PART I

Introduction to Styrenic Polymers

1

Historical Overview of Styrenic Polymers

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1 INTRODUCTION

Styrene has been known from the mid-nineteenth century as a clear organic liquid of characteristic pungent sweet odour. It was also known to have the ability to convert itself under certain conditions into a clear resinous solid that is almost odour-free, this resin then being referred to as 'metastyrol'.

Styrene readily polymerizes in air and it is therefore not surprising that there are a number of early obscure reports referring to its 'polymerization' predating 1900. However, because the concept of polymerization had not yet been proposed (until Staudinger in 1920), many of these early reports referred to the 'oxidation' or 'hardening' of the styrene monomer.

In 1839, Eduard Simon, an apothecary in Berlin, distilled storax resin obtained from the 'Tree of Turkey', (liquid ambar orientalis) with a sodium carbonate solution and obtained an oil which he analysed and named styrol (what we now call styrene) [1]. He recorded the following observation: 'that with old oil the residue which cannot be vaporised without decomposition is greater than with fresh oil, undoubtedly due to a steady conversion of the oil by air, light and heat to a rubberlike substance'. Simon believed he had oxidised the material and called the product styrol oxide. Later, when he realised that it contained no oxygen, the product became known as metastyrol. This puzzled the early chemists as there was no change in empirical formula despite the very pronounced alteration in chemical and physical properties. Unknowingly, this was the first recorded instance of polymerization.

Modern Styrenic Polymers: Polystyrene and Styrenic Copolymers. Edited by J. Scheirs and D. B. Priddy

A few years later, in 1845, Blyth and Hofmann [2] observed that ‘metastyrol’ was formed when styrene was exposed to sunlight, while it remained unchanged in the dark. This is the first report of photopolymerization.

It was established by Blyth and Hofmann in 1845 [2] that ‘styrol’ and its conversion product ‘metastyrol’ had the same elemental composition with an equal number of carbon and hydrogen atoms. After nitration, the N:C ratio was 1:8 for styrol and 1:7 for metastyrol, leading to the conclusion that C_8H_8 had been converted to C_7H_7. However, the conclusion that styrol had polymerized was not reached until 75 years later.

The first samples of polystyrene were characterized by the German organic chemist Staudinger [3]. It was observed that the polystyrene could be fractionated into samples with different solution viscosities and this observation was incompatible with the notion that the substance was a colloidal aggregate. Staudinger challenged the notion that polymeric substances are held together by ‘association forces’. It was Staudinger who first realised that the solid that Simon had isolated from natural resin was in fact composed of long chains of styrene molecules. Staudinger postulated that polystyrene was a high molecular weight polymer. His critics argued that it could not be a high molecular weight polymer because of its solubility in common solvents. He introduced the term ‘macromolecules’ to describe these long-chain compounds. Fierce controversy with his colleagues caused Staudinger to move from the Swiss Federal Institute of Technology in Zurich (ETH) to the University of Freiburg.

In 1929, Staudinger and co-workers also synthesized hexahydropolystyrene by the nickel-catalysed hydrogenation of polystyrene [4,5]. The hydrogenated polystyrene, also known as poly(cyclohexylethylene), had improved oxidative and radiation stability relative to conventional polystyrene.

It was also Staudinger in 1932 who first proposed that the inability of polystyrene to crystallize was due to its lack of stereoregularity which rendered it amorphous. It is its amorphous nature that is responsible for its solubility – though others claimed that polymer solubility was incompatible with very high molecular weight [3].

2 GENERAL-PURPOSE POLYSTYRENE (GPPS)

Styrene readily polymerizes to polystyrene (PS) either thermally or with free-radical initiators. A limiting factor in the commercial exploitation of polystyrene was the high reactivity and considerable heat of polymerization of styrene. The polymerization rate of styrene is exceedingly fast and considerable heat is generated. This was an intimidating obstacle to commercial production of PS since many in the industry were concerned that the large-scale polymerization of styrene may result in a dangerous uncontrolled reaction. The process involved heating styrene monomer in bulk containers. A major limitation of this approach was the need for heat removal from the highly viscous melt. High temperatures can be reached in large mass reactors (>300°C) and thermal degradation of the resultant PS can occur. This problem was later solved by installing heat exchanger tubes in the reaction medium. The first commercial production of PS was in 1931 by BASF.

