Principles of Emulsion Polymerization[1]

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SYNTHETIC POLYMERS, especially those that exhibit rubberlike characteristics and those that can be drawn into fibers, have attracted increasing interest in recent years. Both the technology and the basic knowledge of polymer processes have advanced. This article will be concerned with the fundamental principles of a particular kind of polymerization—namely, vinyl polymerization in emulsion. Even with this limitation, the subject is so vast that only a cursory treatment is possible here. Accordingly, the discussion will be further restricted to those aspects of the subject relating to the author's own work or the work of his associates.

A complete understanding of emulsion polymerization would require a knowledge of a great many branches of chemistry. Obviously, one must recognize the organic chemistry involved to describe how the molecules start growing, how the reaction is sustained, and how the molecular growth finally stops. The kinetics of polymerization processes are also important, both from the point of view of attaining practical speeds and because of their influence on the structure of the product. Finally, in emulsion systems, the phase relationships are of paramount significance by reason of their marked influence on the kinetics and the corresponding control of the possible reactions. We shall now endeavor to discuss each of these topics in turn, with particular emphasis on the kinetics and phase relationships.

THE POLYMERIZATION REACTION

Vinyl type polymerizations, whether they occur in single or multiple phase systems, are characterized by a free radical type of chain growth. To initiate the reaction it is necessary to generate free radicals, either by ordinary chemical decomposition of appropriate catalysts or by photochemical processes. Certain organic peroxides are commonly employed as catalysts, since they can yield free radicals by thermal decomposition (*6*) or by reduction activation (*4, 12*). Denoting the initiating radicals by R · and the monomers by M, we can write the polymerization reaction as

$$\begin{aligned} &R\cdot + M \rightarrow RM\cdot \\ &RM\cdot + M \rightarrow RM_2\cdot \\ &RM_n\cdot + M \rightarrow RM_{n+1}\cdot \\ &\text{etc.} \end{aligned}$$

The chain growth process will not continue indefinitely, however, because certain other reactions can also occur which result in chain termination. In practice, the chain lengths are often controlled by the introduction of chain transfer agents or modifiers (*1, 7, 10*) which operate according to the reaction

$$RM_n\cdot + YZ \rightarrow RM_nY + Z\cdot$$

followed by

$$Z\cdot + M \rightarrow ZM\cdot \text{ etc.}$$

Carbon tetrachloride and certain mercaptans can be effectively used as modifiers for some polymerization reactions. Organic peroxides, in addition to serving as catalysts, can also act as modifiers, especially in the redox system to be discussed later (*13*).

The modification reaction is characterized by the fact that the growing chain abstracts an atom or group from a nonradical molecule, thereby transferring the free radical characteristic elsewhere (*1*). The new free radical can then undergo growth by addition of further monomer units and the cycle repeated. It must not be supposed that the modification reaction occurs at any critical degree of polymerization; instead it is a very random type of reaction, governed largely by probability. This results in marked heterogeneity of molecular weights in the final product.

If no modifier is added to a polymerization system, the molecular weights will tend to be high, but some sort of chain termination must always occur. If necessary, a growing free radical will remove an atom (hydrogen, for example) from a polymer molecule already formed (*9, 11*). This renders the polymer molecule a free radical again, enabling it to grow once more. From probability considerations it is clear that the atom removed from the polymer molecule is unlikely to be at the end of the molecule; accordingly, the secondary growth process will result in the formation of a branch attached to the original molecule. At high conversions the degree of branching can be considerable, and the polymer molecules will tend to look more like trees than like ordinary chains.

