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Emulsion Polymerisation of Non-polar Monomers (Development of Ideas on Kinetics and Topochemistry)

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The kinetics, the topochemistry, and the mechanism of the emulsion polymerisation of non-polar monomers are discussed in the light of results obtained during the past decade. The part played by components of the system, features of the primary reactions, and the theory of emulsion polymerisation are considered. A list of 114 references is included.

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I. INTRODUCTION

Emulsion polymerisation is widespread, technically convenient for the production of monomers, and characterised by several specific features. In its common variants the monomer is dispersed in water, but the polymer is obtained as a latex. All the advantages (and disadvantages) of emulsion polymerisation are due to the heterogeneity of the system, and the possibility of localising the primary reactions in different zones. Improvement of the technology of emulsion polymerisation—the possibility of controlling the structure and working properties of the resulting polymers—is determined by the level to which a general theory has been developed to give a correct interpretation of the kinetic and topochemical features. The difficulty of establishing such a theory is due firstly to the multiphase character of the emulsion system and secondly to the multiplicity of parameters governing the mechanism and kinetics. This diversity is due not only to differences in reactivity of the reactants in specific systems but also to differences in their distribution between the phases. All this complicates the establishment of local zones in which the primary steps take place, as well as the determination of reactant concentrations in these zones, so that kinetic description of an emulsion process becomes difficult.

Thus one of the main problems in a theory of emulsion polymerisation is to establish the sites at which the primary reactions occur and to determine the local reactant concentrations at these sites. It must be noted that a given primary reaction can take place in more than one local zone. Finding a theoretical basis for the presence of local zones, their number, and the distribution of reactants among them, establishing their reactivity as a function of their location—these are the chief tasks of a theory of emulsion polymerisation.

At the present time the greatest certainty has been achieved for the emulsion polymerisation of non-polar monomers, sparingly soluble in water, in the presence of ionogenic emulsifiers and water-soluble initiators. However, existing theories do not give a complete explanation even for this comparatively narrow range of emulsion processes. The new experimental results continually appearing undoubtedly broaden our views and deepen our understanding of the processes occurring in complicated emulsion systems.

The present Review will cover mainly research results published during the past 8–10 years and relating essentially to the emulsion polymerisation of non-polar monomers. Special attention will be paid to work which has not been subjected to detailed consideration in the review literature or has not been discussed at all. Detailed analysis of papers on the emulsion polymerisation of polar monomers will be found in Eliseeva's reviews[1,2].

Before surveying the most recent work on emulsion polymerisation we shall consider briefly existing views based on earlier investigations, as well as some of the main directions in which they have been refined and elaborated.

II. QUALITATIVE PICTURE OF EMULSION POLYMERISATION AND THE SMITH–EWART THEORY

We shall consider the most typical emulsion systems, in which polymerisation takes place by a radical mechanism in the presence of micelle-forming surface-active compounds; the dispersion medium is water, while the disperse phase is a non-polar monomer sparingly soluble in water.

The main principles underlying the technology of emulsion polymerisation in such systems were already known at the beginning of the century[3–5], but ideas on its mechanism were remote from present-day views. It was assumed that polymerisation occurred in drops of the emulsion. Fikentscher[6] was the first to abandon this view and to suggest that polymerisation takes place in the aqueous phase. Later more complete qualitative ideas on the emulsion polymerisation of non-polar monomers were developed[7,8] and supplemented independently[9,10]. We note below only the main principles that follow from this work.

1. Emulsion polymerisation is the usual radical process of polymerisation, the explanation of whose features is that the sites of reaction—micelles and polymer–monomer particles—are discrete volumes.

2. In the initial stage the emulsion system comprises a mixture of micelles of the emulsifier, polymer–monomer particles, and large drops of the monomer.

3. Polymerisation begins only in micelles, which are then converted into polymer–monomer particles, whereas drops of the monomer, in which the process hardly develops, serve

merely as a source of the monomer. Diffusion of the monomer from the drops into the polymer–monomer particles is not rate-determining, so that an equilibrium concentration of the monomer is established in the polymer–monomer particles, which is maintained as long as drops exist.

On the basis of these ideas Smith and Ewart[11] developed a quantitative theory of the emulsion polymerisation of non-polar monomers (more precisely the theory of the emulsion polymerisation of styrene by persulphate in the presence of ionogenic surface-active agents), which was then extended to other systems. Their work, published in 1948, was a most important event in the investigation of emulsion polymerisation, and remains so even to the present time. Hardly any contribution to a quantitative theory of emulsion polymerisation can avoid referring to this work.

Using the principle of quasi-stationarity Smith and Ewart suggested several solutions for the kinetic equation of emulsion polymerisation. The condition of quasi-stationarity for N_n particles containing n radicals can in general be written

$$N_{n-1}(R_i/N) + N_{n+1}k_0a(n+1)/v + N_{n+2}k_t(n+2)(n+1)/v = N_n(R_i/N) + \\ + N_nk_0an/v + N_nk_tn(n-1)v, \quad (1)$$

where R_i is the overall rate of entry of radicals into all N particles (the total number of particles in unit volume), v the volume of a particle, n/v the concentration of free radicals in a particle, a the surface area of a particle, k_0 the rate constant of escape of radicals from a particle, and k_t the rate constant of termination. Thus the left-hand and right-hand sides of Eqn.(1) comprise terms describing respectively the disappearance and the appearance of particles containing n radicals. Smith and Ewart examined three cases.

1. The condition $n \leqslant 1$ corresponds to a high rate of escape of radicals from particles or a small proportion of particles containing a radical. The total number of radicals $R = N_1$, and Eqn.(1) becomes

$$N_1k_0a/v = N_0R_i/N. \quad (2)$$

Since $N_0 \cong N$, we have

$$R \approx N_1 \approx R_iv/k_0a$$

and

$$-\mathrm{d[M]}/\mathrm{d}t = k_{gr}[\mathrm{M}](R_iv/k_0a) \quad (3)$$

or

$$-\mathrm{d[M]}/\mathrm{d}t = k_{gr}[\mathrm{M}]V_pc_r, \quad (4)$$

where k_{gr} is the chain growth constant, V_p the total volume of particles, c_r the total concentration of radicals in the particles, and [M] the concentration of the monomer in a particle. Thus the rate of emulsion polymerisation is proportional to the total volume of particles. However, this case is seldom realised in practice, and does not find wide experimental support.

2. When $n = \frac{1}{2}$, the rate of escape of radicals from particles is small, but the rate of chain termination is high. As a consequence a polymer–monomer particle can contain at most one radical, and each subsequent radical entering the particle causes the instantaneous recombination of two radicals. As a result, only half the particles contain a radical. In view of the assumptions made, the total number of radicals should be $\frac{1}{2}N$. Hence we obtain an equation in which the rate of emulsion polymerisation is proportional to the number of particles:

$$-\mathrm{d[M]}/\mathrm{d}t = k_{gr}[\mathrm{M}]nN. \quad (5)$$

This conclusion is confirmed by numerous experimental results.

3. The case in which $n \gg 1$ is comparatively trivial and is described by relations characteristic of normal radical polymerisation in homogeneous systems. Equation (1) becomes

$$R_i/N = 2k_t(n^2/v), \quad (6)$$

whence after finding n we obtain

$$-\mathrm{d[M]}/dt = k_{gr}[\mathrm{M}](V_pR_i/2k_t)^{1/2}, \quad (7)$$

i.e. the rate of emulsion polymerisation depends solely on the total volume of particles and is independent of their number.

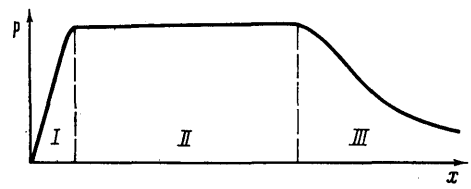


Figure 1. Dependence of rate of emulsion polymerisation on degree of conversion x of monomer into polymer.

The second case is especially interesting, being most often realised in practice and reflecting the features of emulsion polymerisation (for this reason the Smith–Ewart theory is often identified with this case). The qualitative picture and the quantitative theory provide an explanation of the kinetics. The rate curve for non-polar monomers comprises three segments (Fig.1): a comparatively short segment (I), corresponding to an increasing rate of polymerisation R_p, is followed by segment (II), with a constant rate, and segment (III), along which the rate decreases. On the basis of these views section (I), often termed the micellar stage of emulsion polymerisation, can be attributed to formation (nucleation) of polymer–monomer particles and increase in their number. After the micellar soap adsorbed on the particles has disappeared, no new particles are formed, and the R_p remains unchanged along the steady-state segment (II), as all the parameters (k_{gr}, n, N, [M]) are constant. After the monomer drops have disappeared, stage (III) begins, when all the monomer is present in polymer–monomer particles, and the rate of polymerisation falls owing to decrease in the concentration [M] in the particles.

Equation (5) thus describes the steady-state region of emulsion polymerisation, which continues as far as 50–70% conversion depending on the type of monomer. In essence it involves all the kinetic parameters—concentrations of reactants (monomer, initiator, emulsifier) and constants of primary reactions—although only k_{gr} and [M] appear explicitly. The remaining concentrations and constants are included in the parameter N, which according to the Smith–Ewart theory is given by the formula

$$N = k(R_i/\mu)^{3/5}(S_0[\mathrm{E}])^{3/5}, \quad (8)$$

in which μ is the rate of increase in volume of the polymeric particle, S_0 the area occupied by 1 g of emulsifier, [E] the concentration of the emulsifier, and k a constant (varying between 0.37 and 0.53). It is evident that the number of particles depends on the rate of initiation, and hence on the initiation constant and the initiator concentration, as well as the emulsifier concentration. The somewhat unusual powers

to which the emulsifier concentration and the rate of initiation are raised are explained by the circumstance that, with a constant rate of increase in particle volume, the total particle surface should increase with time to the power $\frac{5}{3}$.

