Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Boyer, Raymond F.(1981) 'Anecdotal History of Styrene and Polystyrene', Journal of Macromolecular Science, Part A, 15: 7, 1411 — 1434

To link to this Article: DOI: 10.1080/00222338108056791

URL: http://dx.doi.org/10.1080/00222338108056791

J. MACROMOL. SCI.–CHEM., A15(7), pp. 1411-1434 (1981)

Anecdotal History of Styrene and Polystyrene

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ABSTRACT

A formal history of styrene and polystyrene from 1839 through 1952 appears in the Styrene monograph edited by Boundy and writer but now out of print. Updating of the story by several teams of Dow writers appeared in the Kirk-Othmer Encyclopedia, the Encyclopedia of Polymer Science and Technology, and the SPE Award address of Amos. We propose a more personalized history written from the perspective of one whose 40-year professional career was involved in scientific and technological aspects of the subject. We view this history as a complex interplay of science, technology, industrial activity, management decisions, legal and patent activities, people, and the vagaries of World War II. Germany had an early industrial lead prior to 1941 with a monomer process and mass polymerization techniques. Original work on styrene-butadiene elastomers was another first. Germany also had a scientific lead as academic scientists such as Staudinger, Kern, Schulz, Jenckel, and Ueberreiter became involved in the chemistry and physics of styrene and polystyrene (PS). Mark was first in industry and then in the university. Several United States companies were active with styrene and PS, also prior to 1941. Involvement of the United States in World War II lead to a government decision to produce SBR. This catapulted styrene into a major synthetic chemical. The lead passed from Germany to the

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United States, especially with the large excess capacity for monomer after 1945. Management decisions encouraged diverse large-scale polymer uses for styrene, aided by the low price for the monomer. Through a bizarre series of events (war, people, and legal action), proprietary industrial knowledge in both Germany and the United States had diffused into the domain of public knowledge. Styrene and PS now face the problems of any petrochemical product.

GENERAL INTRODUCTION

There have been several classical histories dealing wholly or in part with styrene [1-3] and several more recent works [4-7]. This account is based on personal observations made during my 40 years at the Dow Chemical Co. in Midland, Michigan. Its intent is to emphasize some of the people-related and chance-dependent aspects of the story.

When I joined Dow in 1935, ethylene was still being made by the dehydration of ethyl alcohol. However, research and development had been completed on a regenerative steam cracker for converting Michigan crude oil into ethylene, propylene, butadiene, and related products. The first commercial plant to do this was constructed during my first year at Dow Chemical. When I retired in 1975, Dow was the worldwide leader in the production of styrene and polystyrene. I was never part of the mainstream of this and I do not wish to imply any credit. The mainstream was carried on mainly by chemists and engineers. However, as a physicist, I was engaged in the characterization of polystyrene, for example, with regard to electrical properties, molecular weight, ultraviolet light stability, and related things. I was in an ideal position to observe what my colleagues were doing.

In addition, I had two major history lessons at Dow. The first occurred in 1962 with Mr. C. B. Branch, then head of Dow International and later to become President and then Chairman of the Board. He called me to his office and asked me, in my then role as Director of Plastics Research, why our research people were not coming up with any new styrenes. I did not know, but promised that I would look into it. I also told him that my colleagues at ICI Plastics Department in Welwyn Garden City, England, were being asked a related question by their management—"Why are you not coming up with any new polyethylenes?" During the next 9-month period, I took an intense look into the early history of styrene and polystyrene at Dow by talking with most of the key figures in the early development of styrene.

Second, in the later 1960s when Dow had decided to initiate patent infringement suits against its major competitors over the impact polystyrene patent [8, 9], I was tagged as one of the key witnesses since I had been in charge of the laboratory in which the process for impact polystyrene was discovered. This gave me an opportunity to review the history of impact polystyrene at Dow and to review all sorts of literature, patent, trade, and scientific, which gave us some idea of what our major competitors had been doing prior to and after the issuance of the Amos, McIntyre, and McCurdy Patent on impact polystyrene (see Ref. 8).

This anecdotal account was written from memory, except for recourse to some material in the references. There is a certain contrapuntal character to this account as I try to interweave what several competitive, and hence interacting, groups were seeking to achieve over a span of about 10 years, with frequent interruptions and changes in direction.

A few comments about the research organization at Dow in the 1935-1940 period will help in understanding the styrene story. There were approximately 12 laboratories, each in a separate building; seven, including analytical, reported to production managers. The remainder, the so-called independent laboratories, reported directly to President Willard Dow. The key ones of concern here were:

1. The Physical Research Laboratory (PRL) under John Grebe, a physicist with strong interests in physical chemistry, instrumentation, and automation.
2. The Organic Research Laboratory (ORL) under Edgar C. Britton, later President of ACS.
3. The Cellulose and Plastics Laboratory (CPL) under William C. Collings and S. L. Bass, both of whom became prominent in Dow Corning during World War II and after.

Founder H. H. Dow had started the philosophy and practice of open rivalry and competition between laboratories and between groups within the same laboratory as a means of arriving at the best process for any given product and/or the best product for a given end use. Examples will appear later. The PRL (of which I was a member) developed Dow's ethylene process, a process for styrene by the dehydrogenation of ethylbenzene, mass polymerization of styrene, and Saran products. CPL developed ethyl and methyl celluloses and also a continuous belt process for PS which was never commercialized. ORL worked on the side-chain chlorination process for styrene and the emulsion polymerization of styrene and styrene-butadiene products. This general situation lead to what I like to call the "Ethyl Cellulose-Saran-Polystyrene Controversy" which dominated conversation among polymer chemists at Dow in the late 1930s.

The CPL believed and preached that ethyl cellulose would become the largest volume plastic in the world because the raw material, cellulose, was cheap and plentiful. The other ingredients were caustic soda to treat cellulose, ethyl chloride to provide the ethyl side groups, and mineral oil as plasticizer. Dow even purchased land on what was then the edge of Midland and started an experimental forest by planting fast growing poplar trees in order to demonstrate that it could eventually, if necessary, have its own supply of cellulose.

The second group, the so-called Saran group. spearheaded by Mr. Ralph Wiley in the PRL, liked to point out that since Saran was about 70% chlorine by weight, and since chlorine only cost about 1¢ per pound, obviously it was going to be the cheapest possible plastic. Therefore, it would become dominant in the world of plastics. Of course, he reckoned without a few factors: the role of density in the selling price, the brittleness of Saran and its poor heat stability, along with a few other factors. While the Saran line of products has been extremely valuable and a profitable one for Dow, it certainly never achieved the sales which its early supporters insisted it could meet.