To prevent premature polymerization of styrene monomer, special inhibitors had to be added so that it could be stored until needed. Polymerization inhibitors were also required to prevent polymer formation during distillation of styrene monomer from ethylbenzene.

Before the large-scale production of PS could occur, a consistent supply of styrene monomer was required. In 1930, Dow started to produce styrene monomer by cracking its ethylbenezene precursor. In 1938, Dow began manufacturing commercial quantities of PS.

The propensity for styrene monomer to polymerize allowed extremely simple and crude polymerization techniques. The first technique used by Dow was known as the 'can process' since it basically involved filling 10 gallon metal cans (Figure 1.1) with styrene monomer followed by heating the cans in a heating bath at progressively higher temperatures for a number of days. After this time the polystyrene (polymerized to approximately 99% conversion) was removed from the can and crushed to a free-flowing powder.

The development of styrene and PS manufacturing technology was spurred on by the advent of World War II. During this time the supply of natural

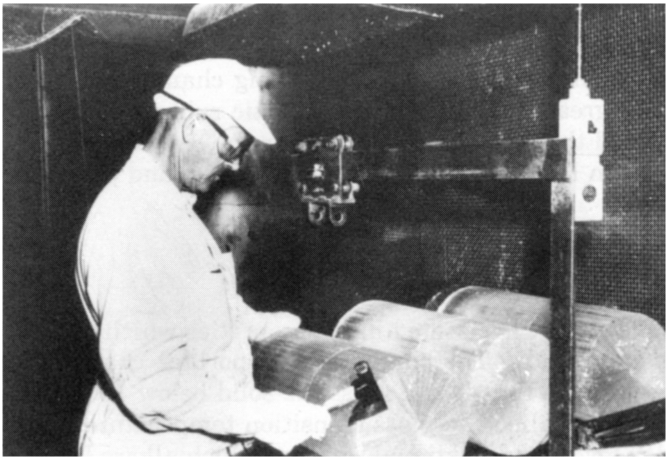

Figure 1.1 Early photograph of the 'can' process for the commercial production of polystyrene. This simple process involved filling 10 gallon metal cans with styrene monomer, thermally polymerizing it in heated baths and then grinding the polystyrene cylinders that formed. (courtesy of Dow Chemical Company)

rubber from the Far East was terminated. The acute rubber shortage accelerated the development of styrene-based synthetic rubber. With the outbreak of the war, the United States embarked on a scientific programme that rivalled the Manhattan Project in its scope and significance. Nearly a billion dollars was spent on research and development of synthetic rubber needed to keep the Allied war effort in motion. The key players such as Dow, Monsanto and Koppers Chemical cooperatively produced record quantities of styrene monomer for the preparation of styrene–butadiene rubber. A staggering 180 000 t of styrene monomer were produced per year towards the end of the War with most being used for the production of the synthetic rubber Buna-S (also known as GRS rubber, where GR stands for government rubber and S for styrene). There was also cooperation between the main rubber-producing companies, Goodyear, B. F. Goodrich, Standard Oil, Firestone and US Rubber.

In early 1942, the American Synthetic Rubber Research Program commenced. Along with the major rubber-producing companies, 11 university research groups, including Carl 'Speed' Marvel at the University of Illinois, Izaak 'Piet' Kolthoff at the University of Minnesota and W. D. Harkins and Morris Kharasch of the University of Chicago, joined the effort to make synthetic rubber work. Their objective was to set up four plants that would produce 30 000 t each of synthetic rubber per year. By the end of 1942, four plants were established but their output was under the target. By the end of 1943, 15 plants were in operation, and supply had begun to meet demand.