Equation (8) can be deduced on the postulate that all free radicals formed in the aqueous phase are captured by micelles, when

$$dN/dt = R_i, \tag{9}$$

The change in volume of a particle in the interval between time τ and t

$$v_{\tau t} = \mu(t-\tau) \tag{10}$$

is accompanied by the change in particle surface

$$a_{\tau t} = \theta(t-\tau)^{2/3}, \tag{11}$$

where

$$\theta = [(4\pi)^{1/3}/3\mu]^{2/3}. \tag{12}$$

The total surface area of all the particles will then vary in conformity with the equation

$$A_p = R_i\theta\int_0^t (t-\tau)^{2/3}\,dt = \frac{3}{5}R_i\theta t^{5/3}. \tag{13}$$

Since $A_p = S_0[E]$ at the instant t_1 of disappearance of free soap or completion of formation of particles, we can write

$$t_1 = (5S_0[E]/3R_i\theta)^{3/5}. \tag{14}$$

Hence the number of particles

$$N = R_i t_1 = R_i^{2/5}(5S_0[E]/3\theta)^{3/5} = 0.53(R_i/\mu)^{2/5}(S_0[E])^{3/5}. \tag{15}$$

It can readily be shown that, in the alternative case in which the radicals formed are captured also by particles attached to existing micelles, the formula for the number of particles will be similar but with a rather smaller value (0.37) for k.

It is noteworthy that the initiator concentration and hence the rate of initiation behave rather unusually in emulsion polymerisation. Primarily they affect the number of particles, the time of formation of which depends on the rate of disappearance of the micellar soap. After the disappearance of micelles no new particles are formed, and the rate of initiation ceases to influence the overall rate of emulsion polymerisation. Thus addition of a fresh portion of initiator in the second stage does not increase the rate of polymerisation, since the number of radicals in polymer–monomer particles cannot then change.

The termination constant k_t does not occur in the kinetic equation, since in the classic form (with $n = 0.5$) it does not limit the processes governing the lifetime of radicals and their number in a particle. If, however, it is postulated that two or more radicals may remain in a particle, this constant will play a decisive role, and its influence on n can be represented by the equation[12]

$$n = {}^4/_3 r^3\pi N_A w_i^{1/2}/k_t^{1/2}, \tag{16}$$

in which r is the particle radius and w_i the rate of initiation. In this case great importance will attach to the viscosity of the polymer–monomer particles, which is apparent in the Trommsdorff effect (increase in rate of polymerisation and molecular mass of polymer due to a decreased termination constant in viscous media). Incidentally, this effect cannot legitimately be used to explain high rates and molecular masses of polymers during emulsion polymerisation on the basis of Smith and Ewart's classic concepts: if we postulate the residence of more than one radical in a polymer–monomer particle, we thereby indicate the possibility of departures from the Smith–Ewart theory.

Publication of the theory was later followed by papers[13–15] discussing such deviations, which still continue to appear with considerations of other problems of emulsion polymerisation. For example, the possibility is examined that colloid-chemical parameters of an emulsion system may influence the constants of the primary reactions, the mechanism of formation and the morphology of the polymeric particles, etc.

To avoid becoming involved in the vast factual material and to minimise confusion in its presentation, we shall attempt to analyse the accumulated experimental results by considering in succession the parameters governing the kinetics and the topochemistry of emulsion polymerisation.

Initially we shall examine the concentration parameters [M], n, and N, analysing the reasons for their variation within certain limits and the topochemical consequences of these variations, after which we shall consider the constants of the primary reactions.

III. NUMBER OF PARTICLES IN EMULSION SYSTEM DURING POLYMERISATION

We shall consider the number of particles in the system, and also the other parameters, primarily in relation to the second stage, which is characterised by a constant rate of polymerisation. This is the most interesting stage from the point of view of theory; it usually extends from 5–10% to 50–70% conversion depending on the type of monomer and the temperature. In order that the rate should become constant, of course, the parameters in Eqn.(5) should also remain constant at this stage.

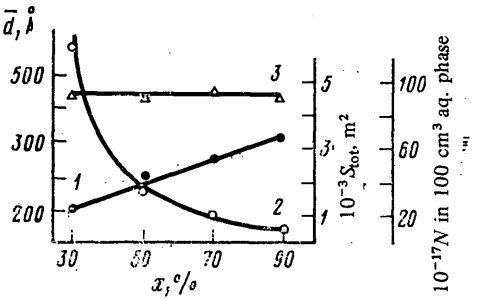


Figure 2. Effect of degree of conversion of styrene[21] on: 1) particle diameter $\bar{d}$; 2) number N of particles; 3) total particle surface S_{tot}.

Constancy of N has indeed been demonstrated in many cases[11,16], as indicated by comparatively recent results for emulsion systems differing from those investigated by Smith and Ewart. For example, in the polymerisation of styrene initiated by the oil-soluble azoisobutyronitrile, N remains constant throughout stage (II).[17] Constancy of the number of particles has also been established[18] in the emulsion polymerisation of styrene in the presence of a mixture of an ionogenic and a non-ionogenic surface-active agent. Unchangeability of the number of particles during stage (II) has been established[19,20] for such an atypical case as the emulsion polymerisation of styrene on potassium peroxodisulphate in the

absence of an emulsifier. Here stabilisation of polymer–monomer particles is achieved by charged SO_4^- end-groups of macromolecules formed by dissociation of the persulphate, and polymerisation is initiated by radical-anions. We shall discuss this work[18–20] in greater detail in connection with the structure of polymer–monomer particles.

However, besides data consistent with the ideas of Smith and Ewart, quite a few results are known that indicate change in the number of particles during the second stage of emulsion polymerisation. First to give a theoretical basis to such phenomena was Medvedev[21], who suggested that adsorbed layers on the surface of latex particles retain in some measure their capacity for interphase exchange among themselves, with a consequent interdependence of polymerisation processes occurring in different proton–monomer particles, so that emulsion polymerisation can be regarded as a quasi-homogeneous process. Medvedev supports this hypothesis with data on the variation in the number of particles, their total surface, and their diameter at various degrees of conversion of styrene and methyl methacrylate[21]. Fig. 2 shows that N falls rapidly with extent of polymerisation, whereas the total particle surface remains constant.

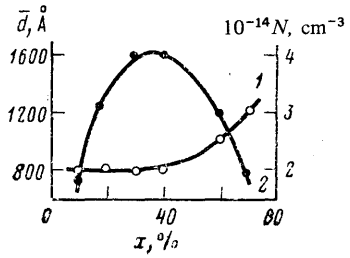


Figure 3. Influence of conversion (0.026 M Alkamon DS in aqueous phase + 0.01 M cumene hydroperoxide in styrene with ratio of monomer to water 1 : 7 at pH 3 and 60 °C [22]) on 1) particle diameter; 2) number of particles.

The Reviewers have also observed[22] variation in the number of polymer–monomer particles during the emulsion polymerisation of styrene, initiated by cumene hydroperoxide in the presence of a cation-active surface-active agent—Alkamon DS $\{C_{12-18}H_{25-37}.O.CH_2.N^+(C_2H_5)_2.CH_3\}CH_3SO_4^-$—although the dependence of N on degree of conversion was more complicated (Fig. 3). However, even in this case the total particle surface remained unchanged after a maximum value had been reached. The increase in the number of polymer–monomer particles until 30% conversion is reached in this sytem can be explained by the very high concentration of emulsifier and extension of the micellar stage to this conversion. The possibility of retaining the micellar soap until high monomer conversions are reached has also been mentioned[23].

The above results show that in several cases Smith and Ewart's postulate that latex particles are discrete is not confirmed. It has therefore been suggested that adsorbed films of emulsifier molecules are the chief site of the primary reactions in emulsion polymerisation. The occurrence of interphase exchange interaction between separate polymer–monomer particles permits the processes to be averaged with respect to the main parameter—the total quantity of soap in the system—and the kinetic scheme to be based on the usual set of reactions of radical polymerisation with reactant concentrations related to the volume of adsorbed films of such particles. In the light of these ideas Medvedev suggested kinetic equations which did not contain the number of particles. For example, with a water-soluble initiator the rate of emulsion polymerisation is given by

$$R_p = k_{gr}[I]^{1/2}[E]^{1/2}[M]^0. \qquad (17)$$

In individual cases Medvedev's theory provides a satisfactory description of qualitative and quantitative aspects of emulsion polymerisation. However, it can hardly be regarded as a more general approach to an explanation and description than is the Smith–Ewart theory, since his conclusions are based mainly on experiments undertaken in the presence of high concentrations of emulsifier and initiator, i.e. under conditions of formation in the early stages of a very large number of particles, which may flocculate because of the rapidly increasing adsorption unsaturation of the system. Similar phenomena can probably take place when the surface-active agent has an inadequate stabilising affect or with a low rate of adsorption of emulsifier on the rapidly formed surface, as occurs in the polymerisation of polar monomers[24]. Furthermore, Medvedev's suggested interphase exchange does not agree well with such a fact as emulsion polymerisation on long-lived radicals in the case of radiation initiation, followed by postpolymerisation after irradiation has ceased[25,26].

Thus Medvedev's theory is not capable of describing the whole variety of phenomena involved in emulsion polymerisation, although it well supplements the Smith–Ewart theory and can justifiably be applied if its limits are intelligently defined. However, it must be stressed that the concept of the discreteness of latex particles in the emulsion polymerisation of non-polar monomers, which usually give well stabilised particles, is more general. For this reason kinetic ideas based on the number of particles in an emulsion system and the number of radicals in them are probably more fertile, and continue to evolve at the present time.