Polystyrene, on the other hand, was like a poor country cousin. It was made by a mass process on an extremely slow production schedule, and had both a high average molecular weight and a broad molecular weight distribution. The injection molding machine at Dow was operated by personnel in the Cellulose Laboratory. They were accustomed to the easy molding of plasticized ethyl cellulose. They stated, authoritatively, that polystyrene could never be used in the injection molding industry because of its poor moldability characteristics. Of course, this was very wrong because ways were found later to lower the average molecular weight, to narrow the molecular weight distribution, to add certain lubricants, and, ultimately, to produce the thermally stable, general purpose polystyrene of commerce which is now molded automatically on a very short cycle injection molding machine.

This was the sort of atmosphere in which polystyrene had to make its way. It is my recollection that the top management of the company favored Ethocel because of the logic of the arguments that could be advanced in its favor. Polystyrene won out in the long run because of its petrochemical origin and liquid processing, on the one hand, and because ethyl and methyl cellulose preparation involved a solids handling process which never was able to achieve the kinds of economics inherent in the production of polystyrene. Also, cotton linters had to be used rather than wood pulp for top quality.

WHY DOW WENT INTO STYRENE AND POLYSTYRENE

Historical study to answer "why no more styrenes" quickly led to the fact that Dow originally did not intend to make polystyrene when its petrochemical program was initiated. In fact, Dow didn't even intend to make styrene monomer. Rather, both products were afterthoughts. Ethylene was wanted for glycols, ethylene bromide, ethylene dibromide, etc., and for vinyl and vinylidene chloride used in the making of Saran. Perhaps one of the most important reasons was to produce ethyl chloride needed for the etherification of alkali cellulose.

The PRL decided that ethyl benzene would be a good product to make. It was speculated that there should be a large market for ethyl benzene as a solvent, electrical fluid, and so on. Such a major market never developed. Then it was realized that styrene could be produced from ethylbenzene. This way, Dow found itself in the way of developing styrene monomer. At that time, both DuPont and Bakelite seemed to have a serious interest in polystyrene. The old record shows that one of the first large sales of styrene monomer was a 5000 pound order to DuPont. Bakelite negotiated a formal arrangement with Dow for purchasing its styrene requirements from Dow. On the strength of this, Dow built a production plant for styrene monomer, capacity slightly under one-half million pounds per year. That is very small compared to today's standards, but was then a major adventure in a new product. DuPont decided not to go into the polystyrene business, even though they certainly had a serious interest in it. Then the Bakelite Co. changed its mind and decided not to go into the production of polystyrene.

In the summer of 1937, in the open field behind the PRL at Dow, were several hundred 55 gallon drums filled with inhibited styrene monomer, sitting out in the sun and being water cooled to try to prevent polymerization. Inhibitor was added to each drum. Dr. Strosacker, the production manager who had authorized the styrene monomer plant, was considered by many to be a fool who had made a colossal mistake.

Dow's answer to its excess monomer was to initiate a crash program for the production of polystyrene. In other words, it was decided that Dow would make and sell polystyrene. This is, if you will, a default decision. The engineers, chemists, and others in the PRL who were placed on this crash program went full speed ahead. For a long time a solution polymerization-precipitation process was very favored because of exotherm control. It could never produce a color-free polystyrene. It was the belief of our laboratory director, Dr. Grebe, that the big outlet for polystyrenes would be in the rapidly growing and coming electronics and electrical industry. Therefore, the quality of polystyrene had to be one of ultimate purity. This seemed to dictate going to a mass process of which I will say more about later.

Of course, a few years later, with the government's decision on GRS, Dow was in an ideal position as far as styrene was concerned. Dr. Strosacker and the people associated with him were suddenly heroes.

THE TWO DOW PROCESSES FOR STYRENE

One major research rivalry in the late thirties involved two processes for producing styrene monomer from ethylbenzene: steam cracking under Dr. Grebe in the PRL and side-chain chlorination followed by catalytic dehydrochlorination under Dr. Britton in the

ORL. The PRL did both research and pilot-plant studies. Dr. Britton's brother, J. W. Britton, a chemical engineer who managed a semiplant unit, operated the side-chain chlorination pilot plant. His semiplant produced Thiokol from Dow's ethylene dichloride for the Thiokol Corp. Later, he was production manage for styrene-butadiene latexes.

According to the styrene monograph [1], the side-chain chlorination process had some attractive features. Moreover, the dehydrogenation process, using superheated steam over a bed of charcoal, was a new venture at Dow, with nothing near the efficiency of today's catalytic cracking.

This petrochemical process was run by the late Mr. Robert R. Dreisbach, whose hobbies included 1) preparation of extensive tables of boiling points for organic compounds as a function of pressure, and 2) insect collecting and classification in terms of their genitals. His books on boiling points are still in use. His insect collection has a permanent home at the University of Michigan.

Robert Dreisbach was among the most colorful of many colorful Dow researchers. Legend has it that his bookkeeping method for materials balance would not bear much scrutiny: the chemical engineer might call it unorthodox, the purist would call it dishonest, the seer might say that it was simply prophetic of the high yields inherent in this petrochemical process. At any rate, his data books and records showed higher overall yields than were reported for the side-chain chlorination process. A retired Dow engineer who worked under him at the time assured me that Dreisbach always included uncracked ethylbenzene recovered by distillation as part of his styrene yield.

My recollection is that monomer from the side-chain process always contained some chlorinated product which ended up on the PS. It would then lose HCl during the molding step, giving rise to mold corrosion, discoloration, and poor electrical properties.

For whatever reasons, the petrochemical process was eventually selected by Dow for its commercial styrene monomer plant. One can only imagine the fate of the Dow styrene process when the synthetic rubber program came along, if it were the side-chain chlorination process. The chlorine demand, with its high capital requirement in chlorine cells and power, would have ruined it.

We might recall at this point that Union Carbide developed still a third process for styrene starting with ethylbenzene. This involved side-chain oxidation of EB, hydrogenation to the alcohol, and dehydration. Although this process had one more step than side-chain chlorination, it was competitive with dehydrogenation into the sixties. The heavy capital investment in chlorine-caustic cells, as compared with liquid O_2–N_2 plants, spelled the capital difference. And there were *no* alkylchlorides to cause corrosion.

