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George E. Ham[a]
[a] G. E. Ham Associates, New York

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Emulsion Copolymerization

GEORGE E. HAM

G. E. Ham Associates
Briarcliff Manor, New York 10510

No other area of polymerization has been the subject of as many studies, especially of mechanism, as that of emulsion polymerization and copolymerization [1, 2]. This fact arises not only from what has been regarded as the distinctive features of emulsion polymerization as a process but also from the highly diverse character of emulsion polymerization arising from the specific nature of the monomers utilized and the polymers produced and their influence on the course of the process itself.

The distinctive features of emulsion polymerization include the following:

1. There must be an aqueous phase present.
2. There is nearly always a separate phase containing monomer, particularly in the early stages of polymerization.
3. For the cases which we will be considering here, an oil-in-water emulsifier is usually employed.
4. Some free radical source such as that provided by chemical initiators like peroxides or persulfates and azo compounds is necessary..

It is now known that the emulsifier may be present in four important places in the system. The emulsifier may be present in soap micelles, or it may be dissolved in water; it is located at the monomer droplet-water interface and finally it is present on the surface of monomer-swollen polymer particles.

The monomer on the other hand is also present in four different locations: in emulsifier-stabilized monomer droplets approximately 1 μm in diameter, dissolved in water, in micelles of approximately

50-100 Å units in diameter, or finally in the monomer-swollen polymer particles.

It is important to separate the distinctive features of emulsion polymerization from the essential underlying features of emulsion polymerization. It is now known that almost any of the foregoing distinctive features can be widely modified and the essential features of emulsion polymerization preserved. For example, emulsion polymerization with styrene may be carried out in the absence of an emulsifier to produce a polystyrene latex. Free radical sources may include not only chemical initiators, usually water soluble, but also high energy sources such as γ-radiation from ^{60}Co. Indeed, polymerization in the absence of any added radical source is possible in thermally induced emulsion polymerization.

The presence of a separate monomer-containing phase can be bypassed in certain cases wherein water-soluble monomers are polymerized from true solution to a polymer latex. Furthermore, although the most important category of emulsion polymerization involves organic-phase-dispersed-in-water types, reverse emulsion polymerization wherein the organic phase is continuous and the water phase is dispersed, employing a water-in-oil type emulsifier, is assuming increasing importance, as in the production of polyacrylamide emulsions dispersed in kerosene or other organic carrier.

Finally, although nearly all emulsion polymerizations involved the presence of an aqueous phase, both continuous and dispersed phase polymerizations have been studied with a production of polymer emulsions which do not even have an aqueous phase present.

Accordingly, it is of some interest to discuss the essential underlying features of emulsion polymerization.

It is now apparent that virtually the only essential feature of emulsion polymerization that gives it its special character is the depression of the termination reaction making possible the production of very high molecular weight polymer. That this reaction also results in the preparation of polymer in a highly convenient form, that is, as a dispersed emulsion from which monomer is readily depleted or removed, although of tremendous industrial advantage, is not really an essential feature of the process.

Of course, the suppression of the termination reaction leads to extremely rapid polymerization rates which also represent a great economic advantage for the process.

The suppression of the termination reaction has been the subject of much study and much debate. It is generally held that a mechanism of the following type exists:

1. Free radicals are produced in the aqueous phase by decomposition of a chemical initiator.
2. Monomeric units add to the initiating free radical slowly in aqueous solution until an oligomer of sufficient molecular weight develops, which possesses some hydrophobic character.
3. The surface-active oligomeric radical so produced is absorbed in one of the numerous soap micelles available.

4. Rapid polymerization occurs, producing a monomer-swollen polymer particle.

5. The process is accompanied by a 100-fold growth of the polymer particle requiring additional emulsifier provided from the dispersed monomer emulsion droplets and from soap micelles by the process of diffusion.

6. At some point the soap micelles disappear due to the depletion of soap required to stabilize the polymer particles formed, marking the end of Stage 1 and the beginning of Stage 2 of emulsion polymerization. Thus, in Stage 1 polymer particles are initiated and in Stage 2 polymer particles grow until monomer or radicals are depleted from the system.

Experience shows that Stage 1 is highly variable depending on initiator type and quantity, monomer and polymer type, degree of agitation, and many other factors. By contrast, Stage 2 is highly reproducible. Once the number of polymer particles has been fixed through depletion of emulsifier, the number of particles remains constant, barring some other factor.

Typically at this stage radicals are being furnished to 1% of the particles each second. Accordingly, on entering a particle, a polymer radical may grow undisturbed for 100 s, that is, until another radical enters the particle. Entry at the surface of a particle by a radical results in immediate termination. In the case of certain water-soluble oligomeric radicals, such as those produced from vinyl acetate or vinyl chloride, the growing radical occasionally transfers out of the particle. However, usually this process can be ignored. It can be stated that radical termination and radical reinitiation depend on the same process, that is, random entry of a radical into a polymer particle with the result of either terminating an existing polymeric radical or initiating a new polymeric radical in the particle. Of course the processes are mutually exclusive; that is, initiation and termination must occur in rigid sequence. Accordingly, since the radical entry process is the same, one may conclude that in the general case one-half of the particles are active and one-half inactive at any given time.