IV. NUMBER OF FREE RADICALS IN A POLYMER–MONOMER PARTICLE

As already mentioned, a single polymer–monomer particle can in principle contain more than one free radical, which is inconsistent with the views of Smith and Ewart. As early as 1957 a theoretical basis was given to such a possibility by Stockmeyer[13], who calculated that such a particle of diameter exceeding 1000 Å can contain several radicals: i.e. the combination of a large particle volume and a high viscosity (with equilibrium swelling at 50 °C the concentration of styrene polymer in a polymer–monomer particle is 43%) makes the presence of several radicals in a particle possible because of the diminished probability of their termination. Subsequently van der Hoff[14], using formula (5) to calculate from data on the emulsion polymerisation of styrene in the presence of cumene hydroperoxide the number of radicals in a polymer–monomer particle as a function of its diameter, showed that even for comparatively small particle diameters considerable departures from $n = \frac{1}{2}$ are possible (Fig. 4).

Since the diameter and the viscosity of a particle (in stage III) increase during polymerisation, the number of radicals in a particle should also increase. Thus a similar calculation for the emulsion polymerisation of styrene has shown[27] that, although the number of radicals does not change very greatly (from 0.5 to 1.0) in the steady state, it rises rapidly after the disappearance of drops of the monomer (stage III) because of a rapid increase in viscosity

in the particle (Fig.5). Similar calculations have been made by other workers[28].

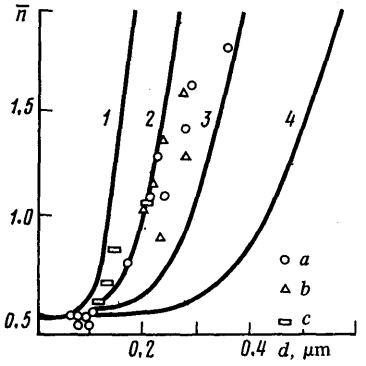


Figure 4. Mean number of radicals in a particle $\bar{n}$ as a function of particle diameter[14] indicated by experimental points for: *a*) $K_2S_2O_8$ at 50 °C; *b*) $K_2S_2O_8$ at 40 °C; *c*) cumene hydroperoxide at 50 °C. The curves have been calculated for different values of lg $[fk_d(I)/k_t]$ (k_d is the decomposition constant of the initiator and f the efficiency of initiation[33]): 1) −12; 2) −13; 3) −14; 4) −15.

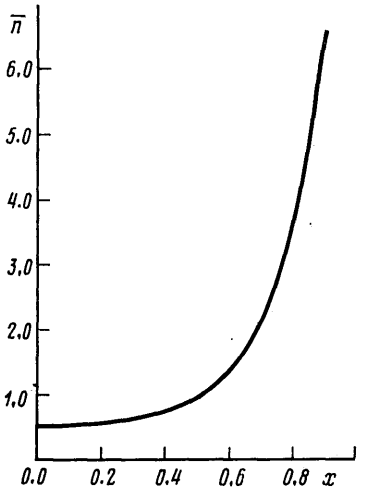


Figure 5. Theoretical dependence[27] of mean number of radicals in a particle $\bar{n}$ on conversion x.

In an investigation of the emulsion polymerisation of styrene (0.01 M) in the presence of cumene hydroperoxide and cation-active surface-active agents (0.026 M Alkamons in aqueous phase, with a 1:7 monomer–water phase ratio at 60 °C) the Reviewers have also shown[12] the possibility of finding several radicals in a single polymer–monomer particle (Table 1), with n dependent not only on particle size but also on rate of initiation. The specific action of the emulsifier made it possible, by varying the pH of the aqueous phase, to increase particle diameter with simultaneous increase in rate of initiation of polymerisation. If a particle contains several radicals, the influence of rate of initiation on n can be described by Eqn.(16).

Table 1. Influence of particle diameter d and rate of initiation w_i on number of radicals n in a polymer–monomer particle during the emulsion polymerisation of styrene[12].

pH	10^3R_p, M (in styrene) s^{-1}	10^8w_i,	$10^{-14}N$, cm^{-3}	$\bar{d}$, Å	n
3	1,62	6,60	1,02	1200	1,61
5	1,91	9,16	0,53	1500	3,27
7	1,02	2,00	0,41	1620	2,22
9	0,70	1,17	0,30	1800	2,12
11	1,40	6,34	0,17	2200	7,47
12	1,92	10,70	0,13	2400	13,4

Thus examination of yet another fundamental parameter of emulsion polymerisation indicates additional limitations on the applicability of the Smith–Ewart theory, associated with the diameter of the latex particles. The theory is fully applicable only to particles of diameter <1000 Å. Nevertheless, Eqn.(5) corrected for the number of radicals describes satisfactorily the steady stage even in the presence of larger particles (for n changes little during stage II), as the rate of initiation remains almost constant[29]).

We note in conclusion that theoretical calculations on the number of free radicals in a polymer–monomer particle are considerably complicated by the possibility of their escape from the latter. This problem is examined in some details in a recent review[30], which notes that the desorption and readsorption of radicals by particles are especially significant in the emulsion polymerisation of polar monomers such as vinyl acetate and chloride, whereas they have little kinetic influence on that of non-polar monomers, e.g. styrene.

V. CONCENTRATION OF MONOMER IN A POLYMER–MONOMER PARTICLE

Consideration of the concentration of the monomer in a polymer–monomer particle—an important parameter of emulsion polymerisation—poses several questions of fundamental significance and widely discussed during recent years—(i) what the concentration is and whether it is an equilibrium value, (ii) whether diffusion of monomer from drops into particles influences establishment of the concentration, (iii) whether the concentration is constant during polymerisation, and (iv) the distribution of the monomer within the particle—to the first three of which the Smith–Ewart theory gives unambiguous answers. The last question, which is ignored in the classical theory, is especially important, since it concerns not only the kinetic aspect of emulsion polymerisation but also the mechanism of formation and the morphology of a latex particle. All the questions certainly apply to the steady state of emulsion polymerisation, since answers to them are given primarily to explain the existence of this second stage. Since Smith and Ewart's ideas have been outlined above, we shall consider only Morton's physical interpretation of the monomer concentration in a particle[31].

The equilibrium swelling of latex particles in the presence of the free monomer is regarded[31] as analogous to the equilibrium in the swelling of a cross-linked polymer in a solvent,

but in the present case the swelling is limited not by intermolecular bonds but by the interfacial energy between particle and aqueous phase. Such a treatment will yield the equation

$$2\Phi_m\sigma/RTr = -[\ln(1-\Phi_p) + \left(1-\frac{1}{\bar{p}}\right)\Phi_p + \chi\Phi_p^2], \qquad (18)$$

similar in form to the well known Flory–Huggins relation[32], in which Φ_m and Φ_p are the volume fractions of monomer and polymer in the swollen particle, σ is the interfacial tension, R the gas constant, T the absolute temperature, χ the monomer–polymer interaction parameter, and $\bar{p}$ the number-average degree of polymerisation.

It follows from formula (18) that the view that the concentration of monomer in a polymer–monomer particle is constant is strictly not entirely accurate, since Φ_m depends on the particle radius and the interfacial tension, which change during polymerisation. Since, however, the increase in particle radius is balanced by that in the interfacial tension, such constancy can be used as a good approximation. Calculations based on Morton's equation show that the concentration varies very little with particle diameter over the range 500–1000 Å, while the emulsifier content of the particle is 2–5% of the mass of monomer[33,34].

Constancy of the monomer concentration in a polymer–monomer particle and its equilibrium character, the latter due to the ability of a polymer particle to swell in the monomer, are supported by a fair quantity of experimental results[35,36], which continue to appear. For example, after separation of drops of monomer and determination of yield of polymer the concentration of styrene in a polymer–monomer particle has been calculated[37] as 5–6 M, which corresponds to the equilibrium swelling of polystyrene in its own monomer[38]. A similar value has been obtained from kinetic data[12], by using the departure from linearity of curves representing the accumulation of polymer at the instant of disappearance of drops of the monomer and from the monomer–polymer ratio. It has been shown also[37] that establishment of the equilibrium concentration of styrene in a polymer–monomer particle is not limited by diffusion, since the rate of diffusion of the monomer into latex particles exceeds its rate of polymerisation by 100–200%, which is entirely consistent with the classical theory of emulsion polymerisation.

Table 2. Emulsion polymerisation of styrene in the presence of ethylbenzene[39]*.

Ethylbenzene, %	c, M	R_{pp}	$[\eta]$, dm^3 g^{-1}	$c^2/[\eta]^{-1}R_{pp}^{-1}$, mole^2 g h dm^{-9}
0	8.69	1.99	1.60	2.4
10	7.82	1.66	0.90	4.1
25	6.57	0.63	0 65	10.5
50	4.35	0.17	0.34	32.7

*Here c is the concentration of styrene in the oil phase, $[K_2S_2O_8] = 0.01\%$, the concentration of sodium dodecyl sulphate in the oil phase is 2 mass %, and the phase ratio of oil to water is 1 : 2.

However, recent papers have indicated that an equilibrium concentration is not established in a polymer–monomer particle even during the emulsion polymerisation of styrene. In particular, the rate of the latter process is lowered by the presence of aromatic solvents to a greater extent than would correspond to the decrease in the monomer concentration (Table 2)[39]. Since the solvent does not diminish the number of particles (on the contrary, the number is slightly increased), it is concluded[39] that the diminished rate is due rather to a lower rate of polymerisation per particle R_{pp}. The latter decrease is attributed to a diminished viscosity in the latex particle and a consequent smaller contribution by the Trommsdorff effect, which may be evidenced by the considerable drop in intrinsic viscosity $[\eta]$ of the resulting polymer with increasing concentration of ethylbenzene. The viscosity decrease cannot be attributed solely to chain transfer to the solvent, since in this respect ethylbenzene is analogous to styrene itself. Calculation of $c^2/[\eta]R_{pp}$, associated with the ratio $k_{gr}/k_t^{1/2}$, shows that its variation at different ethylbenzene concentrations can be due only to change in the bimolecular termination constant if the rate constant of chain growth remains constant, which is quite probable.