The research focus during the War was on refinement, enhancement and incremental improvement of existing processes. For example, if the rubber is allowed to polymerize until no monomer is left then long, branched molecules are produced, which gel and make the rubber difficult to process. To solve this problem, the reaction is only allowed to proceed to 72 % conversion and a thiol modifier, a chain-transfer agent, was used to control molecular weight. It was also observed that the polymerizations have an 'induction period' which varied from batch to batch. During the induction period nothing seems to be happening, then, all of the sudden, the reaction takes off. The researchers at the University of Illinois found that this is due to different fatty acids present in the different soaps needed for the emulsion process. These soaps also cause the solution to foam during the recovery of the remaining monomer. This problem leads to the development of silicone defoamers.

The properties of the Buna-S type rubber are highly dependent on the amount of styrene in the rubber. To determine properties, it is important to know how much styrene had been incorporated. William O. Baker of Bell Telephone Laboratories solved this problem by developing a procedure for determining the amount of styrene using the refractive index of a solution of the rubber.

It was not until after World War II, when styrene monomer capacity could be diverted from its essential wartime use for styrene–butadiene synthetic rubber, that polystyrene became an important commercial plastic. When the War finished the supply route for natural rubber was re-established and there was an oversupply of styrene monomer. The extensive infrastructure for styrene production and the enormous body of process and technical knowledge laid the foundation for the post-War development of polystyrene and styrenic copolymers.

Prior to 1941, Germany had a major technical and industrial lead over the USA, having already established an industrial styrene monomer production process, a styrene–butadiene elastomer process and a mass styrene polymerization process [6]. Figure 1.2 shows the polymerization vessels at I. G. Farben in 1940. Figure 1.3 shows a bank of polymerization kettles. The Germans began the first technical production of polystyrene in 1930 while the first production of polystyrene in the USA was some 8 years later by Dow in 1938.

Interestingly, at the inception Dow did not have a strategic objective to enter into the polystyrene business. Rather, Dow believed that ethylcellulose and poly (vinylene chloride) (Saran) were the commodity polymers of the future. Dow was producing ethylbenzene as a solvent and electrical fluid. However, when the markets for ethylbenzene did not develop it decided to crack the ethylbenzene and produce styrene. After it had stockpiled large quantities of unstable styrene, Dow initiated a 'crash' programme to develop polystyrene. Thus even though Dow did not initially intend to produce polystyrene commercially when its petrochemical programme was initiated it became a logical business decision to do so.

Early on there were numerous technical barriers that made polystyrene difficult to produce and to process. For example, it was made by an extremely slow production process and its high average molecular weight and broad molecular weight distribution made it difficult to injection mould [6]. Dow researchers ultimately developed ways to lower the average molecular weight and added certain lubricants to improve processability, thus making general-purpose polystyrene which fast acquired the reputation of being the easiest thermoplastic to mould.

Other technical barriers were the need to control the exotherm of polymerization and to produce colour-free polystyrene. While the manufacture of styrene seems simple and straightforward, in the early days at Dow there were three major impurities in the styrene monomer apart from residual ethylbenzene. These were phenylacetylene (which acted as an inhibitor for styrene polymerization), divinylbenzene (which caused plugging and fouling of the distillation column for separating styrene from its precursor, ethyl benzene) and sulphur (which caused discoloration of the polystyrene).

Finally, in 1938, the 'crash' programme resulted in the first saleable polystyrene batches. This was produced in metal cans lined with tin to yield high-purity polystyrene. These cans were filled with styrene and immersed in heated waterbaths where the styrene would thermally polymerize. The process was very slow and labour intensive. Further, the exotherm of polymerization was greatest in the centre of each can, which led to a core of lower than average molecular weight. After polymerization was complete, the polystyrene billet was ground up and mixed to distribute the different molecular weight regions [6].