In retrospect, the manufacture of styrene monomer seems routine and very simple. Of course, as with all such things, there was a long period of doubts and difficulties. There were two major impurities in the early monomer aside from ethylbenzene. One was phenyl acetylene which acted as an inhibitor for polymerization but which also gave titrations of greater than 100% styrene, thus leading for a long while to the belief that styrene was really more pure than it actually was. This story is discussed briefly on page 20 of Ref. 1.

The other impurity was a trace of divinylbenzene. This caused the distillation column for separating styrene and ethylbenzene to plug up periodically. I was asked by the production manager of the styrene plant to help out on that problem. I still remember my shock and horror at seeing a large diameter, tall distillation column whose Raschig rings were full of a gelatinous mass that smelled strongly of styrene monomer. The rings had to be chipped out of the column by air hammer which required that the stills be down for several days, once or twice each year. We were able to show that this gelatinous mass had a high sol content and some insoluble material which swelled quite highly. Moreover, the gel seemed to form on the surface of the rings near any air leaks in the port holes of the column. The gel would not wash down the column to the distillation pot and eventually the column plugged, as described.

This incident involving myself was typical of close cooperation between research and production groups. The styrene plant manager, Mr. Richard McClury, was one of many production persons who attended monthly progress reports at the PRL. He knew that I was studying the swelling of cross-linked PS in various solvents to test out the then new Flory-Rehner swelling theory. Hence, he asked me to cooperate. I spent 6 to 9 months on the problem and described my results in a company report.

Once defined, the problem was eventually solved. The production people first of all used more careful distillation to separate ethylbenzene from the higher alkylated benzenes, and better catalysts which allowed the cracking to occur at a lower temperature with less tendency to make divinylbenzene. It was just one of numerous problems that had to be solved on a commercial scale in the late 1930s.

There was also a problem with sulfur which was used in the column to prevent premature polymerization of styrene. However, traces of sulfur would get into the finished monomer and then be incorporated into the polystyrene. We discovered, and subsequently published, the fact that sulfur promoted the ultraviolet discoloration of polystyrene, and that the rate of discoloration, or the amount of color, was directly proportional to the sulfur content [10]. This problem was controlled eventually through use of less sulfur and more judicious choice of where the sulfur was added to the column.

These are just three of many problems that were once of great concern but which did get solved through long and persistent efforts. When the Dow styrene process was needed for the synthetic rubber program, it was already a highly perfected petrochemical process.

In addition to its own facilities in Midland, Dow built and operated monomer plants in Freeport, Texas, and Torrance, California, for Rubber Reserve, and in Sarnia, Ontario, for the Canadian government.

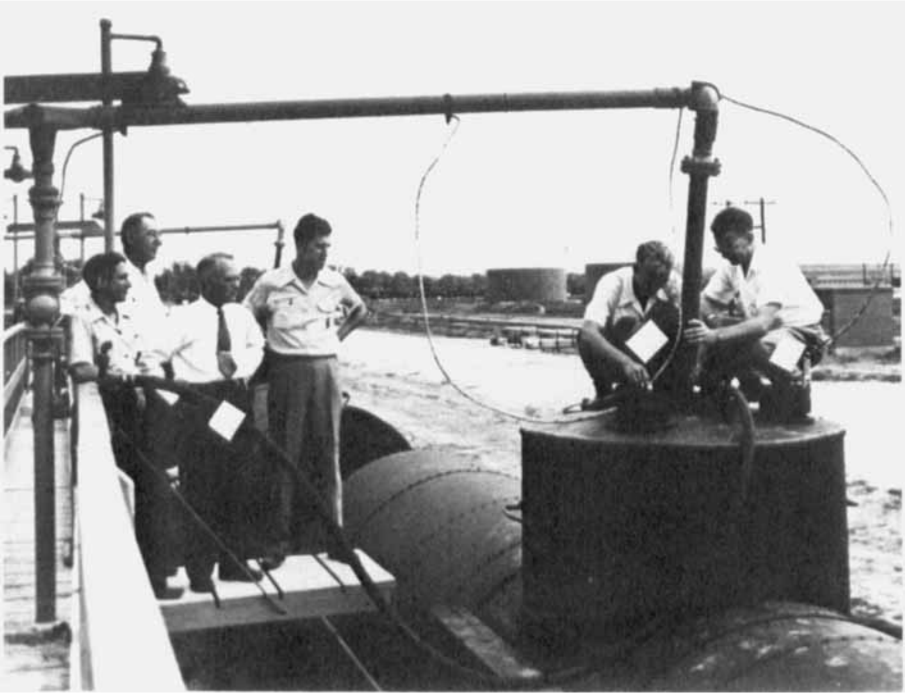

FIG. 1. Loading first tank car of styrene monomer for Rubber Reserve from Texas plant, ca. 1943. White areas, left to right: A. P. Beutel, general manager of Dow's Texas Division; C. B. Branch, chemist, later to become president and board chairman; and K. Bowen, styrene plant superintendent.

Figure 1 shows the loading of the first tank car of monomer at Dow's Texas facility for shipment of a GRS plant. The year was 1943.

THE DOW CAN PROCESS FOR POLYSTYRENE

The net result of the crash program initiated in 1938 in the PRL to produce a saleable grade of polystyrene was the so-called Dow Can Process. In the pilot plant, polystyrene had been made by polymerization in glass bottles starting out small, working up to half gallon and then gallon size, and even two gallon size. Eventually ten gallon capacity milk cans were used. These were lined with metallic tin and thus gave an extremely pure polystyrene.

A large number of these cans filled with styrene were placed on racks which were lowered into water baths. And then, on a long, very slow schedule, the styrene was caused to polymerize thermally. There was always an exotherm at the center of each can as the material thickened, leading to a core of lower than average molecular weight. The finished billets were pushed out of the cans and ground up to distribute the different molecular weight regions of the can.

When metallic tin became scarce during World War II, it was feared that the can process might be doomed. A pilot plant was started up to recover tin from used cans by melting the tin off of the steel cans in hot oil. But Amos and his colleagues discovered that if the inside of newly fabricated bare steel cans was washed with an oil containing a rust inhibitor, the bare metal cans were ideal for polymerizing styrene.

This can process was operated all during the war and turned out 162 million pounds of general purpose PS before it was discontinued around 1950. It was a process that management liked because it had low capital investment. While labor intensive, labor in those days was relatively inexpensive. The process could be easily expanded in capacity by simply adding more water tanks and temperature controllers, and it was really a tremendously profitable operation. There was no question about the high quality of the polystyrene not only for electrical-grade material, for which there was never a big market, but for general purpose molding. One of the key improvements in this can process was the addition of some peroxide catalyst to the monomer. Immediately, the capacity of the plant was doubled because of the faster rates which could be achieved while still controlling the exotherm.