Explaining the observed phenomena in terms of the Trommsdorff effect involves postulating firstly the existence of more than one radical in a polymer–monomer particle, which we have seen to be quite possible for sufficiently large particles, and secondly variation in the viscosity in the particle with solvent concentration. If ethylbenzene and styrene are assumed to be almost identical in thermodynamic properties, changes in viscosity should not have occurred in the particle, since the ratio of monomer plus solvent to the polymer, governed by the equilibrium between the oily phase in the drops and in the particle, would have been constant independently of the presence or the concentration of the solvent. However, the opposite is indicated by the fall in viscosity in the particle with increase in solvent concentration, deduced[39] from the diminution in the gel effect: i.e. replacement of part of the monomer by solvent leads to a ratio of monomer plus solvent to polymer which exceeds that of monomer to polymer when emulsion polymerisation occurs in the absence of a solvent. This result is regarded[39] as indicating non-equilibrium swelling of the polymer–monomer particle, the non-equilibrium character strengthening on passing to the system containing styrene alone (in absence of a solvent).

Other results[40] may also indicate that the swelling of polymer–monomer particles is not an equilibrium process. Halting it by cooling to and maintaining at 10 °C a system comprising styrene with azoisobutyronitrile and Ts-40 (oxyethylated hexadecanol $C_{16}H_{33}O.[C_2H_4O]_{40}H$) results in a higher rate of emulsion polymerisation after the system has been heated to 60 °C than in the normal method of polymerisation. It is supposed[40] that holding the system at 10 °C enables the particles to achieve equilibrium swelling, whereas under the usual conditions the concentration of monomer in a polymer–monomer particle is lower than the equilibrium value. In the Reviewers' opinion, however, these results[40] can have a different interpretation: in particular, the increase in rate after the reaction has been halted can be explained not by an increase in the concentration of monomer in the particle but by a change in the dispersity, e.g. as a result of quasi-spontaneous emulsification. Such experiments would undoubtedly have been more convincing if the reaction had been halted not at the micellar but at the steady stage, when particle formation is complete.

The above results[39,40] were obtained under fairly specific conditions, and can hardly be extended to the majority of traditional emulsion systems. The postulated[39] identity in the thermodynamic properties of the systems formed by polystyrene with styrene and with ethylbenzene appears to the Reviewers not entirely correct, since the parameter χ_1

representing polymer–solvent interaction may differ significantly for these systems. Values of χ_1 for the polystyrene–ethylbenzene system have not been published. Comparison of such systems as those of polystyrene with styrene, toluene, and xylene (with χ_1 respectively 0.33, 0.428, and 0.41)[41] shows that differences in thermodynamic properties between solutions of polystyrene in ethylbenzene and in styrene may be considerable. The above doubts concerning results in Ref.40 are supplemented by the use of a non-ionogenic emulsifier at fairly high concentrations, when formation of a stable structural layer may offer a mechanical barrier to penetration of the monomer into the proton–monomer particle. Nevertheless, as shown above, results obtained for systems with an ionogenic emulsifier at moderate concentrations usually indicate equilibrium swelling of such a particle.

VI. CONCENTRATION GRADIENT OF MONOMER

It is worth paying attention not only to the concentration but also to the distribution of the monomer in a latex particle, a problem hardly discussed at all until recently and arising from the investigations of Williams et al.[29,42–47] The essence of this worker's views is that the monomer is distributed non-uniformly in a polymer–monomer particle: a shell enriched in the monomer surrounds a core in which the polymer is concentrated. Since Williams' conclusions are fundamental in character, we shall consider his results in detail, taking into account the experimental conditions.

Table 3. Dependence of induction period in the emulsion polymerisation of styrene on time of polymerisation by concentration of inhibitor[29]*.

t, min	v, % h^{-1}	Inhibitor, g	τ, min
15	12.0	0.032	32.0
60	14.2	0.008	7.0
60	13.4	0.016	13.0
60	10.6	0.032	36.0
60	10.3	0.032	36.0
120	12.8	0.032	36.0
180	15.4	0.032	36.0

*Here t is the time of polymerisation, v the rate, and τ the induction period.

The "core–shell" theory of the polymer–monomer particle appeared as a consequence of kinetic data for the emulsion polymerisation of styrene on potassium persulphate in the presence of a mixture of sodium dodecyl sulphate and Triton X-100 (octylphenoxypolyethyleneoxyethanol)[42]. Grancio and Williams pointed out that stage (II), i.e. that before disappearance of drops of monomer, terminated at 30% conversion of styrene, whereas the rate of polymerisation remained constant until 50–60% conversion. Thus the concentration of monomer in a particle was roughly halved (from 6.3 M to 3.6 M) along the steady-state segment from 30% to 60% conversion. The number of particles and the number of radicals in them remained unchanged in the steady stage. Invariability of n was regarded[42] as indicated by the absence of an increase in the rate of emulsion polymerisation on introduction of an additional portion of initiator to the system in the steady stage.

Grancio and Williams[29] demonstrated the constancy of the rate of initiation by adding an inhibitor during the polymerisation of styrene (100 g styrene + 0.15 g sodium dodecyl sulphate + 3.0 g Triton X-100 + 0.075 g potassium hydroxide + 180 g water), when the induction period was directly proportional to the inhibitor concentration (Table 3). They adduced the interesting fact that the molecular weight of the polymer increases during the steady stage (Fig.6), contrary to traditional views. They give no clear explanation of the phenomenon, and attribute it to peculiarities of polymerisation in a polymer–monomer particle in the presence of a concentration gradient of the monomer.

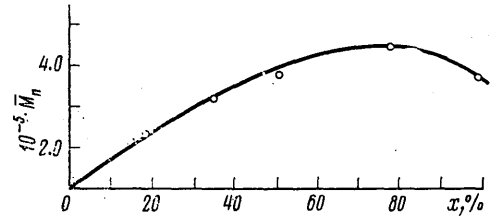


Figure 6. Variation of number-average molecular weight of polystyrene with conversion[29].

Williams explains the kinetic results by constant concentration conditions in the reaction zone, i.e. in the shell, in spite of variation in the monomer concentration calculated on the whole volume of the particle.

Kinetic data were accompanied by direct evidence of the formation of particles having a "core–shell" morphology[46]. Emulsion copolymerisation of styrene and butadiene on a polystyrene latex seed, with equilibrium saturation of the polystyrene particles by monomers added in the second stage, yielded particles comprising a polystyrene core and a shell formed from the added monomers. The structure of the particles was observed on electron micrographs of sections treated with osmium tetroxide.

Since this result appeared inconsistent with the simple thermodynamic incompatibility of polybutadiene and polystyrene, the inoculated polymerisation of styrene was undertaken[46] with a tritium-labelled polystyrene latex as seed, particles of which were saturated with styrene as before. Tritium gives β-rays of moderate penetrating power, which should be completely absorbed by a polystyrene shell 500–800 Å thick. An inoculating latex was therefore obtained having radioactive particles (diameter 1520 Å), on which non-radioactive styrene was polymerised to give a shell 1330 Å thick. The resulting particles were devoid of β-activity, from which it followed that the styrene had polymerised on the surface of the seed particles.

Williams suggested a theoretical explanation of the "core–shell" model on the assumption that the most probable, uniform distribution of polymer throughout the particle is prevented by its thermodynamic properties[45]. The latex particle is a microsystem, to which the laws of macrothermodynamics may be inapplicable. Indeed, only at the centre of a homogeneous particle can a macromolecule adopt the most probable conformation, i.e. one of high entropy. Macromolecules at the periphery, in a zone close to the interface, have diminished conformational entropy. In the "core–shell" model a macromolecule in the shell, which is a dilute

solution of the polymer, is able to adopt the most probable conformation.

The Williams theory has been seriously criticised by several well known investigators. Ugelstad[30] and Friis[27] doubted whether the kinetic data were correct, and considered that Grancio and Williams' results[29] could be explained in terms of the generally accepted increase in the number of radicals in a particle with increasing degree of conversion. Such a suggestion is quite plausible, since latex particles in the work of the Williams group were quite large ($d > 1000$ Å). In experiments with addition of initiator during polymerisation an increase in rate might have been overlooked, for it would have been only 7% under the conditions adopted.

Morton et al.[48] checked the data on the variation in molecular weight of the polymer with conversion and found that they involved experimental errors due to use of an impure specimen of the non-ionogenic surface-active agent—Triton X-100—which tended to oxidise rapidly in the air. The resulting functional groups of peroxy-type acted[48] as chain carriers, and the increase in molecular mass of the polymer could be attributed to their depletion during polymerisation. If Triton X-100 was replaced by an anion-active emulsifier (sodium oleate) or a mixture of dodecyl sulphate and the non-ionogenic surface-active agent Emulphogene BC-840 (tridecyloxypolyethylenoxyethanol), which is resistant to oxidation, no increase in molecular weight of the polymer is observed during the emulsion polymerisation of styrene.

Napper[49] accepts the existence of "core–shell" particles, but attributes formation of such a structure not to a thermodynamically improbable concentration gradient of the monomer across the particle but to specific aspects of the initiation of emulsion polymerisation by persulphates. Breakdown of a persulphate involves formation of radical-anions $SO_4^{\cdot-}$, which when initiating polymerisation fix one end of the polymer chain on the surface of the latex particle as a consequence of the strongly polar properties of the terminal sulpho-group. In inoculated polymerisation the growing macroradical attached to the surface "evacuates" monomer from the core, thereby being polymerised in the shell.

