Chemistry and Technology of Emulsion Polymerisation

Edited by

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List of Frequently Used Symbols

a_e	specific surface area for a emulsifier molecule on a polymeric surface
A	Arrhenius constant of the initiation (A_i), propagation (A_p), termination (A_t) and transfer (A_tr)
$\overline{d}$	average particle diameter, d_n number average diameter, d_s surface average diameter, d_w weight average diameter, d_v volume average diameter
$d_\mathrm{w}/d_\mathrm{n}$	particle diameter non-uniformity factor
E	energy of activation for initiation (E_i), propagation (E_p), termination (E_t) and transfer (E_tr)
f	initiator efficiency
F	efficiency factor for adsorption
ΔG	partial molar free energy of droplets ΔG_d, ΔG_a of the aqueous phase and of the latex particles ΔG_p
H	enthalpy
ΔH	change in enthalpy
j_crit	critical length of an oligomer at which precipitation from the aqueous phase occurs
k	exit frequency
k	rate constant of the initiation (k_i), propagation (k_p), termination (k_t) and transfer reaction (k_tr)
$[\mathrm{M}]$	concentration of monomer, $[\mathrm{M}]_\mathrm{p}$ concentration of monomer in the polymer particles. If this depends on quantities such as radius r, time t etc., the notation is $[\mathrm{M}(r, t, \ldots)]_\mathrm{p}$. $[\mathrm{M}]_\mathrm{a}$ for the monomer concentration in the aqueous phase, $[\mathrm{M}]_\mathrm{a,sat}$ for the saturation concentration in the aqueous phase
$\overline{M}$	average molar mass: number-average molar mass (M_n); weight-average molar mass (M_w)
N	number of latex particles per unit volume of latex
N_n	number of particles with n radicals per particle
N_A	Avogadro constant
n	number of radicals in a latex particle
$\overline{n}$	average number of radicals per particle
n_m0	initially added number of moles of monomer per unit volume
$\overline{P}_\mathrm{n}$	number average degree of polymerisation
R	gas constant

$r_{1,2}$	reactivity parameters in copolymerisation
r_p	rate of polymerisation per particle
r_e	rate of entry of radicals per particle
r_t	rate of termination per particle
r_0	the radius of the unswollen micelles, vesicles and/or latex particles
R_p	rate of polymerisation
S	entropy
ΔS	change in entropy
T	temperature
T_g	glass transition temperature
t	time
V	volume of monomer swollen latex particles
V_m	molar volume of the monomer
v_p	volume fraction of polymer (also ϕ_p)
W	stability ratio
w_p	mass fraction of polymer in the particle phase
$\overline{X}$	fraction conversion of monomer to polymer
X_n	number-average degree of polymerisation, X_w weight-average degree of polymerisation
z-mer	the length of an oligomer in the aqueous phase at which surface activity occurs
α	fate parameter (fate of excited radicals)
χ	Flory–Huggins interaction parameter
δ	solubility parameter or chemical shift
ε	permittivity
γ	interfacial tension
η	viscosity
$[\eta]$	intrinsic viscosity
ν	kinetic chain length
π	osmotic pressure
ρ	entry frequency
ρ_i	radical flux or rate of initiation ($2k_d f$ [I])
μ	volume growth factor
τ_g	time of growth of a polymer chain
ϕ_p	volume fraction of polymer

Abbreviations

AA	Acrylic acid
ABS	Acrylonitrile–butadiene–styrene
Aerosol MA	AMA, sodium di-hexyl sulphosuccinate
Aerosol OT	AOT, sodium di(2-ethylhexyl)sulphosuccinate
AFM	Atomic force microscopy
AIBN	Azobisisobutyronitrile
APCI	Atmospheric-pressure chemical ionisation
ATR	Attenuated total reflectance
ATRP	Atom transfer radical polymerisation
B	Butadiene
BA	*n*-Butyl acrylate
BPO	Benzoyl peroxide
BSE	Backscatter electrons
Buna N	Butadiene–acrylonitrile copolymer
Buna S	Butadiene–styrene copolymer
CCA	Colloidal crystalline array
CCD	Chemical composition distribution
CDB	Cumyl dithiobenzoate
CFM	Chemical force microscopy
CFT	Critical flocculation temperature
CHDF	Capillary hydrodynamic fractionation
CMC	Critical micelle concentration
CMMD	Control molar mass distribution
CPVC	Critical pigment volume concentration
CRP	Controlled radical polymerisation
CTA	Chain transfer agent
CVP	Colloid vibration potential
Cyclam	Tetrazacyclotetradecane
DLS	Dynamic light scattering
DLVO	Derjaguin–Landau–Verwey–Overbeek
DMA	Dynamic mechanical analysis
DNA	Desoxy nucleic acid
DSC	Differential scanning calorimetry
EDTA	Ethylene diamino tetraacetic acid