Eventually, can process know-how was sold to a British firm which wanted to enter the PS market with a small capital investment.

At one point Monsanto operated a batch mass process for PS using filter plate frame units. The finished product came out in the form of blocks of PS about 6 in. thick and the cross section determined by the size of the filter frame leaves. Cooling water was circulated through hollow plates spaced between the blocks. The feed to these units was a syrup of 30-40% PS in styrene from an agitated prepolymerizer. This was more sophisticated than the can process but probably more capital intensive. This unit was destroyed by the explosion of an ammonium nitrate freight boat in the harbor at Texas City in 1947. In hindsight, impact PS could have been made in this unit by adding SBR to the stirred prepolymerizer.

CONTINUOUS MELT PROCESS FOR PS

Following the termination of World War II, research workers in the PRL began studies for a continuous mass polymerization system to replace the labor-intensive can process. Observations made by American teams at I.G. showed what could be done with mass processing [2].

Amos and his colleagues built a series of pilot plants for this purpose. He has discussed this effort in Ref. 6. One unit became the basis for the Stober-Amos patent [11]. It consisted of an agitated prepolymerizer which carried conversion to about 30% solids. A horizontal screw polymerizer increased conversion to about 95%. A vacuum devolatilization step removed monomers, dimers, and timers. An extruder produced strands which were water cooled and chopped into pellets. This unit produced high quality, crystal-clear PS. However, it was not suited for scale-up and never was developed on a commercial scale.

It did become famous as the first unit to produce rubber-modified PS using shearing agitation, as taught in the Amos et al. patent [8]. In today's parlance, the agitation in the prepolymerizer caused phase inversion, resulting in a dilute dispersion of monomer-swollen rubber particles in a concentrated solution of PS as the continuous phase. Styrene grafted to SBR acted as a polymeric emulsifier to stabilize this dispersion. When the about 2 μm diameter rubber particles subsequently cross-linked at high finishing temperatures, the final product was completely thermoplastic and free from "fish eyes" (see page 1423).

Meanwhile, a remarkable engineering design on a continuous process for general purpose PS was proceeding under the late Samuel J. Ludington, one of Dow's most competent design engineers. Amos and his colleagues supplied experimental data on rates as well as heats of polymerization, and on heat transfer coefficients. The final design is shown schematically in Fig. 2.

Two nonagitated horizontal tube tanks, each of about 40,000 pounds monomer capacity, were polymerized alternately using Dowtherm circulated through the tubes to control the exotherm. When Tank 1 had reached high conversion under a nitrogen blanket, a specially designed polymer pump transferred the molten PS at 220-240°C to the bottom receiving tank. Polymerization was then started in Tank 2. Safety features were available in the event of power and/or Dowtherm pump failure. The receiving tank, also unagitated, operated under vacuum to remove volatiles. There was always polymer in the receiving tank so that the extruder-pelletizer sections operated continuously.

There were several remarkable features about this design and the subsequent commercial units:

1. A pilot plant of this design was never built and operated, although prototype components appeared in several pilot plants.
2. A design patent was allowed by the U.S. Patent Office. However, Dr. Charles Strosacker, Production Manager for styrene and PS products, decided that this patent would teach rather than protect. At Dow's request this patent never issued.
3. The first commercial unit was installed at the Dow plant in Sarnia, Canada. The Canadians were anxious to go into the production of polystyrene and they were obviously more adventuresome, or perhaps more hungry, than the Midland production

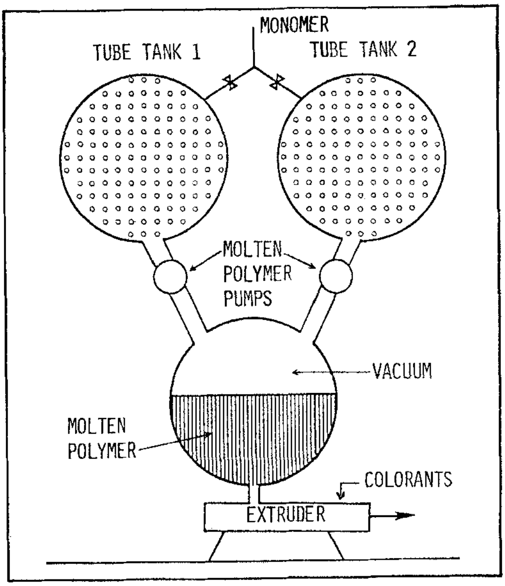

FIG. 2. Schematic cross section through center of three longitudinal unagitated tanks showing Dow's first commercial continuous melt process for PS. Styrene was thermally polymerized alternately in tube tanks 1 and 2, and devolatilized in the receiving tank which was always about half full.

group. They were willing to take a chance on a new, unproven process—a chemical engineer's dream, designed on paper and never having a prototype pilot plant. The unit worked extremely well from the beginning because of the very large heat transfer surface and the efficiency of Dowtherm in heat transfer. It was a really conservative overall design.

Midland was still, I think, enamoured of its low capital investment can process which was turning out prodigious quantities of saleable polystyrene in a perfectly predictable manner. Midland did eventually put in 12 of the tube tank units and operated them for many years. By the time I had retired, these units had produced in excess of a billion pounds of general purpose polystyrene.

4. The commercial success of these unagitated tube tank units without plugging up even after years of operation is a tribute, first to the Amos-Ludington teamwork, but also to the very high purity of styrene monomer, especially with regard to traces of divinylbenzene, and to the extreme thermal stability of PS under nonoxidizing conditions.

Later, when Amos and his group attempted the continuous polymerization of vinyl toluene, they discovered that gel formed on heat transfer tubes, apparently because of chain transfer to ring methyl groups on the polymer. Had polyvinyl toluene been a desirable sales product, it would have required another type of polymerization.

The advent of high impact PS demanded continuous polymerizers with shearing agitation in the first stage for phase inversion. At the same time, agitation in later stages proved advantageous for heat transfer. A patent to Ruffing et al. [12] illustrated the evolutionary changes from the Stober-Amos design. Of course, these multistage units with agitation throughout could be used for general purpose or impact PS as demand dictated.