In reply to the critical comments Williams showed that the "core–shell" morphology is realised even in the initiation of emulsion polymerisation by benzoyl peroxide[46], although the thickness of the shell is substantially less than in the presence of potassium persulphate (respectively 155 and 520 Å) with inoculated polymerisation under similar conditions. In the latter case the size is almost equal to the diameter of the seed.

Gardon[50] also sharply criticised the "core–shell" theory. He considers that there are no thermodynamic grounds for expecting a concentration gradient of the monomer across the latex particle, as the coefficient of diffusion in the swollen polystyrene–styrene system should be $\sim 10^{-9}$–10^{-7} $cm^2\ s^{-1}$, so that polymerisation in the particle will be slower than diffusion. Gardon puts forward several hypotheses to explain the morphology of the particles observed by Williams: (i) the "core–shell" morphology in the system comprising inoculating polystyrene particles with styrene and butadiene is due to the incompatibility of polybutadiene and polystyrene; (ii) with tritium-labelled inoculating polystyrene particles and ordinary styrene the formation of inactive polystyrene in the shell may be expected to be due to reactions of chain transfer to the non-ionogenic emulsifier, a hypothesis supported experimentally, as shown above, by the work of Morton et al.[48]

The "core–shell" theory of particle morphology does not solve the problem of the concentration of monomer in a polymer–monomer particle. If drops of monomer disappear at 30% conversion of styrene, the monomer concentration in the particle should exceed 6 M (at 60 °C), appreciably larger than the equilibrium monomer concentration (~5 M). The reason for the complete transfer of monomer from drops to the particle at such low conversions remains completely incomprehensible, since this process is thermodynamically improbable because of the equalisation, at the instant of establishment of the equilibrium concentration in the polymer–monomer particle, of the chemical potentials of the monomer in the different phases.

Thus kinetic evidence for the "core–shell" morphology is clearly inadequate, and thermodynamic aspects also present several unresolved problems. However, there is no doubt that particles of complicated structure are formed in seeded polymerisation. The particle morphology observed by Williams may be supposed to be due, not to establishment of an improbable concentration gradient of the monomer in the particle, but to the specific conditions under which emulsion polymerisation takes place.

Although the "core–shell" theory involved several incorrect assumptions, a new line of research on emulsion polymerisation—the preparation of polymer dispersions containing particles of complicated structure—was stimulated by the work of Williams and his collaborators. It cannot be asserted that no such investigations had been made previously[51–55], but they have only recently[56–59] become at all purposeful, covering several applied fields of polymer chemistry (production of shock-resistant copolymers, novel types of rubbers, paints and varnishes). Latex particles of layered morphology enable materials of quite diverse properties to be obtained from a given pair of monomers. For example, dispersions of particles having hard cores and rubberlike shells can be regarded as a source of reinforced elastomers. Rubberlike particles having a thin solid-polymer shell give readily processable non-stick rubbers. Particles with a rubber core and a solid-polymer shell provide a typical system for the preparation of shock-resistant copolymers. Application of a thin layer of a soft polymer to a hard core is able to confer good film-forming properties on a dispersion.

Three methods are in practice available for obtaining latex particles of layered morphology in the course of inoculated polymerisation—(i) exploitation of incompatibility between seed polymer and polymer formed in the second stage, (ii) use of monomers that are pore solvents for the seed polymer, and (iii) conducting the second stage of polymerisation under conditions such that the seed particles are unable to swell in the added monomer, i.e. under conditions of competition between rates of diffusion and of polymerisation.

As examples of these procedures we may mention (i) the preparation of shock-resistant ABS copolymers by the emulsion method, (ii) the polymerisation of vinyl chloride or vinylidene chloride, and (iii) the polymerisation and copolymerisation of acrylic monomers. The last process has been developed especially successfully by Eliseeva et al.[58] However, these investigations lie outside the scope of the present Review. We note merely that realisation of the "core–shell" particle model has enabled film-forming dispersions to be obtained with properties considerably surpassing those of dispersions obtained by the random copolymerisation of acrylic monomers or by mixing two acrylic lattices[59].

VII. PRIMARY REACTIONS OF POLYMERISATION IN EMULSION SYSTEMS

The way in which primary actions occur during emulsion polymerisation differs substantially from that observed for homogeneous systems, as is apparent in the values of the constants and in the molecular characteristics of the resulting

polymers. One of the chief distinctions between emulsion and homogeneous systems lies in the possibility of segregating primary reactions in separate phases. This explains the unique feature of emulsion systems that the rate of polymerisation and the molecular weight of the resulting polymer both increase with the concentration of the emulsifier.

Since increase in emulsifier concentration entails an increase in the number of latex particles, the rate of emulsion polymerisation increases. With a constant rate of formation of free radicals in the aqueous phase the increased number of particles leads in turn to a diminished probability of entry of a radical into any polymer–monomer particle: i.e. the lifetime of a radical growing in a particle lengthens, so that the molecular weight of the polymer increases with the emulsifier concentration. We can use this feature of emulsion systems to obtain polymers differing fundamentally in properties from those obtained in homogeneous systems.

1. Initiation

As we have already seen, the number of particles in an emulsion system—one of the chief kinetic parameters—is determined in considerable measure by the rate of initiation. After the stage of formation of polymer–monomer particles is complete, the rate of the process no longer depends on the rate of formation of radicals. Thus introduction of a fresh portion of initiator in the steady stage produces no change in the rate of polymerisation. After completion of particle formation the rate of initiation affects only the frequency of acts of interconversion of particles between "dead" and active states, i.e. the molecular mass of the polymer. All these considerations apply, of course, to cases in which a particle can contain at most one radical.

The initiation of emulsion polymerisation is studied mainly on water-soluble inorganic peroxo-compounds such as ammonium and potassium persulphates, with which initiation is highly efficient (close to unity)[60]. Although many papers have appeared on the kinetics and the mechanism of the breakdown of persulphates in aqueous solution[60–64], the influence of emulsifiers on the rate has remained obscure[65–67]. In the majority of systems the presence of an emulsifier slightly accelerates the decomposition of persulphates. The considerable increase in rate in aqueous media at low pH is due to a change in the reaction mechanism[68,69].

The influence of aqueous solutions of surface-active agents on the kinetics of the decomposition of organic peroxy-compounds, e.g. hydroperoxides, is a more complicated problem. Here the increase in rate of decomposition may be due to several causes. On the one hand, the presence of an aqueous medium leads to the breakdown of association complexes of hydroperoxides, which differ in thermal stability from the monomeric hydroperoxides[70]. On the other hand, the accelerating action of the surface-active agent may be explained by the effects of micellar catalysis[71], which develops during the concentration of bifilar hydroperoxide molecules in emulsifier micelles. The action of an adsorbed film of polymer–monomer particles is probably similar, exerting a concentrating and orientating influence on hydroperoxide molecules and leaving such relatively non-polar initiators as benzoyl peroxide unaffected[72].

Artificial attachment of an initiator in the region of an adsorbed layer of polymer–monomer particles produces, independently of its polarity, a marked change in its rate of decomposition and hence in the rate of initiation of polymerisation. Thus the Reviewers have shown[114] that the graft polymerisation of styrene on particles of an inoculating latex—a copolymer of n-butyl acrylate and 1-t-butylperoxyethyl methacrylate—takes place at considerably higher rates in the emulsion than in the bulk or in a solvent at lower temperatures. It is sufficient to note the mere fact of polymerisation at a high rate under the influence of a dialkyl type of peroxide at an abnormally low temperature (in the bulk hardly any polymerisation occurs under corresponding conditions).

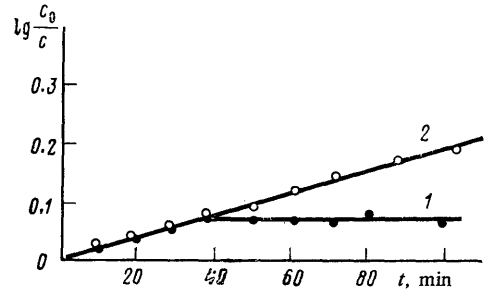


Figure 7. Semi-logarithmic transforms of kinetic curves for the decomposition of peroxy-groups in a copolymer of n-butyl acrylate and 1-t-butylperoxyethyl methacrylate (6.5 mole % of permonomer units in copolymer) in a latex of mean particle diameter 0.100 μm at 60 °C for different distributions of peroxy-groups in latex particles: 1) uniform; 2) predominantly in surface zone[73].

The decisive influence of an adsorbed film on the kinetics of initiator decomposition is also indicated by the difference in the kinetics of the breakdown of peroxy-groups in the copolymer according to their distribution through the latex particle (Fig.7)[73]. The results confirm that under selected conditions breakdown occurs predominantly at the particle surface. With a uniform distribution of peroxy-groups through the particle only the small proportion located at the surface decompose. The surface distribution of peroxy-groups achievable by proportioning the monomers in the preparation of the latex ensures that they will be almost completely decomposed.

Emulsion systems are very convenient for the use of redox initiating systems, in which phase separation of components is possible, so that radical formation can be localised at the interface. Interesting effects are obtained by the use of specifically acting emulsifiers capable of influencing the mechanism of the breakdown of peroxide initiators. Cation-active emulsifiers containing a quaternary nitrogen atom have been investigated in the greatest detail[74–78]. The activating effect of such surface-active agents on the initiation of emulsion polymerisation is attributed by most authors to conversion of the quaternary compounds into tertiary amines[21], whose accelerating action on the decomposition of peroxy-compounds is well known. Such effects were discovered on cationic surface-active agents such as alkylpyridinium halides[74–76]. The unexpectedly high rates of polymerisation in the presence of surface-active aliphatic quaternary ammonium salts were attributed to the formation of tertiary amines[22,77,79] by the Hofmann decomposition of the quaternary compounds. Direct involvement of such compounds in acts of initiation is indicated by the antiparallel dependence, unusual for emulsion polymerisation, of the rate of polymerisation of styrene and the molecular weight of the resulting polymer on the emulsifier concentration (Fig.8)[22].