Smith-Ewart recognized that a steady state was attained and interpreted it in terms of the rate of radical entry into the particles, the rate of radical transfer out of the particles and the rate of termination of radicals in the particles:

Case One: $n \ll 1$
Case Two: $n \sim 0.5$
Case Three: $n \gg 1$
where n = average number of radicals per particle.

Smith-Ewart found that styrene followed Case Two and showed:

$$R_p = k_p[M]N/2$$

$$DP = k_p[M]N/\rho$$

where N = number of particles
ρ = rate of radical entry

As indicated earlier, the nature of emulsion polymerization depends to an important extent on the solubility and reactivity of individual monomers and also upon whether the resulting polymers are soluble in their monomers or in water.

Accordingly, the general classes of emulsion polymerization may be summarized:

By Monomer

1. Water-insoluble:
    - Styrene
    - Butadiene
2. Miscible with water:
    - Acrylic acid
    - Methacrylic acid
3. Limited solubility in water:
    - Acrylonitrile
    - Methacrylonitrile
    - Vinyl acetate.

By Polymer

1. Polymer miscible with monomer:
    - Polystyrene
2. Polymer insoluble in monomer
    - Polyvinyl chloride
    - Polyvinylidene chloride
    - Polyacrylonitrile

SUPPRESSION OF THE CHAIN TERMINATION REACTION

The general mechanistic picture in emulsion polymerization involves initiation of polymerization at the interface of dispersed polymer particles by a polar species, one end of which, an alkali sulfonate group, for example, cannot enter the polymer particle. Accordingly, it is visualized that the polymer radical, until it is terminated by the entry of another similar radical at the polymer surface, grows unimpeded. Thus any individual polymer particle would have at most one active radical polymerizing at any one time. Based on this picture it is obvious why very high molecular weights and long radical lifetimes would result. It is not unusual for the molecular weight of emulsion polymers to be anywhere from twice to tenfold as large as that of corresponding mass polymer as a result. Furthermore, the lifetimes of growing chains can be of the order of 100 s compared to 1 to 10 s for similar mass polymerizations.

However, the thesis that emulsion polymerization is so different and unique needs to be reexamined. For a long time it has been noted that at advanced stages of mass polymerization, as in polystyrene and polymethyl methacrylate, that is, in the range of 80-90% conversion, a new and quite different polymerization behavior is apparent. This so-called Trommsdorff effect leads to an acceleration of polymerization, usually accompanied by a rapid rise in temperature with the production of high molecular weight polymer. In this stage radical termination is suppressed due to the high viscosity of the medium, yet diffusion of monomer at a relatively unimpeded rate to the site of the active radical still occurs. At higher conversions, on the order of 95-98%, diffusion of monomer becomes impeded and the polymerization slows down. Of course, depletion of monomer also causes a slowdown in polymerization. Thus, in conventional high conversion mass polymerizations, a phenomenon not unlike that which has been regarded as unique to emulsion polymerization takes place, that is, the suppression of the termination step.

Another feature which has not received much consideration in emulsion polymerization is that each individual polymer particle is polymerizing to a high unit conversion degree during most of the process. This situation arises from the fact that there is segregation of monomer from polymer, with the monomer principally present in the dispersed monomer droplets in the early stages and only to that degree necessary for maintaining the polymerization within the emulsion polymerizing particle at any stage. Diffusion from the monomer droplet through the aqueous solution to the polymerizing polymer particle takes place with the maintenance of the course of the polymerization. Thus, even at the early stages of polymerization and even more so in the latter stages, each individual polymer particle is polymerizing at a high conversion degree on an equilibrium basis. It is difficult to ascertain just what this conversion level is in individual polymer particles because of the highly dynamic character of the system. However, some indication of this may be obtained from measured phenomenon such as the temperature rise noted with volatile monomers such as acrylonitrile when polymerization is carried out at the boiling point. The fact remains, however, that polymerization under these conditions has a character strongly suggestive of that noted in mass polymerizations as the Trommsdorff effect. Thus the suppression of chain termination, generally attributed to the presence of only one radical in the polymerizing particle at any one time, may in fact be accounted for at least in a qualitative sense by the normal expectations in mass polymerization at high conversion where mobility of polymer radicals is impeded and yet monomer diffusion is still taking place to a high degree.

COPOLYMERIZATION OF WATER-INSOLUBLE AND WATER-SOLUBLE MONOMERS

In 1946 Fordyce, Chapin, and Ham [3] showed that in such copolymerizations in emulsion the copolymer composition was a function of (1) the monomer ratio, (2) individual copolymerization reactivity ratios of the monomers, and (3) the partition coefficient of the monomers in water at reaction temperature.

In such cases, monomer dissolved in water did not contribute to copolymer composition. Correction for dissolved monomer led to good agreement with results obtained in mass and solution copolymerizations.