Other Polymerization Methods for PS

Dow chemists, engineers, and production personnel were thoroughly familiar with suspension polymerization. This method was used commercially at Dow to produce Saran and cross-linked beads for ion-exchange resins. Still later, suspension beads for foaming-in-place by the Badische method were produced. Suspension PS, particularly the Koppers material, had a heat distortion temperature superior to that of Dow PS. This difference was a direct consequence of residual dimers and trimers formed during thermal initiation in the Dow mass process, but not present in the peroxide-initiated suspension process.

The advent of rubber-modified PS was probably the final decisive event in directing Dow effort away from suspension PS. Haward of Shell obtained a patent on rubber-modified PS made by suspension [13]. This product still contained fish eyes because each suspension particle was cross-linked by SBR. Stein and Walter of Monsanto [14] later solved this problem by a prepolymerization step with shearing agitation. The phase-inverted syrup was then converted to an aqueous suspension in which polymerization was completed.

As mentioned earlier, the ORL at Dow did extensive research on emulsion polymerization. Le Fevre and Moll followed this method for years. An emulsion PS made by a batch process became a small-scale commercial Dow product. Moll later operated a continuous emulsion PS process patterned after continuous GRS polymerizers, but it was doomed to commercial failure, especially in a company so heavily committed to mass polymerization.

To the best of my knowledge, emulsion polymerization never succeeded anywhere. British Resin Products in Barry, Wales, with the late Dr. Peter Staudinger as research director, had developed a commercial emulsion batch process. The product was of high molecular weight and gave unusually tough moldings which were difficult to produce by injection molding. This unit was running during my first visit to Barry in 1952. It subsequently burned down following a dust explosion and was never replaced. Instead, via Distrene (a Distillers-Dow joint company), the switch was made to readily moldable Dow mass PS.

I recall that an open mind toward suspension PS prevailed among Dow chemists and engineers. Perfect control of the exotherm and better heat distorsion were positive factors. Suspension drying and pelletizing were energy- and capital-demanding steps not present in the mass process. The exotherm in the Dow process supplied most of the heat needed to produce a molten PS ready for pelletizing. But when impact PS required the prepolymerizing step, the balance switched tremendously in favor of an all-mass agitated process.

RUBBER MODIFIED PS AT DOW

The advent of radar in the early 1940s required a flexible plastic of excellent dielectric properties for jacketed cables. Several of us, mainly O. R. McIntire and myself, worked with natural rubber to modify PS, following the early work of Ostromislensky. NR was either polymerized in styrene or blended with PS. Some promising results were achieved at Dow and elsewhere with such systems.

Meanwhile, Guss and Amidon of the ORL had developed an emulsion process for preparing interpolymer blends by the consecutive polymerization of styrene and butadiene in either order. The resulting product would probably be classified today as an interpenetrating polymer network with some grafting and some cross-linking. These materials combined the high temperature properties of PS with the low temperature flexibility of polybutadiene and the excellent dielectric properties of a hydrocarbon polymer. The government authorized a production plant to produce such material commercially for radar cables. It was given the trade name Styralloy 22. I was its technical sales representative during the war.

Styralloy 22 displaced the NR-styrene interpolymer work at Dow and was in turn displaced by branched polyethylene from ICI. The R&D effort on Styralloy 22 and the production facility for making it were later instrumental in Dow's development of the 60 styrene-40 butadiene emulsion copolymers which became the base of latex paint and paper coatings.

In 1944 or early 1945, John Grebe obtained some soluble GRS and asked me to copolymerize it with styrene. The resulting mass polymer was incredibly tough—far tougher than any such product made with NR. It was also insoluble. It is now known that NR does not cross-link in the presence of styrene radicals, either because of steric hindrance of the methyl side group or absence of vinyl side groups or both. A decision was made to develop a rubber-toughened PS, and Grebe gave this responsibility to O. R. McIntire.

The ultimate result was a can process for high impact PS. The billets from the 10 gallon cans had to be milled extensively to break cross-links so that moldings with relatively smooth surfaces could be made. Even so, the moldings contained blemishes called "fisheyes," consisting of gel particles of rubber in PS.

The material from the unagitated can process consisted of a product which Dr. Turner Alfrey was later to describe as two continuous, interpenetrating phases. One was pure PS, the other was cross-linked rubber filled with discrete particles of PS. This description was based on his examination of electron micrographs. In modern parlance, this also might be called an interpenetrating polymer network although the PS phase was not cross-linked.

Eventually it was found that the addition of certain oils like soy bean oil to the starting mixture would give a somewhat superior product [15]. Still later it was discovered that if the styrene-rubber mixture was carried to about 30% conversion with shearing agitation, it would then be finished off in the cans. This is taught in the patent [8].

Events leading to the Amos et al. patent with shearing agitation [8] were mentioned briefly in the preceding section and extensively by Amos in his SPE Award lecture [6].

When McIntire, one of the co-inventors, first advised me in my then role as assistant director of the PRL that they planned to make a large scale run of 5.5% GRS in styrene using the Stober-Amos apparatus mentioned in the preceding section, I warned him about the cross-linking and the possibility of an exposive run-away reaction via the Smith-Norrish gel effect (a.k.a. the Trommsdorf effect). McIntire advised me that they intended to do it anyway.

There was an incipient loss of control on the first run and the experiment was stopped. After various modifications of the prepolymerizer in the direction of increased safety, and operating at 2/3 of kettle capacity, they resumed the experiment first with 1% rubber, increasing in subsequent runs at 1% increments. This set of experiments was completely successful and formed the basis, along with other experiments, for the Amos et al. patent [8].

Figure 3 illustrates an interim HIPS semiproduction unit using stirred prepolymerizer to 30-35% conversion with can finishing. This unit, hastily constructed from used equipment, produced 16 million pounds of HIPS, as indicated in Table 1, before the first full-scale, continuous agitation HIPS plant came on stream. The several steps included:

1. Cooling SB-R with Dry Ice prior to grinding
2. Rubber dissolver
3. Stirred prepolymerizer
4. Can finishing
5. Grinding HIPS
7. Coloring and pelletizing

Dow's major blunder in rubber-modified polymers was a tardy decision to manufacture ABS resins. A product manager who was convinced that the low price and easy moldability of Dow's HIPS product would drive ABS out of the market, discouraged research groups from working on ABS. The PS Product Laboratory under Amos was ordered

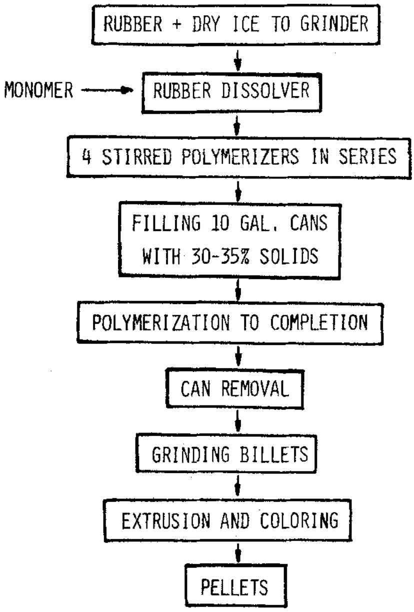

FIG. 3. Interim Production Plant, using continuous pre-polymerization with batch finishing for impact PS.