We can thus consider two specific aspects of the initiation of emulsion polymerisation. Firstly an indirect influence on the overall kinetics can be expressed as the dependence of the number of polymer–monomer particles in the emulsion system on the rate of initiation, which ultimately determines the kinetics of the process. On the other hand, the rate of decomposition of the initiator, and hence the rate of radical formation, depend on the properties of the emulsion system itself, the distribution of initiator between aqueous and oil phases, the possibility of localising acts of initiation in the region of adsorbed layers of emulsifier, and in individual cases direct chemical action of the initiator on the actual acts of radical formation.

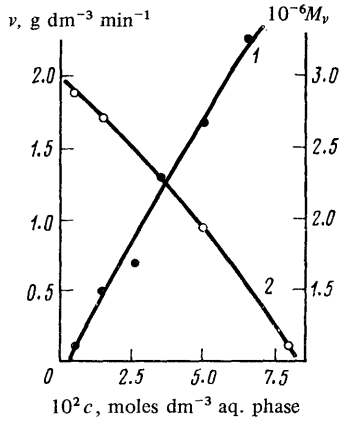


Figure 8. Effect of concentration c of emulsifier (Alkamon DS), with cumene hydroperoxide (0.01 mole cm^{-3} styrene) as initiator and phase ratio of monomer to water 1 : 7, on: 1) rate of polymerisation of styrene: 2) molecular weight of polymer[22].

Since in this work polymerisation was conducted at low temperatures, because of the presence of a redox initiating system, the reliability of these views is doubtful. According to Dunn[82] the low temperatures themselves can explain some regulating effect in the chain-growth steps, for isotactic and syndiotactic additions differ in activation energy[83]. The fact that the ratio $k_{gr}/k_t^{1/2}$ remained unchanged (Fig. 9) when styrene was polymerised in the presence of Alkamons—cationic surface-active agents[12]—in media of differing pH, when the state of the adsorbed layer of emulsifier and the rate of initiation of polymerisation varied greatly owing to passage of nitrogen into the amine state, indicates that the adsorbed emulsifier film had no effect on acts of chain growth.

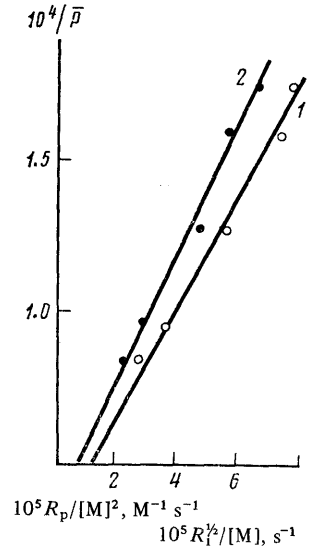


Figure 9. Dependence of reciprocal of polymerisation on $R_p/[M]^2$ and $R_i^{1/2}/[M]$, where the concentration of the monomer in the polymer–monomer particle [M] = 5 M.[12]*

2. Chain Growth

It is usually supposed that chain growth during polymerisation in an emulsion proceeds as in homogeneous systems, i.e. with the same kinetic constants. This postulate enables the chain-growth rate constant to be calculated by means of Eqn.(5) for the rate of emulsion polymerisation. In many cases the results agree well with values of k_{gr} calculated in other ways[34,38,80].

Nevertheless, the view has been expressed that an adsorbed layer of emulsifier has a direct effect on the primary acts of chain growth[21,81]. Such ideas are based mainly on studies of emulsion polymerisation in the presence of *N*-alkylpyridinium halides as cation-active emulsifiers. Thus Medvedev assumed[21] that conducting emulsion polymerisation in an alkaline medium favours conversion of quaternary nitrogen into the amine state with appearance of an initiating centre on the emulsifier molecule. A regular arrangement of charged and uncharged nitrogen atoms on the surface of a latex particle is regarded as ensuring stereocontrol of chain growth and yielding polymers of more regular structure than in the usual cases of emulsion polymerisation.

Specific emulsion systems exist in which such an effect has been quite definitely established. The emulsion copolymerisation of styrene with maleic anhydride in the presence of lecithin as optically active surface-active agent yields an optically active copolymer[84]. However, this result can be explained by separation of the two comonomers in different phases as a consequence of differences in aqueous and mutual solubility. Since maleic anhydride is incapable of homopolymerisation under ordinary conditions, it does not polymerise in the aqueous phase, despite initiation by a water-soluble initiator such as potassium persulphate. Thus copolymerisation can take place only at the interface, i.e.in the region of adsorbed layers of surface-active agent. As a result lecithin exerts a direct influence on chain growth.

Thus the above examples show that under certain conditions surface-active agents can affect acts of chain growth, although in most trivial emulsion systems such an influence is improbable if not impossible.

*It seems that the wrong diagram may have been taken from Ref.12 (Ed. of Translation).

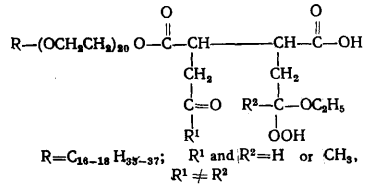
3. Chain Termination

Clearly, it makes sense to speak of bimolecular termination of two growing macroradicals during emulsion polymerisation only when two or more radicals can in principle be present in the polymer–monomer particle. As already noted, this case occurs with sufficiently large particles (of diameter ~1000–1200 Å), in which the primary radical grows to a certain size "without terminating" an already existing macroradical in the given particle, and is able to lose mobility owing to its increase in size and the high viscosity of the particle. Several workers have shown[12,85] that in such cases the termination rate constant k_t has the extremely low values characteristic of polymerisation in highly viscous media. Furthermore, although this constant remains almost unchanged at the steady stage with a constant concentration ratio of monomer and polymer in the particle, it decreases after drops of the monomer have disappeared, owing to enhanced viscosity in the particle, which in turn causes an increase in the number of radicals in the latter[27].

When only one radical can be present in a particle, chain termination by the first radical to enter the particle takes place instantaneously. As a consequence the molecular weight of the polymer is determined solely by the frequency of entry of radicals into a particle, i.e. by the rate of initiation. Since with a high degree of dispersion of the emulsion system this frequency is not too high, the lifetime of a free radical is considerably longer in emulsion polymerisation than when polymerisation occurs in the bulk or in solution. As a result, polymers of quite high molecular weight are obtained by emulsion polymerisation.

Especially interesting effects arise when the generation of free radicals is suddenly arrested (with light or radiation as initiator). In this way the lifetime of a radical present in a polymer–monomer particle may become indefinite, and the use of postpolymerisation effects will yield polymers of exceptionally high molecular weight, provided that chain transfer to monomer, emulsifier, or impurity is not too intense. Polystyrene of molecular weight $>10^7$ can be obtained[25,86] by emulsion postpolymerisation. The latter effects can be used also to obtain graft and block copolymers[25,86–88].

It was supposed until recently that these phenomena—formation of polymers of abnormally high molecular weight and also block copolymers—are possible only with the emulsion system exposed to light or radiation. However, it has now been shown[89–95] that such effects can be obtained also with peroxide initiation of emulsion polymerisation. Quite a high rate of polymerisation is observed in the emulsion polymerisation of methyl methacrylate in the absence of specially introduced initiator[89], i.e. under the influence of peroxides formed by oxidation of the emulsifier, and the molecular mass reaches 7×10^6. Still higher molecular masses (up to 2×10^7) can be obtained by using the initiator



specially synthesised by the Reviewers[114], which possesses well defined surface-active properties.

The emulsion polymerisation of styrene goes at normal rates when the concentration of this initiator is 10^{-6}–10^{-7} M in the monomer. This phenomenon cannot be attributed to a high efficiency of initiation, since separate experiments showed that the efficiency did not exceed a few percent. The reason must be sought in a lengthened lifetime of the radical in the polymer–monomer particle, ensuring the formation of polystyrene of exceptionally high molecular mass (up to 2×10^7). It is as yet difficult to explain satisfactorily the effects arising when acts of initiation are localised in an adsorbed layer of emulsifier. It may be supposed that they are related to additional restriction of the mobility of the growing radical by the attachment of one end to the particle surface, with a consequent decrease in the termination constant. It is noteworthy also that the use of such emulsifying initiators at normal concentrations (0.01 M in the monomer), because of chemical bonding with the resulting polymer, produces polymer dispersions of enhanced resistance to electrolytes, mechanical distortion, and freezing[96].

Very interesting phenomena have been observed by the use of polymeric initiators. Mikulašova et al.[91–94] have investigated the emulsion polymerisation of styrene in the presence of a polymeric hydroperoxide obtained by the oxidation of polypropylene. The hydroperoxide was used as a powder of particle size 0.1–0.55 mm in the presence of triethylenetetramine combined with metals of variable valency to activate breakdown of the hydroperoxide. Styrene was polymerised at 20–50 °C with ionogenic (sodium alkanesulphonates) or non-ionogenic surface-active agents as emulsifier. A feature of this polymerisation system is that the molecular mass of the polymer increases with time. For example, it approximately doubled when the degree of conversion of styrene changed from 4% to 12%. When the polymeric hydroperoxide was replaced by a mixture of polypropylene and t-butyl hydroperoxide, the molecular weight of the polymer did not change with conversion and its value was some 10% of that in the system containing the polymeric hydroperoxide. Use of a polymeric initiator will yield polystyrene of exceptionally high molecular mass (2×10^7) with a very narrow molecular-mass distribution ($M_w/M_n=1.01$). Similar results have been obtained by the same workers[95] by using oxidised powdered graphite or silica to initiate the emulsion polymerisation of methyl methacrylate.

