing a sufficiently accurate model. When a model is available, it may be used for predictive process control of the reactor. Several researchers in chemical engineering are now working on this topic, and much of it has appeared only during the last 10–15 years. The group of Asua has published many works in this field and is presently one of the most active in emulsion polymerisation process control. The details of these processes will be treated further in Chapter 4.