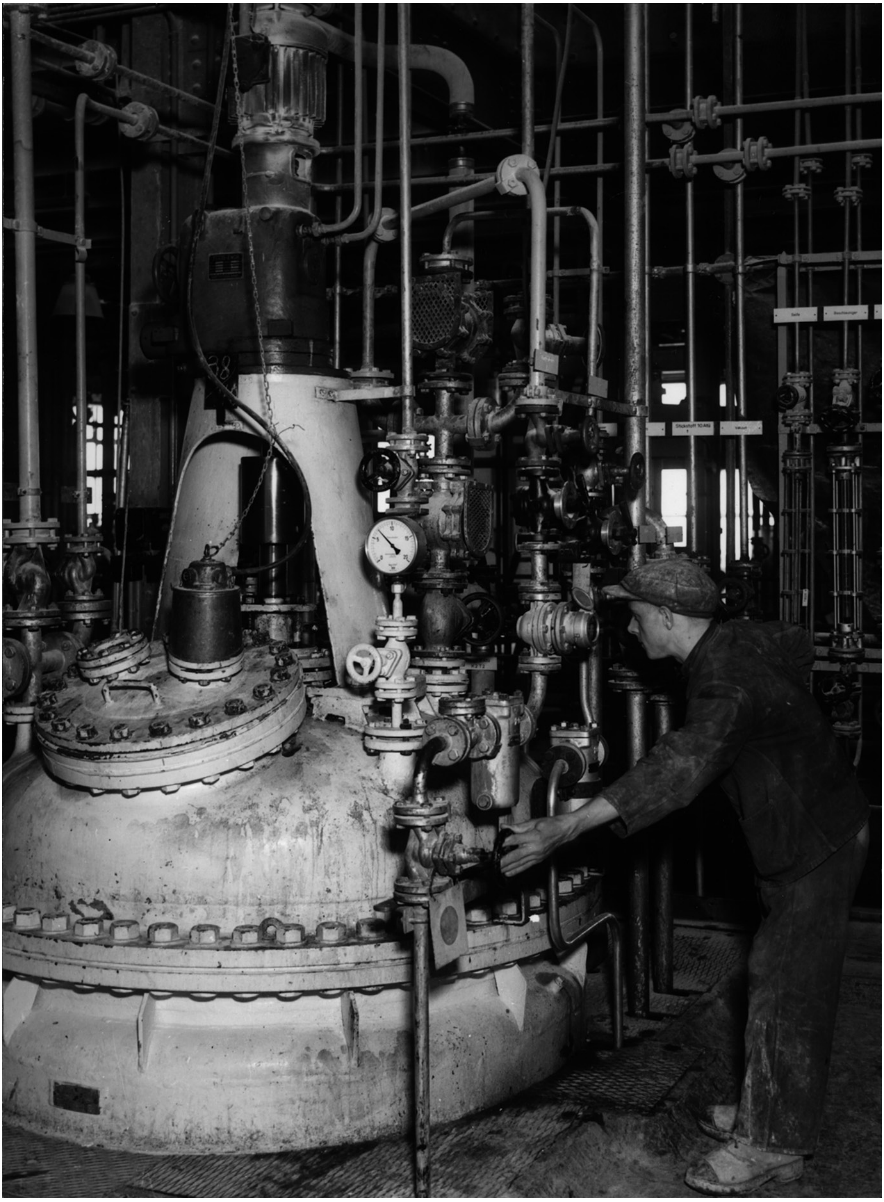

Figure 1.2 Photograph taken in 1940 of a styrene polymerization vessel inside the I. G. Farben plant in Ludwigshafen, Germany (courtesy of BASF, Ludwigshafen)