TABLE 1. Cumulative Dow United States Production of General Purpose and Impact Polystyrenes (millions of pounds)

Method	General purpose	Impact	Cumulative through
All Can Process	162	1	1950
Tower Process[a]	3	-	1950
Tube Tank Process	175	-	1950
	2000		1970
Agitated prepolymerization			
Can finishing	-	16	1950
Continuous finishing	-[b]	1173	1964
		2011	1968

[a] Discussed in Ref. 6.

[b] Dow global rate of production of GP polystyrene is 500,000,000 per year in stirred polymerizers (1971).

not to waste time making ABS by the Amos et al. patented process. Another group bootlegged R&D on a suspension process for ABS with support and encouragement from me. When Plastics Management finally realized that it could no longer ignore ABS, the only available process was the suspension route. A semiproduction plant was built.

Meanwhile, Amos and his group bootlegged runs in his continuous mass pilot plant with shearing agitation. The product was so superior to the suspension process that the latter was soon abandoned. The Amos product was then manufactured in commercial HIPS plants with an acrylonitrile content lower than that of regular ABS. It was affectionately called "the poor mans ABS." But by this time, ca. 1965, other companies, notably Marbon's patented process [16] for grafting styrene plus acrylonitrile monomer into polybutadiene, had gained an impressive market lead. Many other companies obtained related grafting patents for ABS.

This ABS history, which seems like my washing dirty linen in public, came out during the infringement proceedings. It was alleged that Dow's main purpose in wanting to sue Monsanto over the ABS claim in the patent [8] was to acquire Monsanto's commercial know-how on ABS.

Table 1, which I prepared from statistics assembled for the patent infringement trials in Los Angeles, shows the production of PS and HIPS by the several mass methods discussed in the preceding three sections. ABS statistics were not included.

Finally, two conclusions emerge from this story on rubber modified PS's:

1. Dow's original overwhelming success in the market place with Styron 475 brand HIPS was the result of a sustained effort to combine the properties of PS with a rubber. Again, there was competition between groups, namely, the can process in the Styrene Polymerization Laboratory (a post-World War II R&D group) and the shearing agitation work in the PRL.
2. Judge Gray's decision that the use of stirring during polymerization was obvious [9] was a capricious one based on lack of appreciation of the background facts. Amos has presented the statistics (Fig. 19 of Ref. 6) showing the surge in patents teaching agitation which were issued after the Amos et al. patent appeared in 1954. One need only compare the Haward and Elly nonagitated suspension polymerization patent [13], which was issued in 1954, with the Stein and Walter patent [14] of 1958.

STYRENE SECRETS

After the styrene monograph [1] appeared, Boundy and I received various comments, especially from European polymer chemists, expressing amazement that Dow would permit publication of such a book containing so much proprietary information. Still later, we were chided by a new generation of Dow management people for giving away Dow's crown jewels in such a convenient package. The truth is that there were few styrene secrets in 1952 and almost no PS secrets by 1960. This resulted from a bizarre series of events, both national and international, largely connected with World War II.

1. When World War II started, and the United States Government decided to engage in the synthetic rubber program with styrene and butadiene known as GRS, the Dow Chemical Co. rather generously agreed to make known, under suitable licensing arrangements with its competitors, any and all of its information on how to produce styrene monomer. Union Carbide had a side-chain oxidation process and did not wish to participate in the Dow process. Koppers participated in part. Monsanto did so in full, and so on. The story of who built styrene plants, where, and of what capacity is documented in Chapter 5 of Whitby's book [3].
2. The original SBR work was done in Germany and was known to Standard Oil of New Jersey through a technical exchange agreement prior to 1940. This German know-how must have helped determine the direction of the United States rubber effort.
3. Next, shortly before World War II ended, Allied investigating teams went to Germany to interview German personnel engaged in all aspects of the chemical and plastics industry. In particular, all of the secrets of I. G. Farbenindustrie about styrene and polystyrene became known, and were subsequently published in government reports and finally in the book German Plastics Practice [2]. There is no question in my mind that at the time the Germans (this is the group now known as BASF) were well ahead of Dow Chemical, and probably of anyone else in the world as far as making polystyrene, although their efforts were seriously hampered by the war. Dr. R. H. Boundy, first director of Dow's Plastics Department, was on one investigating team; Dr. Goggin, founder of Dow's Plastics Technical Service Department, was on the other.
4. When World War II ended, the American plastics industry knew to within a thousandth of a cent the cost of making styrene monomer by the Dow process. This was detailed in reports that went to the government. Of course, these did get circulated and were known. There is very little question that Dow had the best styrene monomer process, the most economical process, especially with the help of the Shell dehydrogenation catalysts. But the styrene monomer plant which Dow built and operated in Torrance, California, for Rubber Reserve was later sold to Shell by Rubber Reserve; and the styrene plant which Dow built in Sarnia, Ontario, for the Canadian government's synthetic rubber program was acquired by the Polymer Corp. Then, too, some of Dow's highly trained personnel who operated these monomer plants drifted away to other companies when the production

of SBR dropped at the end of World War II and the need for monomer decreased. One of Dow's best engineers joined Foster Grant to help them build and operate their own monomer plant.