At this stage it is well to discuss another phenomenon frequently encountered in polymerization, namely, cross-linking. For reasons to be discussed presently, cross-linking should be considered different from branching, even though superficially they appear to have similar characteristics. Cross-linking occurs during polymerization, when a growing polymeric free

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[1] Based on a paper presented at the 23d National Colloid Symposium, held in Minneapolis, Minnesota, June 6–8, 1949.

radical chain adds on a polymer molecule instead of a monomer, the addition involving some residual unsaturation in the polymer (*9, 11*). Butadiene polymers can obviously undergo cross-linking, since only one double bond is lost for each monomer unit in the primary chain growth process. Since the polymer itself has a great deal of unsaturation, it is not at all improbable that at high conversions the free radicals will react with polymer instead of with monomer. Although branching tends to build up treelike structures, cross-linking goes further than this, for it ultimately gives rise to networks. When cross-linking occurs there is either a decrease in the number of molecules or a building up of network structures. When the network is big enough, the resulting polymer system becomes an insoluble gel, which can, however, be swollen by appropriate liquids, especially those that would be solvents for the non-cross-linked material. Direct evidence for cross-linking has been obtained by studies of molecular weights as functions of conversion (*11*). Such investigations have shown that in some of the advanced stages of the reaction there is an actual decrease in the number of polymer molecules with increasing conversion.

KINETICS OF POLYMERIZATION REACTION

An ordinary vinyl type polymerization taking place in dilute solution might be expected to be first order with respect to monomer concentration. The specific reaction rate constants will, of course, depend upon the catalyst used and upon the nature of the processes involved in generating and removing free radicals. For emulsions, on the other hand, the kinetics are considerably more complicated. It is found empirically that for a great many emulsion polymerizations the reaction appears to be zeroth order up to as high as 60 percent conversion, after which the rate falls off rapidly. The copolymerization of butadiene and styrene to make GR-S synthetic rubber follows such a pattern (*12*). It must not be inferred, however, that all emulsion polymerizations are zeroth order, for some systems do exhibit marked departures. The zeroth order behavior which is frequently observed suggests that the concentration of monomer in the reaction locus remains substantially constant.

LOW TEMPERATURE REDOX POLYMERIZATION

Vinyl type polymer growth reactions frequently involve several reaction possibilities, with the result that the polymer does not have a uniform structure. Diene polymers in particular exhibit such structural variations, since a monomer unit might appear in the polymer in *cis* or *trans* forms, if the addition was 1–4, or it might appear to have added in 1–2 or 3–4 fashions, the latter two being distinguishable only if the diene is unsymmetrical. Besides the aforementioned branching and cross-linking, still other "side reactions" are possible. At high temperatures there is a tendency for randomness in accordance with the general effect of increased temperature on relative reaction probabilities. At low temperatures, on the other hand, certain specific reactions may be favored, with the result that the polymer structure will be more nearly uniform. If this uniformity should manifest itself in more desirable polymer properties, and this is often the case, then a low temperature polymerization would appear to be in order. The so-called "cold rubber," which is prepared at low temperatures by a redox system, is in fact superior to ordinary GR-S.

Unfortunately, the catalyst systems developed for higher temperature reactions (say, 40°–70° C) generally do not function at reduced temperatures (around 0° C). This is readily understood if peroxides are used as catalysts and thermal decomposition is relied upon to produce free radicals for initiating the polymerization (*6*). Accordingly, it would be highly desirable to employ some method to activate peroxide systems at low temperatures. If enough free radicals can be generated at low temperatures, then the reaction can be made to proceed with a practical over-all speed without losing high quality in the product.

If $[\mathrm{R}\cdot]$ represents the total free radical concentration, and $[\mathrm{M}]$ that for the monomer, then the over-all polymerization reaction rate will likely be given by

$$\frac{d[\mathrm{M}]}{dt} = k[\mathrm{R}\cdot][\mathrm{M}],$$

where k is the specific reaction rate constant for chain growth. It is clear that the effective velocity is proportional to $k[\mathrm{R}\cdot]$, so that even if k is reduced by lowering the temperature, $[\mathrm{R}\cdot]$ might be sufficiently increased to compensate.