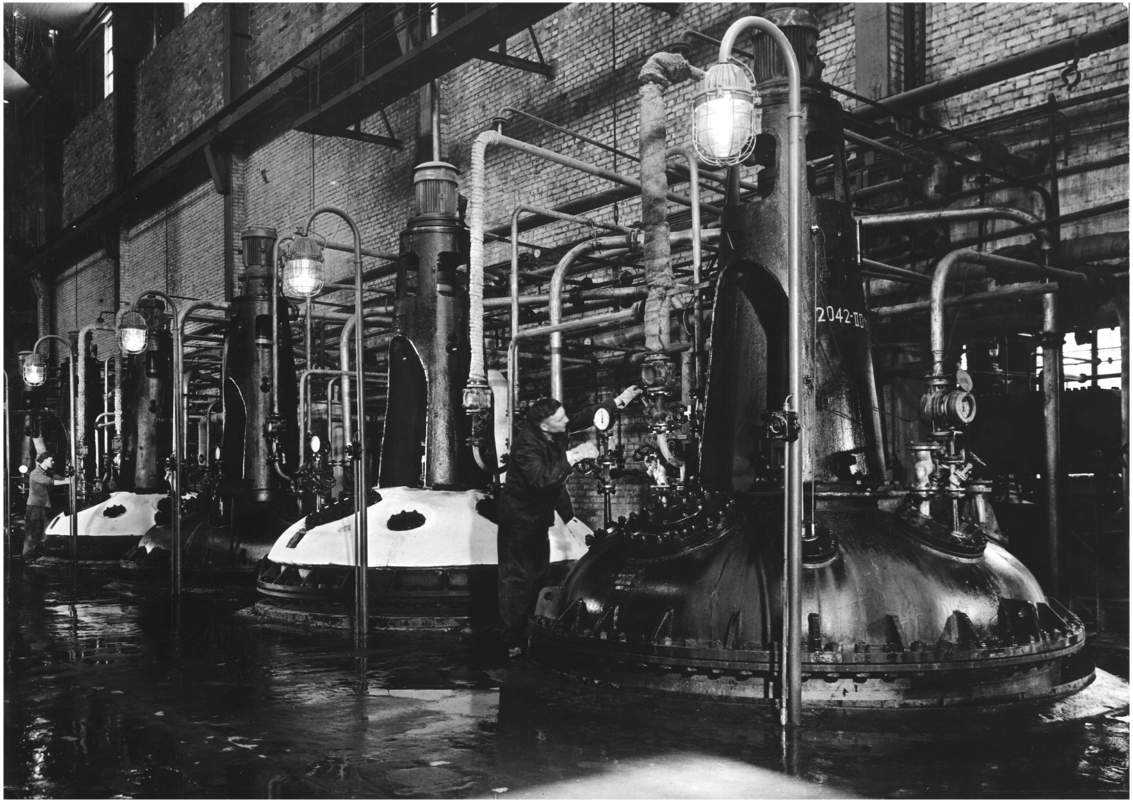

Figure 1.3 Reaction kettles in the BASF polystyrene production plant (courtesy of BASF, Ludwigshafen)

Although the can process was very slow, it lent itself to easy expansion of production output by simply adding more cans and heating baths. It was also discovered that by adding some peroxide catalyst to the styrene monomer the production throughput could be increased significantly. In fact, this innovation led to a doubling of Dow's plant capacity since faster polymerization rates could be achieved while still controlling the exotherm [6].

While the USA was progressing with the can process, Germany had already developed a continuous process for the mass polymerization of styrene.

After World War II, researchers from Dow visited the German polystyrene plants and were surprised to learn of their scale and sophistication. One of the key people on the investigating team that went to Germany was Dr Goggin, founder of Dow's Plastics Technical Service Department. The American teams that visited I. G. Farben after the War recorded their findings in a historic report [7]. This report clearly showed the advantages of a continuous production process for polystyrene. Further, the first industrial production of SAN was in 1936 also by I. G. Farben in Ludwigshafen.

