

PROGRESS OF STYRENE PRODUCTION

Willard Dow

Dow Chemical Company, Midland, Mich.



STYRENE is contributing to the synthetic elastomer program as a basic material, and the general outline of how it will be utilized is well known. Many of the statistics on production schedules and quantities have been released for general publication. The story of the commercial development of styrene to the point that the process was ready when the large-scale need for it materialized has not been told. It is an interesting story and can furnish no aid or comfort to the enemy. It is believed constructive to review the development of styrene in hindsight with the thought that a lesson may thereby be learned as to other chemicals.

The literature on styrene is voluminous. It extends back more than a century, both as to the monomeric and polymeric substance. Experiments relating to several methods for making the monomer were reported prior to 1900. As early as 1928 some polymeric styrene of German origin was finding its way into this country and was being experimented with as a molding material. The properties of molded specimens permitted no doubt of the desirability of the material as a plastic. Yet in 1931, when our research on styrene began, there were available on the American market only limited quantities of relatively impure monomeric styrene.

The styrene development in the United States is an example of the method of carrying on research by supplying chemists with plenty of so-called patient money while maintaining a prayerful attitude. In this respect, our commercial development of styrene is really a tribute to the ingenuity and foresight of American chemists. It is distinctly the opposite of the development of so many chemicals which have had their origin in a stewpan on the kitchen stove tended by a nontechnical individual with an avid curiosity. It may be added that our styrene development did not originate with a purchased German process.

Our first approach to the problem of making monomeric styrene involved a process leading through β -phenylethyl alcohol. Ethylbenzene was formed from benzene and ethyl chloride, and the ethylbenzene was then chlorinated to yield a mixture of α - and β -chloroethylbenzene. The beta compound was separated and hydrolyzed to give β -phenylethyl alcohol, which was then dehydrated with an alkali to yield a relatively pure styrene.

There is, of course, a fundamental fault with this process, arising out of the fact that the chlorination of ethylbenzene normally yields a mixture of monochloroethylbenzenes very high in the alpha compound. Before the production of styrene could be accomplished on any substantial scale at a reasonable cost, the yield of styrene from both the alpha and beta compounds had to be materially increased.

IN ANOTHER laboratory, work was being done simultaneously on the process now used by us for making styrene,

which does not involve a chlorination step. At one stage of the development the two processes appeared to present substantially equal possibilities, and we were confronted with the question of which process to concentrate upon in an endeavor to produce the material. Let us assume for a moment that the process involving chlorination could have been worked out to produce styrene at the same cost as the one now used and that we had elected to develop this process. When the present need for styrene arose, we would have found ourselves with a process requiring huge quantities of chlorine which might well have forced the production of a polymeric elastomer probably inferior to the styrene-butadiene type because of lack of sufficient styrene. It should be added that work was continued on the process involving the chlorination step for some time after the decision to use the cracking process was made. However, such work only substantiated the correctness of our decision in that we ultimately found better economies were actually obtained by the cracking method.

The story of the development of our present commercial method for the manufacture of styrene begins in 1933. For some time prior to that year, considerable research on the cracking of hydrocarbons to yield unsaturates such as ethylene had been in progress in our laboratories. At least three methods had been worked out. A group of research workers, not associated with the cracking problem, had been in a position to observe most of this work. Some of these men were experienced organic chemists, and the thought of large quantities of relatively inexpensive ethylene stimulated their imagination. In their background of experience they had accumulated a store of knowledge on the Friedel-Crafts reaction, and they could see the possibility of cheap ethylbenzene. Before their eyes were satisfactory cracking processes and the possibility of dehydrogenating ethylbenzene to styrene seemed to merit investigation. The problem was fully recognized and the solution appeared to be reasonably simple. It was not! Even when guided by such knowledge as could be gained from the literature, added to the technical "know-how" of the investigators, it required over three years and the efforts of a large group of chemists and engineers to work out the process to the point where a satisfactory product was obtained.

The ethylbenzene reaction did not require too much time and effort, and the basic work on producing this intermediate material was completed in two or three months. A great deal of subsequent research was necessary to perfect the process and make it commercially useful. Various cracking procedures were tried, and then concentrated effort was put upon the process, involving mixing the preheated vapors of ethylbenzene with highly superheated steam. It was found that high yields could be obtained by this procedure without producing free carbon or tar in the condensed reaction product.

THE next step was the separation of the styrene from other products of pyrolysis. This purification was a tedious problem, and in many instances we thought it was solved only to discover that the polymer formed from monomer we thought pure would still blush and craze. In one instance it was reported the problem was licked. Some days later this proved to be the story: Five gallons of the best monomer were taken to an excellent still, and an attempt made to clean up the product once and for all. The run was made under ideal conditions, and the product was analyzed at short intervals by the bromide-bromate titration method for unsaturates. When the analysis showed a purity of 99.9+ per cent, this fact was reported. No immediate report was made that the purity ultimately went to 104 per cent. That is how the presence, theretofore undetected, of phenylacetylene was recognized. Monomer purity is the most important single thing to be considered in the preparation of styrene polymers and copolymers, particularly as to the styrene-butadiene copolymer.

The incident of finding a monomer still column suddenly full of solid polystyrene was a real headache, until it was discovered that sulfur would prevent this. If you want to spend money like the proverbial sailor, as well as gain a respect for the sheer cussedness of styrene, try the problem of continuous polymerization of the monomer.

On hot working the polymer in molding and compounding operations, we sometimes get molecular degradation with a consequent viscosity decrease and loss of strength and toughness. Also, we occasionally have the problem of discoloration on drying the polymer to remove the last traces of monomeric styrene. Investigation of this problem revealed that certain hydrocarbon-substituted catechols prevent such discoloration and degradation, and permit reproducibility of properties in polymers. As a safety measure, therefore, we have found it advisable to incorporate *tert*-butylcatechol in the order of 1 part in 20,000 parts of monomeric styrene as a stabilizer.

It was necessary early in the development to determine the probable toxicity of the monomer. We find that monomeric styrene may be handled with the same precautions now observed in the handling of common aromatic hydrocarbon solvents. It is worth noting that the extreme eye and nose irritation produced in man at a concentration of 1300 parts per million affords a definite safeguard against voluntary exposure to acutely hazardous concentrations of monomeric styrene vapor. Concentrations up to 400 p. p. m. do not produce appreciable eye and nose irritations in man and appear to present no serious industrial hazard; therefore this figure is suggested tentatively as the permissible limit for repeated exposures.

IT IS interesting to make a brief comparison of the Dow method with some of the other processes considered for the production of ethylbenzene to be used in making styrene. One proposed process utilizes benzene and 95 per cent alcohol as starting materials. These are reacted in the presence of a

solid catalyst containing phosphoric acid at temperatures around 600° F. and pressures of the order of 250 pounds per square inch. Another process advanced is similar, except that ethylene is substituted for alcohol.

In both of these processes benzene and ethylene must be recycled several times, and the yield of ethylbenzene is claimed to be about 200 pounds per pound of catalyst. Both processes require nitration-grade sulfur-free benzene, which has a 1° F. boiling range. In contrast to such processes, the one which we have developed will actually use ethylene in admixture with other hydrocarbons in concentrations as low as 38 per cent ethylene, provided the gas is nearly propylene-free. Of course a more concentrated ethylene is desirable if it can be economically obtained. The operating temperature of our process is only about 190° F., and the pressure is relatively low, 15 pounds gage. Aluminum chloride is used as a catalyst, and 75-100 pounds of ethylbenzene can be obtained per pound of catalyst with a nitration grade of benzene. Scrap aluminum can be used in preparing a satisfactory catalyst, as well as cheap bauxite. Our process can use a less pure benzene with a boiling range of 2° F., with no substantial adverse effect on the quantity of ethylbenzene obtained per pound of catalyst.

The presence of sulfur in the benzene is not objectionable in our process, inasmuch as the aluminum chloride catalyst used promotes the formation of hydrogen sulfide gas which is vented from the system. Small amounts of unsaturates can also be tolerated in the benzene. The yield of ethylbenzene which can be obtained by operating according to our continuous procedure is nearly theoretical. No ethylene is recycled in the Dow process. A particular advantage arises out of the substantial dealkylation of any polyethylbenzenes formed simultaneously with monoethylbenzene. Procedures have been satisfactorily worked out on a pilot plant scale for recovering as high as 80 per cent of the spent aluminum chloride catalyst and are now being extended to commercial plant operation.

Although over 95 per cent of our present production of polystyrene is going directly into war uses on priority ratings of A-1-I or higher, styrene is distinctly not a "war baby". It will continue to find use as a basic material in elastomers. We visualize the refinement of the material and its expanding use as a moldable thermoplastic. It is peculiarly adapted to fabrication by the procedure known as injection molding. It is strong, tough, and exceedingly attractive because of its crystal clarity as well as its unlimited color possibilities. We look forward confidently to the future of styrene in the radical improvements in consumers' goods which will occur upon the cessation of hostilities.

BIBLIOGRAPHY

- (1) Dow Chemical Co., U. S. Patents 2,110,829 (1938); 2,181,102 (1939); 2,198,595, 2,222,012, 2,225,543 (1940); 2,240,764 (1941).
- (2) *Oil and Gas J.*, Aug. 6, 1942, p. 14.