EHMA	2-Ethylhexyl methacrylate
EPA	Environmental Protection Agency
ES	Electrozone sensing
ESA	Electrokinetic sonic amplitude
ESD	Equivalent spherical diameter
ESEM	Environmental scanning electron microscopy
ESI	Electrospray ionisation
FESEM	Field emission scanning electron microscopy
FFF	Field-flow fractionation
FLGN	Feeney, Lichti, Gilbert and Napper
FTD	Functionality-type distribution
FTIR	Fourier-transform infrared
GC	Gas chromatography
GPC	Gel permeation chromatography
HASE	Hydrophobically modified alkali-swellable emulsions
HDC	Hydrodynamic chromatography
HDPE	High density polyethylene
HEC	Hydroxylethyl cellulose
HEMA	2-Hydroxyethyl methacrylate
HEUR	Hydrophobically modified ethylene oxide urethanes
HOST	Homogeneous start
HIC	Hydrophobic interaction chromatography
HPLC	High performance liquid chromatography
HUFT	Hansen, Ugelstad, Fitch and Tsai
i-LC	Interactive liquid chromatography
IR	Infrared
IVC	Intrinsic-viscosity distribution
K	Kelvin
LC	Liquid chromatography
LD	Laser diffraction
LE	Light extinction
LIST	Line start
LRP	Living radical polymerisation
LS	Light scattering
MA	Methyl acrylate
MALDI	Matrix-assisted laser desorption/ionisation
MFFT	Minimum film forming temperature
MMA	Methyl methacrylate
MMD	Molar mass distribution
MONAMS A5	1-(methoxycarbonyl)eth-1-yl initiating radical
MS	Mass spectrometry
NIR	Near-infrared
NMP	Nitroxide-mediated living radical polymerisation
NMR	Nuclear magnetic resonance
NR	Natural rubber

OM	Optical microscopy
PCH	Phenyl-cyclohexene
PCS	Photon correlation spectroscopy
PDI	Polydispersity index
PDMS	Poly(dimethylsiloxane)
PE	Polyethylene
PEO	Poly(ethylene oxide)
PGA	Poly(glycolic acid)
PHD	Pulse height distribution
PHS	Poly(hydroxystearic acid)
PLA	Poly(D, L-lactic acid)
PLP	Pulsed-laser polymerisation
PLGA	Poly(glycolic–*co*–lactic acid)
PMMA	Poly(methyl methacrylate)
PNIPAM	Poly(*N*-isopropylacrylamide)
PPO	Polypropylene oxide
PRE	Persistent radical effect
PS	Polystyrene
PSA	Pressure-sensitive adhesives
PSD	Particle size distribution
PTA	Phosphotungstic acid
PTFE	Poly tetrafluorethylene
PTV	Programmed temperature vaporiser
PVAc	Poly(vinyl acetate)
PVC	Pigment volume concentration
QELS	Quasi-elastic light scattering
RAFT	Reversible addition fragmentation transfer
RCTA	Reversible chain transfer agents
RI detector	Refractive-index detector
S	Styrene
SAM	Self-assembled monolayer
SANS	Small angle neutron scattering
SAXS	Small angle X-ray scattering
SB	Styrene–butadiene
SBLC	Styrene Butadiene Latex Council
SBR	Styrene–butadiene rubber
SDS	Sodium dodecyl sulphate
Sed-FFF	Sedimentation field-flow fractionation
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
SFM	Scanning force microscopy
SPM	Scanning probe microscopy
SPOS	Single-particle optical sensing
SRNI	Simultaneous reverse and normal initiation
SSIMS	Static secondary ion mass spectrometry
STM	Scanning tunnelling microscopy