Central to Germany's development of polystyrene technology was Herman F. Mark (Figure 1.4). Mark worked at I. G. Farben Industrie for 6 years from 1927 to 1932, first as a research chemist (1927–28), then as Group Leader (1928–30) and finally as Assistant Research Director (1930–32). Because of the changing political climate, Mark moved to the University of Vienna, where he became Professor of Chemistry and Director of the First Chemical Institute (1932–38). While at I. G. Farben Industrie, Mark played a major role in the development of styrene monomer and PS. Mark patented a process in 1929 for the production of styrene from ethylbenzene via catalytic dehydrogenation [8].

The German Chemical giant I. G. Farben developed the continuous tower process for PS in the 1930s. The German PS polymerization plant shown in Figure 1.5 overcame the problem of the polymerization exotherm and thermal runaway by using a tank reactor with heat-transfer tubes criss-crossed through it. The reaction temperature was gradually increased and controlled, and polystyrene was removed via an auger. This design was later improved by prepolymerizing in stirred kettles prior to the tower process (Figure 1.6).

After the War, Dow began to focus on constructing its own continuous mass polymerization plants for PS. Known as the tube tank process, it consisted of two nonagitated horizontal tube tanks containing arrays of tubes through which a heat-transfer fluid (Dowtherm™) flowed in order to control the exotherm of polymerization (Figure 1.7). Each tank had a capacity of 18 000 kg of styrene monomer and represented a batch process, but when alternately sequenced the process was continuous. When the styrene in tank 1 had reached high conversions, a special polymer pump pumped the molten polystyrene at 220–240 °C to the bottom receiving tank. Polymerization was then started in tank 2. The bottom receiving tank was under vacuum to remove volatiles such as unreacted monomer and also dimers, trimers and other oligomers. There was always polystyrene in the receiving tank so that the extruder and pelletization process could operate on a continuous basis [6]. The exotherm in the Dow process supplied most of the heat needed to produce a molten PS ready for pelletization. These units were extremely successful because of the very large heat transfer surface and the efficiency of the Dowtherm™ heat transfer fluid. Twelve such tube tank plants were installed and operated at the Dow site in Midland, Michigan and they produced prodigious quantities of polystyrene over many years [6].

Figure 1.4 Photograph of Herman F. Mark taken in 1936. Mark worked at I. G. Farben Industries in Germany for 6 years, from 1927 to 1932, and played a major role in the industrial development of styrene monomer and polystyrene (courtesy of BASF, Ludwigshafen)

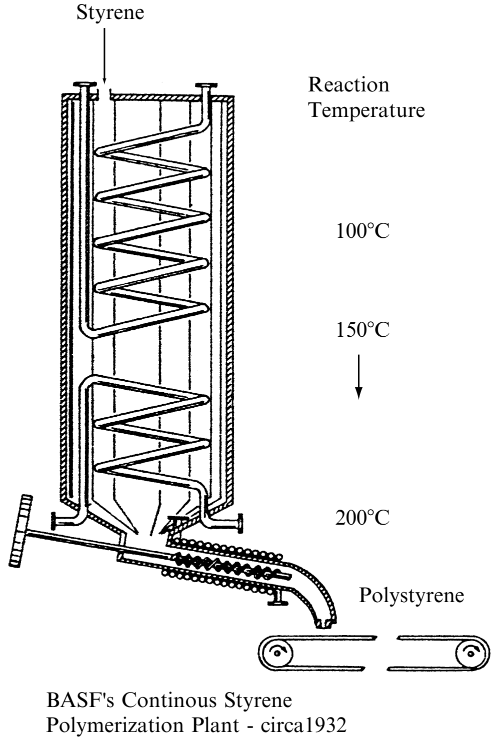

Figure 1.5 Schematic of BASF's early tower process for the continuous polymerization of styrene. This configuration was designed by C. Wulff and E. Dorrer in the early 1930s. Polymerization was thermally initiated and the exotherm controlled by heat transfer tubes (courtesy of BASF, Ludwigshafen)

In the following years, other methods of polymerizing styrene were developed such as suspension polymerization by Koppers Chemical, which was first introduced in the 1940s and which showed rapid development in the 1950s. The suspension polymerization process is still in use for the production of PS [9], although it has been largely replaced by more economical techniques such as continuous mass polymerization.