Systems studied included styrene-acrylonitrile, styrene-methacrylonitrile, styrene-fumaronitrile, styrene-itaconic acid, and styrene-vinyl chloride.

Since then, this behavior has been noted in vinylidene chloride-acrylonitrile [4]; styrene-methyl methacrylate [5]; vinylidene chloride with acrylonitrile, methyl acrylate, and methacrylonitrile [1b, p. 152]; and vinyl chloride with homologous acrylates and acrylic acid [1b].

For many years it has been noted that the addition of certain reactive water-soluble monomers to emulsion polymerizations of one or more water-insoluble monomers will often lead to an acceleration of the polymerization rate in emulsion. For example, the rate of vinylidene chloride polymerizations in emulsion has been enhanced by the addition of such monomers as acrylonitrile and methyl acrylate as reported by Fowler [6].

In other studies [7], vinyl chloride (70) and butyl acrylate (30) copolymerizations in emulsion were enhanced in rate by the addition of some amounts of itaconic acid, monomethyl itaconate, dimethyl itaconate, fumaric acid, monomethyl fumarate, dimethyl fumarate, and acrylic acid. These studies were reported by Ley and Fowler; see also Hopff and Storck [7].

CORE-SHELL LAYERING IN EMULSION

Considerable interest has been evidenced in core-shell copolymers. Such copolymers are of increasing commercial interest because they represent an opportunity to combine the mechanical and barrier properties of core polymers with the dispersion, adhesion, and film-forming properties of shell polymers. Thus, for example, kerosene dispersions of acrylic polymers such as poly-MMA may be obtained by following a core polymerization of MMA with a shell polymerization of a long-chain oil-soluble acrylate. A stable kerosene dispersion of polymer results.

These practical considerations and results have been accompanied by a secondary controversy surrounding the general subject of equilibration of monomers in polymers in growing emulsion particles which might negate the effects of layering. It has been argued for example that, following the production of core particles, attempts at layering by the addition of another monomer might lead to sufficient diffusion into the polymer particle so that true layering would not occur.

A variety of studies in recent years has confirmed the possibility of producing core-shell polymers. Keusch and Williams [8] showed that in seeded batch polymerizations, additional monomer did not penetrate from the monomer-rich shell to the core even when 48 h was allowed for the swelling of the latex particles. Further studies by Chung-Li, Goodwin, and Ottewill [9] showed that when particles with a diameter of 2140 nm were employed, no swelling of the latex polymers took place after 12 h at 60°C. Even after 69 h, equilibrium swelling had not been attained. Such behavior would be particularly expected in polymer at high conversion. Thus, such swelling data provide a strong indication that polymer emulsion particles <u>do</u> polymerize at high conversions when at equilibrium. The present evidence is that the monomer concentration is relatively constant (and low) in the shell of the particle where polymerization is occurring and that monomer is not uniformly distributed throughout the polymer particles.

CONTINUOUS AND SEMICONTINUOUS POLYMERIZATION PROCESSES

Note should be given to the major importance of continuous and semicontinuous polymerization processes in the polymer industry. Even as early as the 1940s synthetic rubber latices were polymerized in sequential batch reactors. More recently in the late 40s, 50s, and 60s, semicontinuous batch polymerizations were carried out, in which most of the water, emulsifier, and initiator required was charged initially and some or none of the monomer was added initially, the remainder being added throughout the course of the reaction. In the case of copolymer manufacture the addition of monomer throughout the reaction is often in the same proportion as that desired in the final product. Due to the special character of copolymer reactivity ratios, one may rapidly obtain an equilibrium monomer ratio in the reactor which will yield copolymer corresponding in composition to that of the monomer being fed at any instant.

More recently, completely continuous polymerizations have attained industrial importance in which all reactants are fed into the reactor, sometimes of a tubular design, where the reaction is maintained at polymerization temperature with suitable agitation. In this process, stripping of monomer takes place downstream from the reaction zone in a suitable stripping zone, after which the desired polymer emulsion goes to storage.

In semicontinuous polymerization, experience has shown that even when monomer mixtures equal in composition to that of the desired polymer are added throughout the run, in the absence of original monomer addition, equilibrium copolymer is rapidly attained. The point of attainment will, however, depend upon such factors as rate of addition, catalyst concentration, monomer reactivity, etc.

One study, not necessarily done under conditions leading to most rapid equilibration, has utilized a variety of monomer mixtures including butyl acrylate-butyl methacrylate, butyl acrylate-styrene, styrene-acrylonitrile, and styrene-butyl acrylate-acrylonitrile. This work has been reported by Snuparek and Krska [10]. In this study, at what was indicated as low feed rates, it was found that the copolymer composition became equal to that of the feed after about 20% conversion.

Semicontinuous, delayed addition, and continuous stirred tank reactor systems are widely used in the manufacture of resins for synthetic fibers (acrylonitrile copolymers), plastics and barrier resins (acrylonitrile copolymers), surface coatings (acrylic ester-vinyl acetate copolymers), synthetic elastomers, and other vinyl polymers of industrial importance.

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