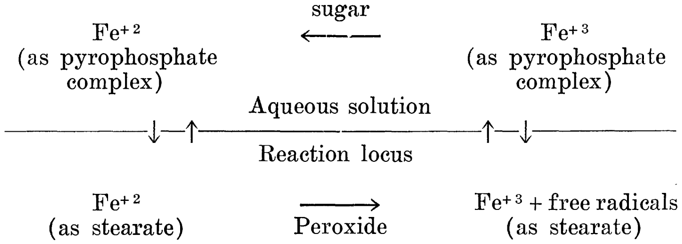
The necessary increase in $[\mathrm{R}\cdot]$ can be brought about by reduction activation involving ferrous iron. In analogy to the conclusions of Haber and Weiss (*2*) on hydrogen peroxide, we can write (*13*) that

$$\begin{aligned}
&(\mathrm{RCOO})_2 &&+ \mathrm{Fe}^{++} \rightarrow \mathrm{RCOO}^- &&+ \mathrm{RCOO}\cdot + \mathrm{Fe}^{+++} && (1)\\
&\mathrm{RCOO}\cdot &&+ \mathrm{Fe}^{++} \rightarrow \mathrm{RCOO}^- &&+ \mathrm{Fe}^{+++} && (2)\\
&\mathrm{RCOO}\cdot &&+ \mathrm{M} \rightarrow \mathrm{RCOOM}\cdot && && (3)\\
&\mathrm{RCOOM}_{n-1} &&+ \mathrm{M} \rightarrow \mathrm{RCOOM}_n\cdot && && (4)\\
&\mathrm{RCOOM}_n\cdot &&+ (\mathrm{RCOO})_2 \rightarrow && && \\
& && \qquad \mathrm{RCOOM}_n\mathrm{R} + \mathrm{RCOO}\cdot + \mathrm{CO}_2 && && (5)
\end{aligned}$$

Reaction (1) is the desired reduction activation reaction. Ferrous iron rapidly reacts with peroxide to form acid ions, free radicals, and ferric iron. Reaction (2), which is not desired, involves the reduction of the free radical to a stable acid ion. In the presence of monomer, however, reactions (3) etc. can occur to form polymer. Reaction (5) is a modification reaction in which the peroxide acts as the modifier.

The reaction between ferrous iron and peroxides is very rapid, so that in practice certain additional controlling agents must be present. The benzoylperoxide redox system contains in addition to iron and peroxide some soap and pyrophosphate. The pyrophosphate appears to control the iron concentration by complex formation and the soap renders the iron capable of entering the reaction locus. Finally some reducing sugar is generally added to a redox system, so as to reduce (possibly by indirect means) the ferric iron back to the ferrous state.

Considerable evidence (*13*) leads one to believe that the iron undergoes a cycle as follows:



If pyrophosphate is absent, the reaction between the iron and peroxide is too fast; if soap is absent, the iron is not brought into contact with the peroxide, with the result that no reaction occurs. The peroxide is only slightly soluble in water, but can be present in the oil phase (monomer) or in the soap micelles distributed throughout the water.[2]

Locus of Reaction

The most significant contributions to our knowledge of the locus of reaction in emulsion polymerizations have been made by Harkins and co-workers (*3, 8*). These investigators have come to the following conclusions. Two types of loci are involved: (1) soap micelles in which the polymerization starts, and (2) the polymer particles themselves.

The soap micelles contain a core of oil and in that core the reaction starts. The polymer molecules thus started then grow into the aqueous phase (the soap becoming adsorbed to the polymer). By diffusion through the aqueous phase, monomer enters and dissolves in the polymer particles, thus providing more material for polymerization. Accordingly, most of the polymerization takes place in the polymer-monomer particles, and the monomer droplets in the emulsion serve only as reservoirs for reactants.

According to Harkins (*3*) the aqueous phase can serve as a secondary locus for initiation, but the particles so formed ultimately enter the second stage described above. As the reaction proceeds, the monomer droplets get smaller and smaller until at about 60 percent conversion (for GR-S) all the monomer is dissolved in polymer particles. After that the effective concentration of monomer in the reaction environment falls off rapidly, with the result that the kinetics soon depart from zeroth order.

It is significant that after 60 percent conversion the growing free radicals encounter relatively more polymer molecules and less monomer, with the result that branching and cross-linking then occur (*11, 12*).

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[2] The author is indebted to Prof. I. M. Kolthoff of the University of Minnesota for pointing out that the reduction activation step occurs somewhere in the water layer, which is here presumed to be the oil core of the soap micelle. This interpretation is a modification of that given in (*13*).

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