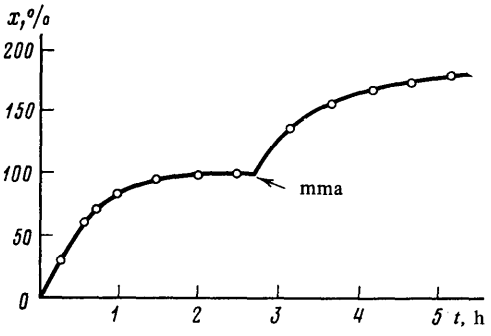


Figure 10. Kinetic curves for the polymerisation of styrene and that of methyl methacrylate (mma) on "live" polystyrene during emulsion polymerisation initiated by polypropylene hydroperoxide[90].

Another feature is the possibility of obtaining block copolymers[90]. Introduction of a second monomer following complete depletion of styrene led to a resumption of polymerisation

(Fig. 10). Formation of block copolymers has been proved by turbidimetric titration[90].

The above facts are regarded[90-94] as evidence of polymerisation without termination of growing radicals, i.e. by a mechanism of live chains. In the first stage of a suggested two-stage mechanism chain growth takes place on the surface of polypropylene, when under certain conditions grafts of polystyrene do not take because of the special mechanism of initiation by polypropylene hydroperoxide and triethylenetetramine[91]. As the molecular weight of polystyrene increases, it becomes more incompatible with polypropylene. As a result the macroradical becomes detached from the polypropylene surface and passes into the aqueous phase, to form on absorption of a monomer and stabilisation by the emulsifier a polymer–monomer particle. In the second stage the process continues in the particles by a "non-terminable" mechanism, since primary radicals from the aqueous phase do not penetrate the particle, and their formation within the particle is also excluded.

The suggested mechanism explains the results, but cannot yet be accepted without question. Other workers[97,98] have used methods similar to those of Mikulašova et al. to obtain block copolymers of vinyl chloride, but have interpreted their results on a different basis. Two types of radical-forming groups—hydroperoxy and peroxy—are present in oxidised polypropylene[97,98]. The former, which are less thermostable, initiate the emulsion polymerisation of styrene or acrylic esters in the first stage at 30–40 °C. In the second stage, after introduction of the second monomer, the process continues at 50 °C on the more thermostable peroxy-groups, whose presence in the polymer isolated after the first stage was demonstrated in separate experiments. It was also shown that such a polymer is able to initiate polymerisation not only in an emulsion system but also in the bulk, although the latter requires a higher temperature (70 °C).

In contrast to the concept of "live" radicals, the polyfunctional nature of the polymeric initiator is used[97,98] to explain the observed effects. However, the proposed mechanism is not entirely consistent with the molecular-weight characteristics of the resulting polymers. The narrow molecular-weight distribution and the M_w/M_n ratio close to unity, observed in the work of Mikulašova, are not achieved in polymers obtained on polyfunctional initiators with peroxy-groups varying in thermal stability[99], and are more typical of processes occurring on long-lived active centres without chain termination.

We note in conclusion that chain-terminating reactions are considerably slower in emulsion systems than in homogeneous polymerisation, owing to the low termination rate constants and the isolation of growing radicals in individual particles. These circumstances ensure the formation in emulsion polymerisation of polymers having exceptionally high molecular masses, and in limiting cases the occurrence of polymerisation without chain termination.

VIII. TOPOCHEMISTRY

We shall now consider the sites at which latex particles are generated and the mechanism of their formation. We have already discussed this problem in terms of the views of Harkins[7,8] and of Yurzhenko[9,10] on the appearance of particles in emulsifier micelles, a quantitative basis for which was given by Smith and Ewart. However, micellar nucleation of particles under the influence of primary radicals is by no means the only possible mechanism, is unable to explain several features of emulsion polymerisation, and is quite inapplicable to certain specific systems, e.g. emulsion polymerisation in the absence of an emulsifier. The problem of the nature of the primary radical entering the micelle was ignored in the early work. Nevertheless, the need to pose this question is evident in the initiation of emulsion polymerisation by persulphates, which generate active centres of radical-anion type. It is difficult to imagine that the highly polar charged species SO_4^- is capable of penetrating a similarly charged micelle (anionic surface-active agents have been used in almost all studies of the topochemistry of emulsion polymerisation).

These difficulties led to the view that emulsion polymerisation was initiated directly in the aqueous phase, oligomeric radicals were formed and penetrated into micelles (because they were sufficiently hydrophobic) or were precipitated into the aqueous phase on reaching a critical molecular mass, and nucleation took place by a non-micellar mechanism[100-102]. The fundamental ideas of the theory of homogeneous nucleation were developed by Fitch[101,102] and based on the postulate that radicals were formed in the aqueous phase and captured by already formed particles at the same rate. He proposed an equation in which the rate of capture of radicals ρ_c was proportional to the total particle surface. The theory was used to describe the polymerisation of methyl methacrylate in very dilute aqueous solution. In the absence of an emulsifier the primary particles are stabilised by ions formed on decomposition of the initiator. According to the theory of the homogeneous nucleation of particles the addition of an emulsifier does not increase the number of particles formed but merely tends to enhance the stability of the primary particles and prevent their flocculation. The theory was developed primarily for polar monomers readily soluble in water, but was later applied also to such sparingly soluble monomers as styrene.

Roe suggested[103] that particles are formed also outside micelles in the emulsion polymerisation of styrene, and their formation ceases at the instant when the total particle surface reaches a value at which the emulsifier concentration in the aqueous phase becomes lower than the critical concentration of micelle formation. He showed that this hypothesis leads to the same formula for the number of particles as does the Smith–Ewart theory.

Peppard showed[104] that the Fitch theory is fully applicable to the emulsion polymerisation of styrene at low emulsifier concentrations. At higher concentrations nucleation takes place both in the aqueous phase and in micelles. This theory assigns great importance to the rate of capture of oligomeric radicals by particles. In deducing the equation for this rate Fitch used collision theory, and assumed that every collision between a radical and a particle leads to capture. The rate of capture of radicals is then given by the equation

$$\rho_c = \pi r^2 L w_i N,$$

where L is the mean distance a radical diffuses in the aqueous phase before it grows to a size at which it separates from this phase as a primary particle.

Barrett has shown[105] that the Fitch formula presupposes movement of the oligomeric radical along a straight line, so that the probability of its collision with a primary particle is greatly underestimated. The rate of capture of radicals can be calculated from diffusion theory on the assumption that their adsorption is reversible, by means of the equation

$$\rho_c = 4\pi r D_j N R_j,$$

in which D_j is the coefficient of diffusion of long-chain radicals in the aqueous phase and R_j their concentration in this phase. This formula indicates a higher rate of capture of radicals than that calculated by means of the Fitch expression.

The theory of homogeneous nucleation has now been fairly well developed, but no direct experimental evidence of the existence of surface-active radicals has yet been found. One of the most convincing indications of their formation in the aqueous phase is the decrease in surface tension during the initial stages of emulsion polymerisation[106]. A recent investigation[107] of the polymerisation of styrene in aqueous medium in the presence of potassium persulphate (with an alkanesulphonate as emulsifier) at a low monomer concentration has given results that can be regarded as kinetic proof of the homogeneous nucleation of particles. In the initial stage the rate of polymerisation corresponds to an order of reaction 0.5 with respect to the initiator. The molecular mass of the resulting polymer is proportional to the initiator concentration to the power −0.5 up to 20% conversion. These results indicate bimolecular termination of growing chains, which is characteristic of steady-state kinetics of radical polymerisation in a homogeneous system. Hence it may be concluded that in the initial stage polymerisation takes place under homogeneous conditions, i.e. in the aqueous phase. In later stages the process moves from the aqueous phase into the resulting polymer–monomer particles, as is evident in the kinetics: the rate of polymerisation increases owing to the higher monomer concentration in the particles than in the aqueous phase, while the order of reaction with respect to the initiator falls to 0.26 at 30% conversion.

Table 4. Variation of particle diameter and number in unit volume with conversion[20] (0.870 M styrene + 3.69 mM $K_2S_2O_8$ at 70 °C).

t, min	x, %	$\bar{d}$, Å	$10^{-12}N$, cm^{-3}
15	0.4	700	1.90
30	0.8	930	1.23
60	2.1	1500	1.02
112	5.8	2140	0.97
175	12.9	2820	0.95
232	21.6	3250	1.04
292	32.3	3770	1.00
342	47.6	4120	1.12
1440	90.6	5030	1.18

A mechanism of homogeneous nucleation is more evident in emulsion polymerisation without an emulsifier. Interesting results indicating the existence of oligomeric radicals and the formation of primary particles on their precipitation from the aqueous phase have been obtained by Wilkinson et al.[19,20,108,109], who measured particle diameter and molecular weight of the polymer from low monomer conversions in the emulsion polymerisation of styrene in the presence of potassium persulphate. Table 4 shows that N changes appreciably only in the earliest stages of polymerisation. The molecular mass changes abruptly also only at the start of polymerisation, formation of a polymer of molecular mass ~1000 being observed in the earliest stages[20]. This last fact can probably be regarded as direct evidence of the presence of oligomeric radicals in the polymer system.

Another interesting phenomenon observed by Wilkinson et al. is the abnormal particle structure revealed on electron micrographs, shown diagrammatically in section in Fig.11. Such particles were observed by means of a scanning electron microscope, and their formation was attributed to removal of monomer from the inner region of a particle during vacuum preparation of the specimen. Particles having this structure were observed when specimens of latex were withdrawn at comparatively low conversions (~40%). This structure is supported also by results for the sorption of nitrogen by polymer particles after removal of monomer from them[19]. The total particle surface calculated by the method of Ref.17 exceeds by 17% the surface calculated from electron-microscopic data on the assumption that the particles are spherical in form.

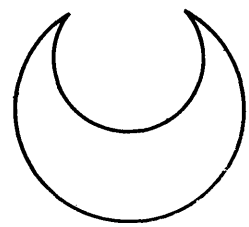


Figure 11. Structure of abnormal particle[17].