It is interesting that the polystyrene produced by suspension polymerization, particularly the Koppers material, had a heat distortion temperature superior to that of the Dow polystyrene [6]. This was attributed to the measurable levels of residual dimers and trimers in the Dow product due to its thermal initiation and which were absent in the peroxide-initiated suspension process.

The suspension polymerization process has a number of distinct advantages over competitive processes. It allows excellent control over the polymerization temperature and a lower viscosity reaction medium. Furthermore,

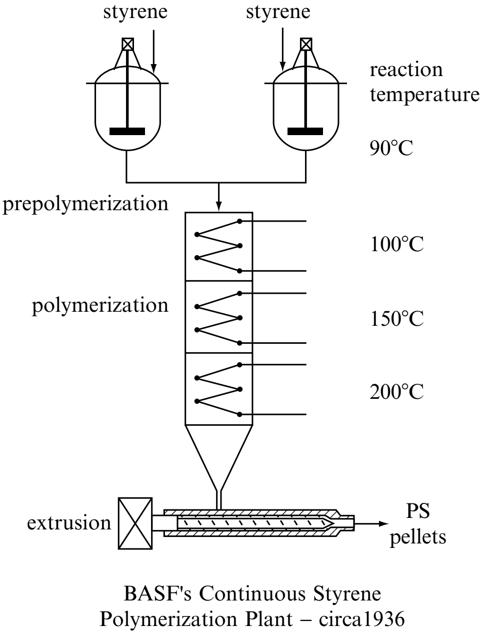

Figure 1.6 Schematic of BASF's improved tower process for the continuous polymerization of styrene. In this design (dated 1936) the styrene was first polymerized up to 30–35 % conversion in a stirred kettle and then transferred to the tower reactor for polymerization up to 97 % completion (courtesy of BASF, Ludwigshafen)

expandable polystyrene and high-impact polystyrene are also produced by this technique.

3 FOAMED POLYSTYRENE

The concept of cellular polystyrene was first reported in 1935 by the Swedish inventors Munters and Tandberg [10], who filed a patent entitled 'Foamed Polystyrene'. Ray McIntire, a young researcher at Dow Chemical, is credited with inventing Styrofoam. McIntire said his invention of foamed polystyrene was accidental. His invention came as he was trying to find a flexible electrical insulator around the time of World War II. He worked at developing a rubber-like substance that could serve as an electrical insulator. Although polystyrene was a good insulator it was far too brittle. McIntire tried to make a new rubber-like polymer by combining styrene with isobutene, a volatile liquid, under pressure. He tried combining styrene with isobutene, but he accidentally

