

## A General Theory of the Reaction Loci in Emulsion Polymerization

William D. Harkins

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## Letter to the Editor

**T**HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few halftone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$3.00 per page) will not be made and no reprints will be furnished free.

### A General Theory of the Reaction Loci in Emulsion Polymerization\*

WILLIAM D. HARKINS  
University of Chicago, Chicago, Illinois

**I**N the study of the kinetics of emulsion polymerization no adequate attention had been given to the loci of reaction until the work of this project was begun in January, 1943. On the basis of work by H. F. Jordan and R. H. Ewart on the disappearance of soap early in the reaction, the writer had gained the idea earlier that the principal locus for the *initiation* of polymer particle nuclei is the soap micelles. Very quickly it became evident that there are two types of loci:

- A. Loci for initiation of polymer particle nuclei
  1. Soap micelles, and
  2. Monomer droplets
 the relative efficiency of which depends upon the amount of soap and other factors.
- B. Locus for formation of most of the polymer
  3. Monomer in the polymer-monomer (latex) particles. Some polymer appears in the emulsion droplets also.

#### 1. LOCUS FOR NUCLEI FORMATION IN THE OIL LAYERS OF SOAP MICELLES

Monomer diffuses continually from the emulsion droplets into adjacent soap micelles, where it forms monomer (oil) layers which polymerize continually. (Fig. 1.) Thus, a layer of isoprene-styrene 16Å thick, as shown by x-ray measurements, disappeared (thickness = zero) upon heating in the presence of a catalyst, while the polymer appeared outside in the aqueous phase (R. W. Mattoon and R. S. Stearns). Upon shaking with more monomer the initial thickness is restored, though the amount of *micellar* soap has been decreased, as indicated later.

Recently, M. L. Corrin has found that the *apparent* density of heptane solubilized in a soap solution is higher than that of liquid heptane at all concentrations below saturation, but becomes at saturation equal to that of the liquid.

#### 2. MONOMER EMULSION DROPLETS

The evidence that monomer droplets constitute a locus is less direct, but during the two and a half years of in-

vestigation of reaction loci considerable evidence, too extensive to be presented here, has been obtained, which shows that they also constitute a locus for the *initiation* of polymer nuclei. These are formed in an emulsion of a monomer in an aqueous solution of an emulsifying agent, even when micelles are absent, and with sufficient agitation slowly even in the absence of any efficient emulsifier.

### 3. THE LATEX PARTICLES

The latex particles (polymer swelled by monomer) constitute, after their initiation in and escape from the other loci, the locus in which nearly all of the polymer is formed. The monomer of the emulsion droplets diffuses continually through a thin diffusion layer into the adjacent polymer-monomer particles, where it polymerizes continually. In general, the ratio of monomer to polymer in these particles decreases with the yield of polymer.

All hydrocarbon particles (monomer or latex) in an aqueous soap solution are surrounded by an adsorbed monolayer of soap molecules packed with moderate tightness at a soap concentration of 0.1 molar. The polar ends are oriented toward the water and the hydrocarbon ends toward the hydrocarbon particles (Fig. 1). Since the polymer-monomer particles are in general very much smaller spheres than the emulsion droplets, the area on which the soap is adsorbed increases rapidly as the material of the monomer droplets is transformed into monomer-polymer (finally polymer) particles.

As a result the soap of the micelles is rapidly changed into adsorbed soap, so the micelles disappear at a yield (conversion), often rather low, of polymer, which increases with the initial amount of soap present. Above this yield the monomer droplets remain as the only locus for the *initiation* (or formation) of polymer particle nuclei.

At a higher yield the monomer emulsion droplets disappear completely, since the monomer has now diffused wholly into the polymer (latex) particles. Above this yield it is obvious that the only locus of polymerization is

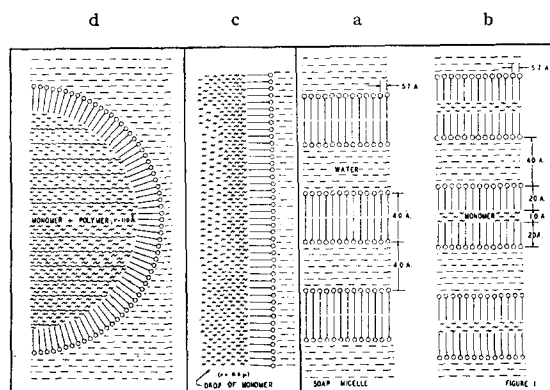


FIG. 1. While the figure is drawn to scale, the actual dimensions vary considerably. The thickness of the water layer increases with decrease of soap concentration, that of the double layer of soap with length of the soap molecule.

- a. Idealized structure of a soap micelle,
- b. Same with layers of oil, often 15Å thick,
- c. Monomer droplet: monomer diffuses into micelle, or into
- d. Monomer + polymer particle and also gives some polymer at its interface; this usually passes into the aqueous phase.

these latex particles (locus 3). The yield at which the micelles disappear decreases as the initial amount of soap decreases, and this causes the monomer droplets to play a relatively more prominent role in the *initiation* of polymer nuclei.

Since the area of the micellar oil layers increases with the initial amount of soap, the number of polymer particles initiated also increases. Thus, for a given yield the size of these particles decreases as the initial amount of soap is

increased, while without soap the particles are in general very large. Much interesting evidence in favor of these concepts has been obtained by others not mentioned above: Dr. W. Heller, H. B. Klevens, B. Adinoff, and H. Oppenheimer.

This outline is far from a complete description of the theory.

\* The work reported in this paper was done in connection with the Government Research Program on synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.