Wilkinson et al. explained the results in terms of a mechanism of the emulsion polymerisation of styrene in the absence of an emulsifier[20] involving formation in the early stages of a large number of primary particles of a polymer of low molecular weight. This is followed by flocculation of the primary particles to give stable particles, in which the usual emulsion polymerisation initiated by oligomeric radicals then proceeds. Thus the core of a particle is enriched with a polymer of low molecular weight. Since the solubility of the monomer in this polymer is higher, the inner region of the particle has a higher monomer concentration than has the outer region: i.e. a concentration gradient of the monomer is established in the polymer–monomer particle, although the concentrations themselves have equilibrium values in corresponding regions of the particle.

In a novel topochemical picture of emulsion polymerisation—the formation of polymer–monomer particles without involving emulsifier micelles—the particles are generated not in micelles but directly from drops of monomer[40] by quasi-spontaneous emulsification in conformity with the views of Taubman et al.[110] Transfer of monomer from drops to particles then takes place not by diffusion through the aqueous phase but as a result of direct contact, when obviously particle–particle contact is also possible.

Support for these views was sought[40] by using a new technique to obtain electron micrographs of latices at low conversions. The latex was frozen above the freezing point of styrene, and then the monomer was completely polymerised by exposure to fast electrons. Three kinds of particles—small (150 Å) corresponding in size to solubilised micelles, medium (600–800 Å) corresponding to polymer–monomer particles, and large (5000 Å) to drops of the monomer—can be observed on the photomicrograph. The polymerisation of styrene was conducted in the presence of the ionogenic surface-active agent E-30 (sodium pentadecanesulphonate) (4 wt.%) and azoisobutyronitrile (0.15 millimole in 1 ml of styrene) at 60 °C. As emulsion polymerisation proceeded, the size of the large particles diminished, that of the medium particles increased, and the small particles remained

unchanged. On addition of fresh portions of surface-active agent at conversions of 15% and 40% new polymer–monomer particles were formed significantly larger than micelles but smaller than the previously formed particles, with a consequent bimodal particle-size distribution (Fig.12).

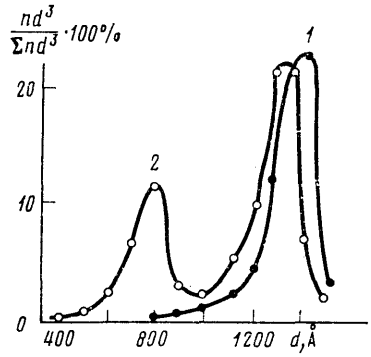


Figure 12. Size distribution of latex particles in presence of 0.15 millimole of azoisobutyronitrile in 1 cm^3 of styrene: 1) without additive; 2) after addition of Ts-40.[40]

However, these ideas are not consistent with such a well known fact as the abrupt increase in rate of emulsion polymerisation when the emulsifier concentration passes through the critical limit of micelle formation, which indicates that micelles play a definite part. Results of this type have been published recently by Smirnov et al.[111] Study of the traditional system comprising styrene with potassium peroxodisulphate and potassium laurate showed that in the region of this critical concentration a break occurs in the dependence both of rate of emulsion polymerisation and of number of particles on the concentration of surface-active agent. With regard to the results on additions of emulsifier during polymerisation, the comparatively large size of the newly formed particles can be explained by the greater rate of polymerisation in them consequent on the more developed surface and the higher probability of capture of monomer and free radicals.

The mechanism by which the small particles retain their size during polymerisation is not entirely clear. It may be supposed that the micellar stage of polymerisation was not yet complete [fairly high concentration (4%) of surface-active agent], but the phase ratio unfortunately was not given[40]. Furthermore, fine particles can be formed by the escape of radicals from polymer–monomer particles and nucleation by a homogeneous mechanism. Since homogeneous nucleation is possible at any stage of polymerisation, the apparent retention of size due to small particles may be caused by their continual regeneration during the process and flocculation with each other and with existing particles. Nucleation of particles in the aqueous phase has been used by Ugelstad et al.[112] to explain the formation of new particles finer than drops of the microemulsion obtained in the presence of the emulsifying system comprising a long-chain aliphatic alcohol with an ionogenic surface-active agent; the effect is observed whether the polymerisation of styrene in microdroplets is initiated by water-soluble or oil-soluble initiators.

Thus the results presented in Ref.40 undoubtedly indicate that microemulsification may make a certain contribution to the mechanism of the generation of polymer–monomer particles, but is not the sole cause and probably acts together with a micellar mechanism.

In a more recent study[113] on the same materials Pravednikov, Gritskova, et al. have developed the above ideas, while accepting the emphasis on the site at which polymerisation occurs in a polymer–monomer particle once formed. They worked with an oil-soluble initiator, and considered that effective polymerisation was possible only in cases in which the radicals formed were rapidly fixed in a polymer matrix, since under ordinary conditions the presence even of the two radicals produced by breakdown of a single initiator molecule cannot occur in a small polymer–monomer particle. However, the monomer content of such a particle is quite large, amounting to ~50% of its mass, and such a strongly swollen gel can hardly ensure effective fixation of radicals. This contradiction was explained on the hypothesis that the polymer separated out and formed a film at the particle–water interface. Thus a particle comprises a core strongly swollen in the monomer and a surface layer containing a small quantity of monomer, radicals being fixed in this layer.

Virtually the same arguments—bimodal molecular-mass distribution (with 10^{-6} M_n respectively 0.17 and 4.0) and formation of particles of abnormal structure—were used to support these hypotheses[113] as by Wilkinson[19,20], but with a different interpretation of the results. According to these workers[113] the polymer of low molecular weight is formed in the central region of the polymer–monomer particle as a result of rapid termination of unfixed radicals; the main site of polymerisation is the shell of the particle.

However, formation of a polymer of low molecular weight during emulsion polymerisation can be explained more simply by chain transfers to impurities that may be present in the reactants, phenomena that have been reported recently with styrene[48]. Furthermore, it is difficult to imagine the formation of a "low-molecular polymer" of molecular weight 170000 by the suggested[113] mechanism, since in a small particle termination would occur almost instantaneously with formation merely of oligomeric molecules. Since chain transfers take place predominantly in the early stages (their contribution should diminish as the carrier becomes exhausted), Wilkinson's explanation—greater solubility of the monomer in the core enriched with the lower polymer—can be accepted for the formation of abnormal particles.

Concluding our discussion of the mechanism of nucleation we note that local zones of particle generation in an emulsion system may vary depending on the specific conditions. In the absence of an emulsifier nucleation can occur only in the aqueous phase, i.e. by a homogeneous mechanism. In the presence of high emulsifier concentrations micelles form the chief site of nucleation. In the formation of microemulsions initiation of polymerisation and hence formation of polymer–monomer particles take place directly in microdrops. Even in the last two systems, however, it is probably impossible to eliminate the contribution of homogeneous nucleation.

For ordinary emulsion systems it is difficult to state unambiguously the site of polymerisation in an already formed particle (whether throughout or predominantly near the surface). However, the process can be localised predominantly in the outer zone of the particle by establishing special conditions (e.g. lower rate of diffusion of monomer into the particle). As a consequence it is entirely possible to realise a "core–shell" particle model, especially with inoculated emulsion polymerisation, when the polymer of the seed particles is thermodynamically incompatible with the polymer formed from the monomer introduced into the seed.

IX. CONCLUSION

The present Review cannot claim full coverage of published information on the theory of emulsion polymerisation that has appeared even during the past decade. The volume of information on such polymerisation increases steadily, the range of problems discussed widens, and at the same time investigators are returning to fundamental theoretical problems posed more than thirty years ago, attempting in individual cases to revise the basis of classical ideas. We have tried to examine only some of the most interesting lines of development of the theory of emulsion polymerisation.

Research on emulsion polymerisation during recent years has been characterised by experiments under special conditions enabling a specified topochemical and kinetic pattern to be modelled. Investigations in special model systems are extremely promising, since they enable individual parameters to be fixed that often are not entirely definite under ordinary conditions, and the sites at which primary processes occur to be established more precisely. Smith and Ewart's concept that the number of particles in an emulsion system is the principal kinetic factor in emulsion polymerisation remains most fruitful in current as in earlier work. Great attention is now paid to the structure of polymer–monomer particles and the site of polymerisation. The possibility under certain conditions of localising chain growth in particle shells indicates that particles of complicated structure may be formed.

The work surveyed thus shows that extremely diverse phenomena are observed during emulsion polymerisation, which cannot yet be explained in terms of a single theory. However, if we confine our attention to monomers that are sparingly soluble in water, the basis for a general theory probably does exist. The most practicable method is evidently still to seek general relations between conditions and the most important parameters (number of particles, local zone in which process occurs, primary constants). The classic Smith–Ewart theory, where such relations have been established, can be extended only to a limited number of systems. There is probably no need to revise this theory radically, as several authors attempt to do; it is advisable to define more clearly the limits of its applicability. Refinements and developments of certain of its principles are necessary and useful for obtaining more general ideas on emulsion polymerisation.

The work surveyed in this Review is not yet able to introduce full clarity into the theory of emulsion polymerisation, but is undoubtedly of both theoretical and practical interest, since it opens up new opportunities for the emulsion synthesis of polymers. In this connection we must again mention the work of Williams et al., which stimulated research on the preparation of polymer dispersions containing particles of layered structure, and the investigations of Mikulašova et al. on emulsion polymerisation in the presence of polymeric initiators, which enabled block copolymers to be obtained in emulsion systems. Research on emulsion polymerisation in the presence of multifunctional emulsifiers merits attention, in particular on surface-active initiators, which ensure the formation of polymers having exceptionally high molecular weights and latices that are highly resistant to various factors.

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