5. The next major breech came when Dr. J. Lloyd McCurdy decided to quit Dow in 1958, along with an engineer who worked for him and a plastics salesman. Dr. McCurdy was a co-inventor on the Amos, McIntyre, and McCurdy impact polystyrene patent [8]. He was also at that time Assistant Production Manager for general purpose and impact polystyrene and related products in the Midland location. It seems probable that he had taken with him a tremendous amount of his own file material relating to production know-how because shortly after he left, he began constructing production plants to make general purpose polystyrene, and later, impact polystyrene. These plants were sold to companies which wanted to get into the polystyrene business. At a still later period, he began selling engineering drawings showing exactly how anyone skilled in the art could construct an impact polystyrene process using the Dow know-how and the shearing agitation which was covered in the Amos et al. patent. Dow purchased from his assistant, through a third party, plans for its own impact polystyrene process. The cost was $1,500.00 in late 1969. I have seen these drawings and I therefore know that they did exist. Dow's agent purchased them for the pending patent infringement trial, just to prove that they could be bought on the open market.
6. Dow and Distillers of London formed a joint company, known as Distrene, for the manufacture of PS in the United Kingdom based on Dow know-how. Both general purpose and later impact PS were produced at the plant in Barry, Wales. Around 1958 a Distrene employee, ignorant of or disregardful of the Dow-Distillers secrecy agreement, described to a technical writer major details about Dow's continuous process for HIPS. A flow sheet was published in a British technical journal. Angry letters went back and forth between Midland and London but the secret was out.
7. When Dow started its lawsuits against various competitors concerning alleged infringement of the Amos et al. patent [8, 9], the lawyers on the opposing sides initiated a process called discovery in which they interviewed key persons on their opponents side and demanded access to all sorts of information which normally was highly classified and well guarded by the individual companies. Since Dow later lost its lawsuits against Monsanto and the combined suit against Dart Industries and Standard Oil of Indiana, the net effect of this whole legal proceeding was that many, many intimate details of Dow's, of Dart Industries, of Monsanto's, of Standard Oil, and of other companies were widely known to everybody else. The trial in Los Angeles, in the spring of 1970, was open to the general public,

if anyone wished to attend [9]. The Monsanto trial in Cincinnatti in 1969 was a closed trial.

In brief, there were no secrets about styrene monomer by 1952, and none about HIPS after the Amos et al. patent was issued in 1954, thereby ending the desperate search by Dow's competitors to match Dow's 475 brand HIPS [9].

Ironically, Prof. Bruno Volmert, University of Karlsruhe, but at Badische in 1954, testified at the Amos patent trial in 1970 [9] that Badische engineers considered the Amos et al. patent as unworkable, and refused to duplicate it. BASF then licensed the Dow HIPS process.

WHY NO NEW STYRENES?

In May 1963 I reported back my findings on the question posed by Mr. Branch. I had talked directly in the intervening 9 months with most of the key figures in styrene development. Joseph C. Frank, a chemical engineer who was superintendent of the first styrene production unit, still had his files and records intact. I had a largely factual presentation with a minimum of speculation.

I had a most distinguished audience including H. D. Doan, H. H. Dow, R. H. Boundy, and C. B. Branch from the Board of Directors and all key figures in R&D. I started with the history of styrene at Dow as recounted in the section entitled "Why Dow Went into Styrene and Polystyrene." Dow went into styrene (and PS) for the wrong reasons and lucked out with the synthetic rubber program. We ended up after World War II with a large excess of monomer capacity which forced action. All of the subsequent big uses for styrene and PS had not been anticipated (SBR; styrene-polyesters; injection moldable PS; Styrofoam; foaming-in-place beads, film, and foil; latex paint) when Dow decided to produce styrene and PS.

I presented patent statistics showing that through 1946 DuPont had more issued patents in the styrene field than did Dow, and must have had a much bigger R&D effort (see Fig. 1.1 of Ref. 1). Yet DuPont did not go into PS.

One R&D manager told the group that he had learned authoritatively from a DuPont man that a market survey carried out by DuPont around 1940 showed that there was no market for styrene or PS big enough to attract DuPont. This well may have been apocryphal. However, it is plausible that had such a market study been made, it would have come out with exactly those results because the styrene demand was negligible prior to 1940. It is more likely that DuPont was so occupied with the development of nylon, Lucite, and chloroprene that polystyrene by comparison seemed quite unattractive.

I emphasized that the high efficiency of the monomer process (90+%) in 1963 was undreamed of in 1937. Robert Dreisbach became the object of ridicule when he wrote in an internal report, ca. 1935, that styrene monomer would eventually sell for 10¢ a lb. It was then selling for about 40¢.

I pointed out that the very expensive R&D bill for styrene came out of profits on the sale of caustic soda, phenol, etc. In those days, all income and disbursements went to and from one big, common till in the treasurer's office. Today there are many tills.

I cited the history of vinyl toluene, another Dow monomer, which succeeded for the wrong reasons. Around 1950, research and other groups persuaded Dr. R. H. Boundy, then manager of the Plastics Department, that vinyl toluene would be a desirable sales product, in part because of vinyl toluene's higher boiling point. Boundy's successful argument to get approval from fellow Board Members was that vinyl toluene would likely succeed but that the plant to produce it could always be used for styrene. The resulting commercial plant was operated on a turnaround basis to produce both vinyl toluene and styrene. In fact, within the first few years, during a styrene shortage, it produced sufficient styrene to pay for the entire plant. Vinyl toluene eventually required the facilities full time. It was not a "new styrene" in 1963 but still a valuable and successful product.

I noted that excess styrene capacity after World War II 1) spurred the development of new uses for styrene, and 2) led to a series of price reductions in the selling price of general purpose PS. PS actually crossed and then rode down the price-volume curve for all plastics, as shown in Fig. 4.

I summarized by listing five major factors which militated against "new styrenes."

1. Market analysts who rightly could and did prove the absence of a sizable market for any totally new product.
2. Cost analysts who calculated return on investment (R.O.I.) at an early stage when process improvements and capital cost reductions were not yet achieved. Top management had established precisely stated R.O.I. goals for different types of products, and expected them to be followed.
3. Key decisions made by middle management personnel who could not afford to be wrong. They relied completely on the market survey results and the R.O.I. calculations.

(I characterized the above 3 types as the "Abominable No Men.")

4. Middle management decisions, when confronted by research with a new type of potential product, saying: "Dow is not in that line of products and doesn't intend to get into it"; or, "Company A, who is a good monomer customer, would be offended and no longer buy monomer from us." I recall one instance when a middle management person made the latter decision whereas a top management man shortly thereafter declared that Company A couldn't care less if Dow produced such a product. But mostly such decisions don't get as far as top management.