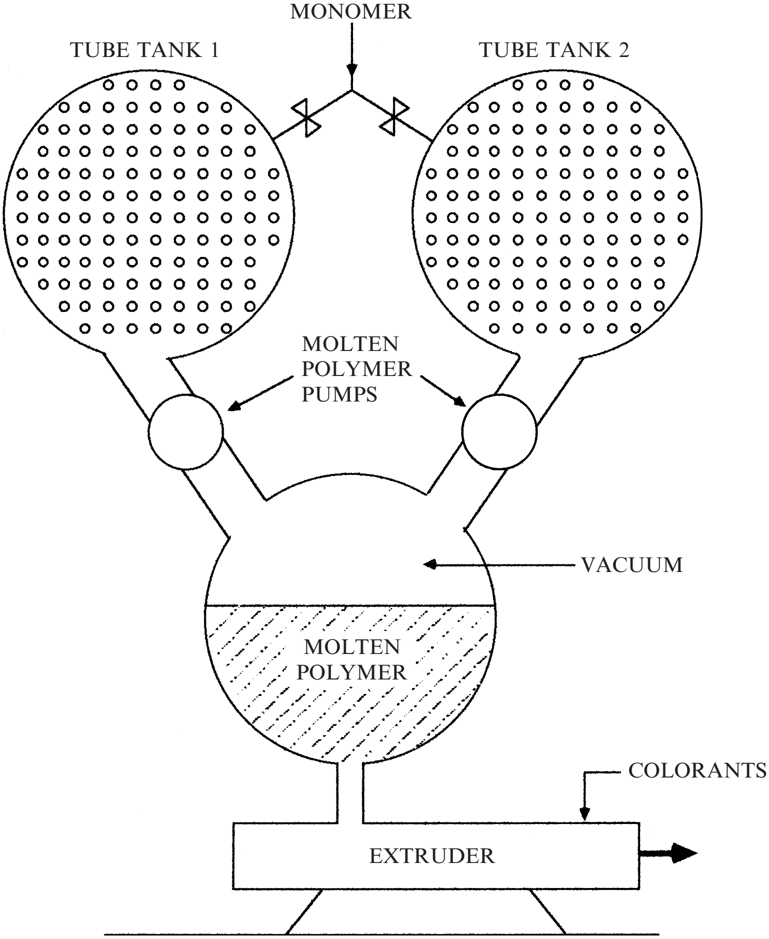

Figure 1.7 Schematic of Dow's 'tube tank' process which represents the first commercial continuous polymerization process for polystyrene in the USA. The figure shows a cross-section through the centre of three longitudinal unagitated tanks. Styrene was thermally polymerized in tube tanks 1 and 2 and then devolatilized in the bottom receiving tank, which was always about half full and under vacuum [adapted from Boyer, R. F., *J. Macromol. Sci. Chem.*, **A15**, 1411 (1981)]

added too much of the latter – and was surprised to see that the isobutene formed tiny bubbles. The result was a foamed polystyrene with a cellular microstructure, 30 times lighter than regular polystyrene. McIntire stayed with Dow Chemical until his retirement in 1981. The word Styrofoam is still trademarked by Dow, and it technically only applies to a kind of insulation used for building materials. Today, however, many companies produce products made of PS foam, and the brand name Styrofoam is commonly used to describe them all.

It was only in the early 1940s that commercial production of cellular polystyrene began. In 1942, Dow began research on an extrusion process for the production of PS foam using a low-boiling chlorocarbon (methylene chloride) as the blowing agent. The product was extruded into large foam logs, which were then cut into boards and planks. This material was given the trademark Styrofoam™ in 1943 [11]. This foam was rapidly adopted by the US Coast Guard and US Navy as a buoyancy medium and insulation material.

BASF developed its own process for foaming polystyrene in the early 1940s (Figure 1.8). This process was later refined by the improved suspension polymerization process which produces foamable polystyrene beads. A blowing agent (typically pentane) can be introduced during the polymerization of styrene or introduced later in a separate impregnation step under pressure and heat [11]. All major PS foam bead producers took out a license from BASF for this patented technology [12–14]. Figure 1.9 shows a promotional illustration from 1952.

The single most important factor responsible for the rapid commercial growth of expandable PS is its ability to be steam-moulded into lightweight, closed-cell, low-cost foams suitable for beverage cups, packages, ice buckets, picnic chests, insulation board, etc [11]. (Figure 1.10).

Figure 1.8 Early photograph (ca 1948) showing some of the earliest polystyrene foam (Styropor™). Foamed polystyrene has unrivalled low-density and thermal insulating properties (courtesy of BASF, Ludwigshafen)

„Das leichteste Schiff der Welt ist das STYROPOR-Schiffchen“.

Das leichteste Schiff der Welt…

ist das STYROPOR-Schiffchen, dessen praktische Darstellung auf dem BASF-Stand anläßlich der Kunststoffmesse 1952 in Düsseldorf in erster Linie den Ingenieur und Techniker interessierte. Es ist 15 cm lang und wiegt ganze 5 Gramm, womit bereits eine der wesentlichen Eigenschaften von STYROPOR gekennzeichnet ist: sein geringes spezifisches Gewicht (von 0,025 an). