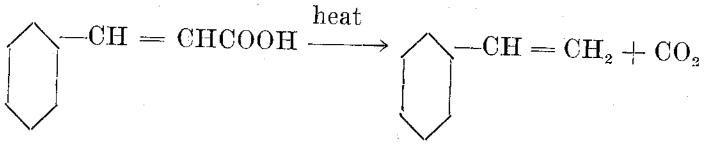
Illinois Academy of Science Transactions, Vol. 46, 1953

SOME FACTORS INFLUENCING THE SUSPENSION POLYMERIZATION OF STYRENE-DIVINYLBENZENE MIXTURES

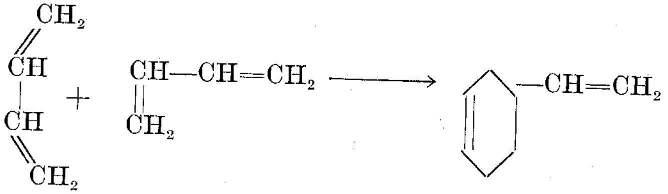
C. R. MELOY
University of Illinois, Navy Pier

Styrene, which occurs in liquid storax, is a fragrant, honey-like substance found in various plants, and was first isolated by Bonastre in 1831. Several methods of synthesizing the compound have been developed since that time. The decarboxylation of cinnamic acid by distilling is said (1) to produce styrene in yields of 38 to 41 percent.



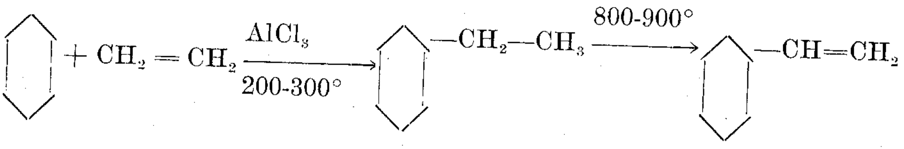
Heating of acetylene produces some styrene in addition to benzene: $4CH{\equiv}CH \xrightarrow{heat} C_6H_5CH = CH_2$. The dehydration of β-phenylethylalcohol also yields styrene: $C_6H_5CH_2$-$CH_2OH \rightarrow C_6H_5CH = CH_2 + H_2O$.

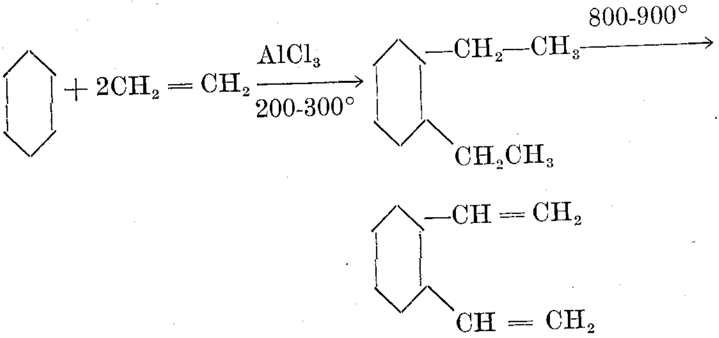
A method worked out by Weizmann and co-workers in 1948 starts with butadiene formed from petroleum. This dimerizes through a Diels-Alder reaction:



The dehydrogenation of the vinylcyclohexene then yields the styrene. This is said to be more effective than coal pyrolysis as a source of styrene.

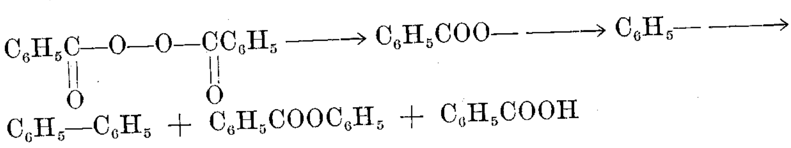
The present commercial method used by Dow and other manufacturers (2) involves the vapor-phase union of benzene and ethylene to produce ethylbenzene—along with some diethylbenzene—followed by dehydrogenation:





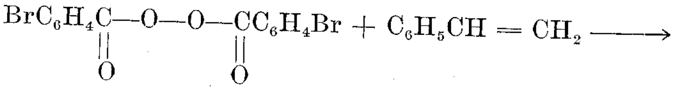
The polymerization of styrene was probably observed before styrene had been isolated. Evidence for this lies in the name applied to certain trees of the witch hazel family. These trees, of the genus Liquidambar, exude styrax. The first light-induced polymerization of styrene seems to have been the work of Blyth and Hofmann about 1845 (3) although Simon (4) is supposed to have polymerized it by heating it to 200° about six years earlier. This polymer, possibly the first of the synthetic resins, did not come into any practical use in this country until 1937, when a suitable method of producing monomer at low cost was worked out. Because the manufacture of synthetic rubber has resulted in a large capacity to produce styrene, the cost has been reduced to a point where it is the lowest priced transparent resin. The more common polystyrene resins are sold as molding granules.

The polymerization of styrene is catalyzed by oxygen, various oxidizing agents—notably peroxides—and by light. The reaction is rapid in an emulsion, such as 5 percent sodium oleate, and leads to the formation of high molecular weight polymers. The absence of low molecular weight products and the added fact that distyrenes and tristyrenes do not polymerize to polystyrene suggests a chain reaction mechanism involving free radicals. If dibenzoyl peroxide is used as catalyst it gradually decomposes thus:

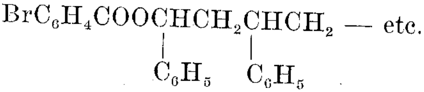


$$C_6H_5\underset{\overset{\|}{O}}{C}—O—O—\underset{\overset{\|}{O}}{C}C_6H_5 \longrightarrow C_6H_5COO— \longrightarrow C_6H_5— \longrightarrow$$
$$C_6H_5—C_6H_5 + C_6H_5COOC_6H_5 + C_6H_5COOH$$

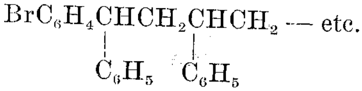
One evidence for the formation of free radicals is the transient color appearing during the early stages of the polymerization. That these free radicals become attached to at least one end of the chain is shown when a marking group such as an atom of bromine, present in the peroxide, can be detected in the polystyrene:



$$BrC_6H_4\underset{\substack{\| \\ O}}{C}—O—O—\underset{\substack{\| \\ O}}{C}C_6H_4Br + C_6H_5CH = CH_2 \longrightarrow$$

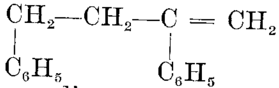
(1)


$$BrC_6H_4COO\underset{C_6H_5}{C}HCH_2\underset{C_6H_5}{C}HCH_2 — \text{etc.}$$

(2)


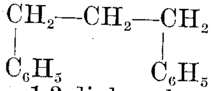
$$BrC_6H_4\underset{C_6H_5}{C}HCH_2\underset{C_6H_5}{C}HCH_2 — \text{etc.}$$

The structure of polystyrene can be deduced from the four products of destructive distillation (in addition to styrene itself):



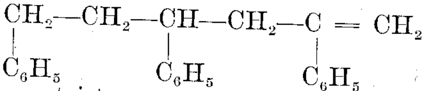
$$\underset{C_6H_5}{CH_2}—CH_2—\underset{C_6H_5}{C} = CH_2$$

distyrene



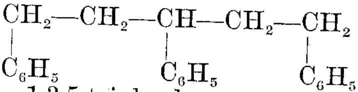
$$\underset{C_6H_5}{CH_2}—CH_2—\underset{C_6H_5}{CH_2}$$

1,3-diphenylpropane



$$\underset{C_6H_5}{CH_2}—CH_2—\underset{C_6H_5}{CH}—CH_2—\underset{C_6H_5}{C} = CH_2$$

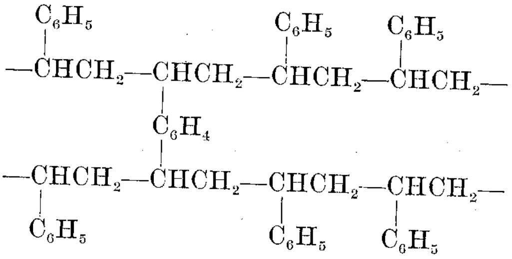
tristyrene



$$\underset{C_6H_5}{CH_2}—CH_2—\underset{C_6H_5}{CH}—CH_2—\underset{C_6H_5}{CH_2}$$

1,3,5-triphenlypentane

Like the other vinyl resins styrene groups are joined head-to-tail to form long chains. As is to be expected, these are thermoplastic. However, minute amounts—as little as 0.002 to 0.003 percent—of divinylbenzene added prior to polymerization yields a relatively nonthermoplastic, insoluble resin. The effect has been compared to that of sulfur in the vulcanization of rubber. Cross-linked polymers result from the presence of a second functional group attached to the benzene ring:



If the copolymerization of styrene and divinylbenzene is carried out in aqueous suspension in the presence of certain stabilizers, the product may show up in the form of beads or "pearls." Fryling and Harrington (5) and Hohenstein and Mark (6) point out that suspension polymerization is in reality bulk polymerization on a small scale. Actually only a few monomers, mostly vinyl compounds, seem to possess properties suitable for suspension polymerization.

Taylor (7) suggests that mechanical agitation subjects the monomer to a viscous drag causing elongation to a thread-like form with subsequent degeneration into drops. By means of the reverse process of coalescence, the drops tend to revert to a monomeric mass. Clusters of droplets, not fused but held together by weak residual forces, tend to disperse with agitation. Snell (8) points out that effective surface-active agents alone are capable of deflocculating the aggregates of droplets.

The effect of the suspension stabilizer becomes most important at the onset of polymerization when the droplets become tacky. A protective monomolecular film, resulting from the selective adsorption of stabilizer at the interface, prevents cohesion of monomer. Hutchinson and Staudinger (9) indicate that the "tacky" stage encountered here is absent or much less pronounced in the polymerization of other vinyl compounds such as the vinyl esters and the acrylic ester type of compound. The tendency toward stickiness makes it more difficult to control globular diameter as the diameter of the beads increases. The largest beads may be as much as 50 times the size of the smallest, and uniformity is particularly difficult to get when beads of more than 1 mm. diameter are desired.

Winslow and Matreyek (10) tried both inorganic and organic suspension stabilizers. Of the former, bentonite and tricalcium phosphate produced opaque beads by surface roughening. The organic dispersants used were all typical hydrophilic polymers:

Methyl cellulose
Polyvinyl alcohol
Polyvinyl methylether
Polyethylene glycol
Polymethacrylic acid
Carboxymethyl cellulose
Starch
Gelatin
Apple and citrus pectins
Sodium alginate

Using 40-50 percent divinylbenzene mixtures they found polyvinyl alcohol to be among the most effective stabilizers.

The polymerizations described in this paper were carried out in a 2-liter pyrex resin kettle with a three-neck ground-glass cover. The kettle was suspended in a water bath—a 4-liter beaker—heated by an electric hot plate. A variable speed stirrer of the cone-drive type was used. A reflux condenser and thermometer completed the required equipment.

The suspension stabilizer was stirred into 1500 ml. of water while the latter was being heated. When the specified temperature (95° in the early runs, 80° or even room temperature in the later runs) was reached, the monomer containing the dissolved dibenzoylperoxide was added in one portion. Stirring could be stopped during the addition, but after the induction period (5 to 10 minutes at 95°) continuous stirring was required until polymerization was nearly complete. This induction period could be shortened by distilling the monomer in order to remove the inhibitor, tert-butyl catechol. No other detrimental effect of the inhibitor was observable, however.

Polymerizations were complete in two to two and one-half hours. The increase in density of the beads so that they would sink when the stirring was interrupted showed the reaction to be finished. Closer control of specific gravity could be obtained by using brines of known specific gravities instead of water for the dispersion medium.

The beads were filtered while hot through a 100-mesh screen, thoroughly washed, and dried at 105° for 3 hours or longer. When dry the beads were weighed and screened to determine size distribution. Screening was difficult because the dried beads tended to acquire an electrostatic charge. Dusting with graphite will eliminate the problem, although cautiously breathing on the beads is simpler and avoids the blackening caused by graphite.

In all, some one hundred polymerizations were carried out. Of the stabilizers listed by Winslow and Matreyek, the following were tried:

Carboxymethyl cellulose
Polyvinyl alcohol
Sodium alginate
Starch
Gelatin

In addition glucose, casein glue, animal glue, soap solution, and such commercial products as Antarox and Tween (polyoxyethylene sorbitan monooleate) were tried. Of this list only animal glue and gelatin gave desirable results and the latter was used in most of the polymerizations. Edible-grade gelatin did not seem any more effective than technical-grade. Styrene monomer was commercial-grade stabilized with tert-butyl catechol. The divinylbenzene, available from Dow Chemical Company, was of two grades, 20-25 percent and 40-50 percent. Typical compositions given were as follows:

	Percent 20-25	Percent 40-45
Divinylbenzene	23.4	43.7
Ethylvinylbenzene .	30.7	43.5
Styrene	10.4	....
Non-polymerizables	35.5	12.0

For the most part the beads were uniformly spherical (fig. 1), but occassionally, in the larger size ranges oval beads and fused beads were observed. Fusion was particularly noticeable when stabilizers other than gelatin or glue were employed.

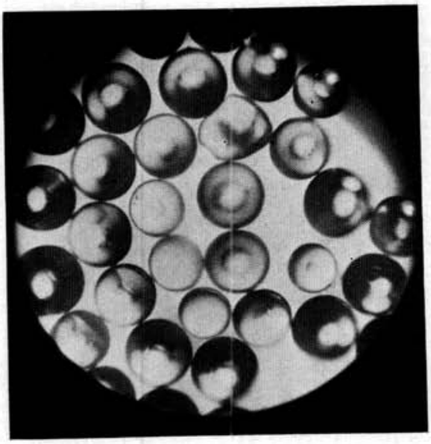


FIG. 1.

At the start a stabilizer concentration of 1 percent was used. This was gradually decreased without ill effect until only 0.5 grams of gelatin was used in 1500 ml. of water, a concentration 0.033 percent. An attempt to reuse the gelatin gave poor results. The beads showed opacity and considerable powdery material was present.

The ratio of catalyst to monomer was held at 1 percent, and the ratio of monovinylbenzene (styrene + ethylvinylbenzene) to divinylbenzene was 10 to 1 in most runs.

The amount of monomer used seemed to influence the size of the beads (fig. 2). The amount of monomer could be increased from 50 grams per 1500 ml. of water to 300 grams and even higher.

The most important single factor other than the type of stabilizing agent was the stirring. Both the rate of stirring and the type of stirrer used influenced the size and appearance of the product. Too slow stirring lets the monomer droplets coalesce and form large chunks of polymer. Too rapid stirring breaks the monomeric liquid into such fine droplets that microscopic beads result. In general smaller beads result from more rapid stirring (fig. 3).

No statement about stirring rate can be made without specifying the type of stirrer used. Four types used were: 4-blade propeller types, one with blades directed for upward and one with blades for downward motion of liquid; spiral type; and anchor type designed to fit exactly the resin kettle. The down-draft stirrer gave smaller beads than the up-draft type, even at lower speed. The spiral type could not be speeded up sufficiently to prevent coalescence. The anchor stirrer was so efficient at moving the entire body of the liquid that the stirring rate could be reduced to 120 r.p.m., whereas the rate used in the propeller type stirring varied between 250 and 450 r.p.m.

A student experiment in pearl polymerization has been worked out which, unlike one described in the literature (11), does not require 7 to 8 hours of continuous stirring or redistillation of monomer. The apparatus, with the possible exception

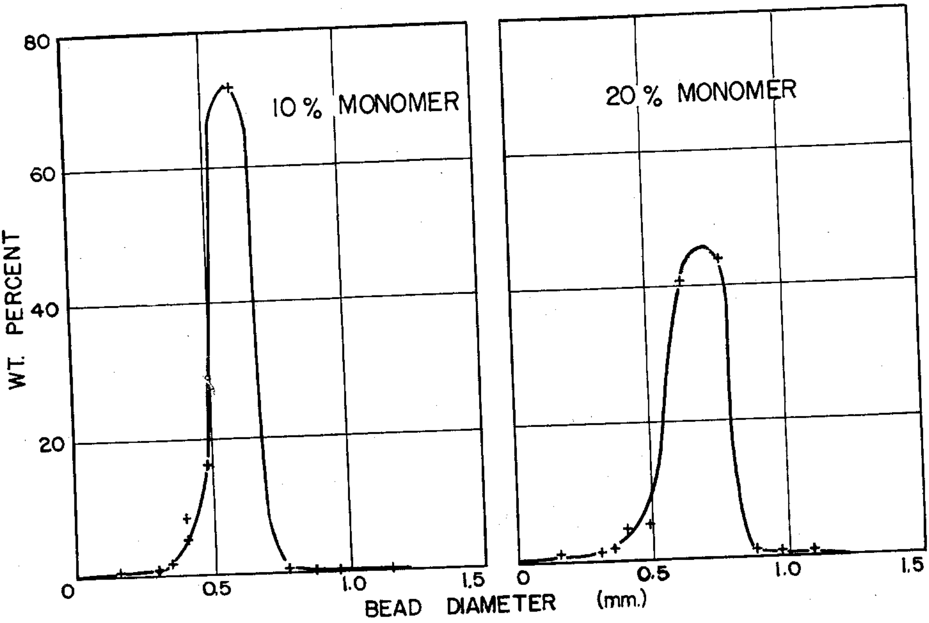


FIG. 2.

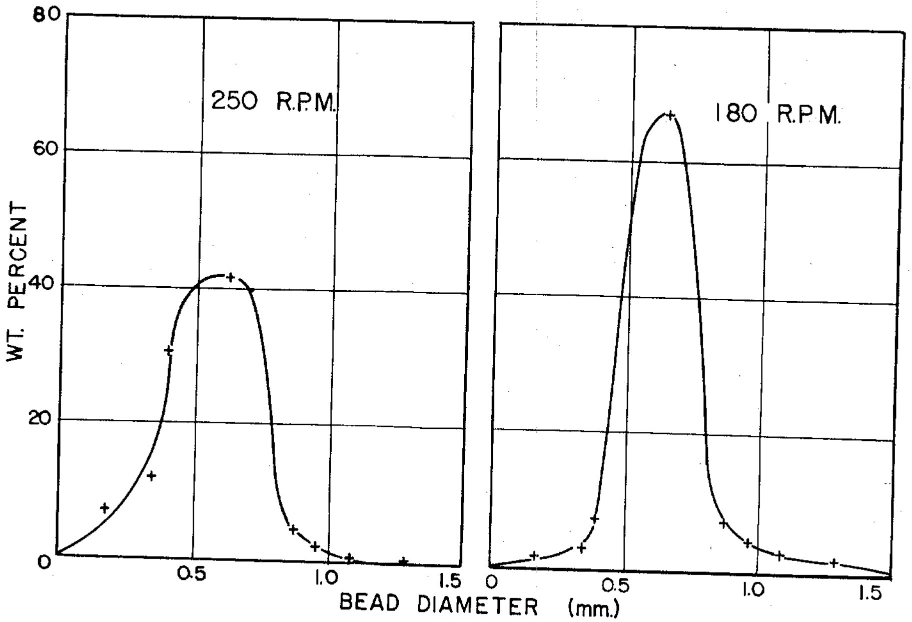


FIG. 3.

of the stirring motor, makes use of equipment normally found in the student's locker. The directions, which were given out to the students in mimeographed form, are as follows:

NOTE: It is imperative that the polymerization be carried through in one period. Set up the apparatus during one period, label it, and start the reaction at the beginning of the next.

In a 500 ml. 3-neck, round-bottom flask equipped with a stirrer, thermometer, and condenser place a suspension of 0.1 to 0.2 gm. of gelatin in 300 ml. of water. The flask is then set in a water bath. (A 1-liter beaker should suffice. It is desirable to put a few glass beads or boiling chips in the beaker to prevent bumping.)

Adjust the stirring rate to approximately 200 r.p.m. and heat the water bath. Meanwhile measure out between 0.1 and 0.2 grams of benzoyl peroxide and dissolve it in a mixture of 10 ml. of styrene and 2.5 ml. of divinylbenbene. When the temperature of the water suspension reaches 75-80° add the mixture of monomer and catalyst. Do not discontinue stirring after this until reaction is complete.

The temperature should rise to 97-98°. Continue at this temperature for 1 hour, stop stirring, remove water bath and, when sufficiently cool to handle, pour entire contents of flask onto a Büchner funnel. Wash 2 or 3 times with hot water, suck dry, and place polymer in a small flask in an oven set at 105°. Examine some of the dried product under the microscope; hand in the remainder in a small stoppered test tube.

QUESTIONS:

1. Could you observe when gelation occurred? How?
2. What happens to the specific gravity of the material during the polymerization?
3. Describe the product. Are the beads clear? What color are they?
4. What electrical properties do you observe?

The beads obtained were generally small but fairly uniform and in good yield. Yields, based on monomer, usually run over 90 percent. In a few cases, when the stirring was accidentally interrupted, the polymer set up as a mass.

REFERENCES CITED

1. Organic Syntheses, Collective Vol. I (1941), p. 440. The method, adapted from Böeseken and Bastet, Rec. Trav. Chim. *32*, 190 (1913), involves heating a mixture of cinnamic acid and hydroquinone under a 24 cm. column for 3½ to 5 hours. The temperature at the head of the column is kept below 130°.
2. Ostromuislenskii and Shepard: U.S.P. 1, 541, 175.
3. Blyth and Hofmann: Ann, *53*, 314 (1845).
4. Simon: Ann, *31*, 267 (1839).
5. Fryling and Harrington: Ind. Eng. Chem. *36*, 114 (1944).
6. Hohenstein and Mark: J. Polymer Sci. *1*, 127 (1946).
7. Taylor: Proc. Royal Soc. (London) *146A*, 501 (1934).
8. Snell: Ind. Eng. Chem. *35*, 107 (1943).
9. Hutchinson, H. M., and Staudinger, J. J. P.: U.S.P. 2, 566, 567 (1951).
10. Winslow, F. H. and Matreyek, W.: Ind. Eng. Chem. *43*, 1108 (1951).
11. D'Alelio, G. F.: Experimental Plastics and Synthetic Resins (1946), p. 72.