TEM	Transmission electron microscopy
TEMPO	2,2,6,6-Tetramethylpiperidine-l-oxyl
Texanol®	2,2,4-Trimethyl-1,3-pentanediol-diisobutyrate
TGIC	Temperature-gradient interaction chromatography
THF	Tetrahydrofaran
TOF	Time-of-flight
TREF	Temperature-rising elution fractionation
UAc	Uranyl acetate
UV	Ultraviolet
VAc	Vinyl acetate
VCH	Vinyl-cyclohexene
VOC	Volatile organic compound
W	Watt
XPS	X-ray photoelectron spectroscopy
XSB	Carbo**x**ylated **s**tyrene-**b**utadiene dispersions

Introduction

The increasing need for environmentally benign production methods for polymers has resulted in a further development and implementation of the emulsion polymerisation technique. More and more companies switch from solvent-based polymer production methods to emulsion polymerisation. New polymerisation mechanisms, such as controlled radical polymerisation, are combined with the emulsion polymerisation technique, encountering specific problems but also leading to interesting new possibilities in achieving special nanoscale morphologies with special properties. In the past years many people have been trained in the use of the emulsion polymerisation technique. Many courses on the BSc, MSc and the Ph.D. level as well as special training for people in the industry are given all over the world. Despite this, no recent book exists with the purpose of supporting courses in emulsion polymerisation.

This book is aimed at MSc students, Ph.D. students and reasonably experienced chemists in university, government or industrial laboratories, but not necessarily experts in emulsion polymerisation or the properties and applications of emulsion polymers. For this audience, which is often struggling with the theory of emulsion polymerisation kinetics, this book will explain how theory came about from well-designed experiments, making equations plausible and intuitive. Another issue experienced, especially in the industry, is that coupling theory and everyday practice in latex production is really hard. This is another aim of the book; showing how theory works out in real life.

The basis for the contents of this book can be found in the course, 'Emulsion Polymerisation', taught for many years at the Eindhoven University of Technology in the framework of the Foundation for Emulsion Polymerisation. In the last 10 years many people have contributed to shaping the afore-mentioned course and therefore laying a basis for this book: Ian Maxwell, Jenci Kurja, Janet Eleveld, Joop Ammerdorffer, Annemieke Aerdts, Bert Klumperman, Jos van der Loos and last but not the least Ton German. Most of the contributors to the chapters are members of the International Polymer Colloids Group, a group of experts around the world that meet on a regular basis and form a unique platform for sharing knowledge in the field.

The book is focusing on emulsion polymerisation in combination with both conventional and controlled radical polymerisation. Except for miniemulsion polymerisation, more exotic techniques, such as inverse emulsion polymerisation, microemulsion polymerisation and dispersion polymerisation are not covered. Chapter 1 gives a historic overview of the understanding of emulsion polymerisation, while also focusing on the solution of the kinetic equations. In Chapter 2 an introduction is given in the radical (co)polymerisation mechanism, explaining kinetics and the development of molecular weight and chemical composition. In Chapter 3, the basic elements of emulsion polymerisation are explained, again focusing on rate of reaction and molecular mass distributions. In Chapter 4, emulsion copolymerisation, process strategies and development of morphology is explained. In Chapter 5, the implementation of controlled radical polymerisation mechanisms in emulsion polymerisation is discussed. Colloidal aspects of emulsion polymerisation are discussed in Chapter 6. In Chapter 7, an overview of the molecular characterisation techniques of (emulsion) polymers is given whereas in Chapter 8 the characterisation techniques available for particle size, shape and morphology are reviewed. In Chapters 9 and 10, bulk and specialty applications are discussed.

We hope that this book will become a standard textbook in courses in emulsion polymerisation.

Chapter 1
Historic Overview

Finn Knut Hansen

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 natural polymers, such as cellulose, proteins, rubbers etc. Of these, natural rubber occurs in the form of a latex that is defined as a 'viscid, milky juice secreted by the laticiferous vessels of several see-bearing plants, notably *Castillia elastica*' etc. (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 these areas the most important sources of natural rubber. The latex that is obtained from this tree is usually called 'natural latex' and is a colloidal suspension of rubber particles stabilised by protein. The rubber content of the latex is between 32% and 38% by weight, the protein 1–2%, different natural sugars about 2% and inorganic salts about 0.5% (Hauser, 1930). The rubber particles vary largely in size from quite small, c.50 nm, up to 1–2 μm. 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 eventually resulted in the word 'latex' being also used to refer to 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 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 books have been written on the early developments in emulsion polymerisation, and have been a natural starting point for this text. One of the first reviews is that of Hohenstein and Mark (1946). The following is a direct quotation from their work (reprinted from *Journal of Polymer Science*, 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, Ostromislensky, 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 and 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.*, 1936b, Balandina *et al.*, 1936a, Berezan *et al.*, 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 *et al.*, 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 3 years, except for brief references in the books of Mark and Rafft (Mark and Rafft, 1941) and of Scheiber (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 *et al.*, 1944a, Hohenstein *et al.*, 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 *et al.*, 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.