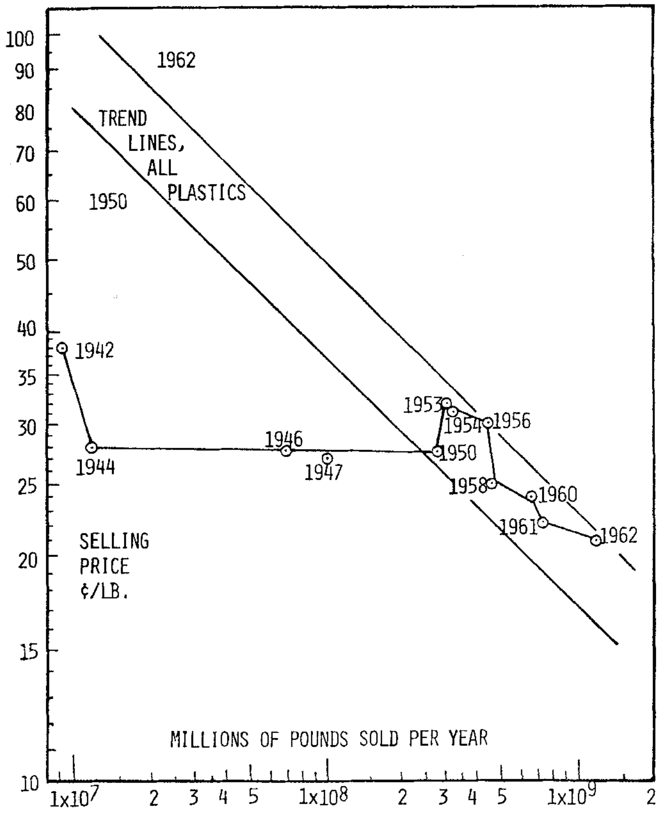

FIG. 4. Price-volume history for general purpose PS in relation to 1950 and 1962 price-volume trend line for all plastics. The price increase between 1950 and 1953 represented a period of short supply. The period from 1956 to 1962 marked the beginning of intense market competition. (Plot prepared by the writer, Spring 1963).

The above may sound like a defense of research and development groups at the expense of middle and top management. Therefore I would like to quote and illustrate the dictum of Thomas Wolfe: "You can't go home again." There were numerous irreversible changes at Dow between 1935 and 1963.

1. The burgeoning plastics industry exploded into a vacuum in the mid to late thirties. It was difficult to make mistakes. Today, many potential new products can succeed only by displacing existing products.
2. World War II created demands for styrene for SBR: Saran film for packaging machine guns, Styrofoam for floatation, Ethocel

for proximity fuzes, and the Styralloy product already named (which became the basis for SB latexes). Other companies had similar experiences. Nylon, neoprene, PMMA, PE, Thiokol, to name a few.

3. Chemical industry profits were considerably higher then and management welcomed new investment opportunities.
4. Key decisions were then made by top management types, many of whom were board members. Dow was a small company then, annual sales around $40,000,000.
5. Policy and procedures were less rigidified then. A research person could go directly to President Willard Dow with his potential new product. Dr. Dow might intervene for him.

The factors just discussed were and/or are not unique to Dow Chemical Co. but appear to be typical of the chemical industry here and abroad.

The moral of the styrene story seemed to be that a combination of simple chemistry, sound research, and aggressive management, with a certain amount of luck, should be a winning combination, and could lead to "new styrenes."

I ended by suggesting to the group that a product, X, a monomer then in research, had the elements to become another styrene. A week later, Mr. Branch, who was then Executive Vice President, gave R&D personnel permission to build a pilot plant. This was done and promising markets were soon being developed. Ten years later, against the wishes of many development persons who were trying to develop these new markets, the project was killed by a unilateral decision by one member of middle management.

At this point, the logarithmic growth rate of monomer sales in pounds per year for product X was almost identical to the styrene monomer growth rate prior to the start of the synthetic rubber program.

A major reason for terminating the project was intense pressure from a profit center manager who did not want to absorb the million dollars a year which the project was still losing. My recommendation at the time, based on the styrene monomer lesson, was to go from the quarter million pound per year pilot plant to a 25 million pound production plant. This advice was ignored.

"Why no new styrenes?" Perhaps I simply backed a loser in monomer X.

CONCLUDING REMARKS

This is a personalized account of styrene and PS at Dow and how it evolved from dubious status in 1937 to a leading product family which carried Dow's name around the world. I have recounted elsewhere the global and economic aspects of styrene and PS on pages 440-447 of Ref. 5, with statistics to 1968-1969.

I am certain that styrene and PS were destined to succeed. Certain accidents of history, such as World War II, accelerated the pace of development but not necessarily the end result. Even if Dow had failed, say by choosing side-chain chlorination, other companies such as Badische, Carbide, Koppers, and Monsanto were also in successful motion.

We elected not to emphasize the science and technology aspects, except as they fitted into our anecdotal approach. Science and technology received ample treatment in Refs. 1, 2, 5, and 6.

ACKNOWLEDGMENTS

Dr. Sylvia Stoesser, a Dow chemist during the styrene monomer days, and later an assistant to the Editors for the monograph [1], was kind enough to read an earlier version and give me her views. Dr. J. Lawrence Amos made extensive comments on the original version. Factual errors noted by him were corrected. We differed in our recollections of some events. I accept full responsibility for the present version.

I am indebted to former Dow engineer, Mr. Kenneth Bowen, for Fig. 1. Retired chemical engineer, Walter Roush, reminisced at length about the early styrene days in a research history session ca. 1978 at which Amos and I were also present.

There were scores of individuals involved in the ethylbenzene-styrene-polystyrene effort at Dow. We have named only a few. Grebe and Dreisbach won, respectively, the SPI gold and silver medals for their role in styrene-PS. Amos won the SPE international award and gold medal in 1973 for his work with PS and rubber-modified PS [6]. Boundy managed Dow's styrene participation in the Rubber Reserve Program and became the first head of Dow's Plastics Department. Most key workers are recognized in the patent literature.

I am personally indebted to Dr. L. A. Matheson, formerly an Assistant Director of the Physical Research Laboratory. He was my first supervisor at Dow. He introduced me to polymers via a study of light and heat stability of PS and Saran, coupled with a search for chemical stabilizers. I also express my gratitude to L. C. Chamberlain, also an Assistant Director in the Physical Research Laboratory. He became Dow's first Director of Plastics R&D from 1945-1952, and then assistant to Dow's first Research Director, Dr. Boundy, from 1952-1973. In both roles, he was exceedingly helpful to my career in polymers.

W. C. Goggin, founder of Dow's Plastics Technical Service group, third head of the Plastics Department, and later chief executive of Dow Corning, was a close associate, as both co-worker and supervisor, during my long association with styrene-PS and other Dow plastics.

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Note Added in Proof. A detailed analysis of the Amos et al. trial in California on impact PS has appeared by G. Freeguard and J. T. Wallace, Chem. Ind. (London), pp. 104-112 (February 1980).