In 1945, Hohenstein, Siggia, and Mark (Siggia *et al.*, 1945) published an article on the polymerisation of styrene in agitated soap emulsions, and Huges, Sawyer and Vinograd (Huges *et al.*, 1945), Harkins (Harkins, 1945), and Harkins with a number of collaborators (Harkins *et al.*, 1945) 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 *et al.*, 1944b, Vinograd *et al.*, 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, Kolthoff and Dale, 1945, Price and Adams, 1945, Siggia *et al.*, 1945, Vinograd *et al.*, 1944); (b) solubilised in the soap micelles (Harkins, 1945, McBain, 1942, McBain and Soldate, 1944) 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 extract tells much about our initial understanding of the emulsion polymerisation mechanisms, even as, at that time, a quantitative theory was not yet developed. Also, the basic understanding of the relative importance of the aqueous, organic and micellar phases was somewhat lacking. But these topics will be treated thoroughly throughout this book. At this point must be mentioned, the very important so-called GR-S recipe for synthetic rubber. Even if the production of synthetic latexes were 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 (1939–45) 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).

The American Chemical Society has declared this programme 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, the recipe is quite simple, and each ingredient has its specific function (Table 1.1). The 3 : 1 ratio (5.8 : 1 molar) of butadiene and styrene gives the polymers 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 stabilisation of the particles, whereas the potassium persulphate acts as initiator. The traditional soap used was a commercial fatty acid soap containing mainly C_{16} and C_{18} soaps, but the effect of different soaps from C_{10} to C_{18} was investigated. The role of the mercaptane has been debated, and it has been frequently stated that the mercaptane and persulphate form a redox couple. However, the most accepted role of the mercaptane is as an inhibitor and chain transfer agent: to inhibit the formation of crosslinked, *microgel* particles during the polymerisation.

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 persulphate	0.30

When rubber is used in end products, such as car tyres etc., it is crosslinked in its final shape, a process called vulcanisation. This used the tetra-functionality of the butadiene (two double bonds), but this crosslinking is, naturally, not wanted during the emulsion polymerisation. Adding (among others) mercaptane to avoid this crosslinking action thus controls the process. The process is also stopped at 60–80% conversion and the monomers are removed by flash distillation. The GR-S rubber recipe has been modified from the 'mutual' recipe over the years, especially by lowering the polymerisation temperature to 5°C which 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 persulphate is too slow as an initiator at such low temperatures, this required the development of more active (redox) initiator systems.

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 have been 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 that the American synthetic rubber programme 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 United States was used in many other industrial emulsion polymerisation systems that begun their development both before and after the war. Another example of this is neoprene rubber, polychloroprene [poly(2-chloro-1,3butadiene)]. 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, such as gloves and shoe soles. However, World War II removed neoprene from the commercial market, 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 polyvinyl chloride (PVC) was patented by Fikentscher and co-workers 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 sulphonated organic derivatives such as the sodium salts of Turkey Red Oil and di-isobutylnaphthalene sulphonic 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 United States during the 1930s and eventually in the United Kingdom 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 United States and the United Kingdom, 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 by (what became) KemaNord in 1945 and in Norway by Norsk Hydro in 1950. This has been the origin of the Norwegian occupation 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 (1946). It appeared in a series of publications between 1945 and 1950 (Harkins, 1945, 1946, 1947, 1950; Harkins *et al.*, 1945). Harkins' interest was chiefly the role of 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 (Figure 1.1). The essential features of the theory are as follows (Blackley, 1975):

1. The main function of the monomer droplets is to act as a reservoir.
2. The principal locus of initiation of polymer particles is monomer swollen emulsifier micelles.
3. The main locus of polymerisation is the initiated polymer particles. During polymerisation, the 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 explicitly state how the water soluble initiator would be able to initiate the monomer swollen, 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 capable of going 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 a major leap forward in emulsion polymerisation. This is described further in Section 1.2.2.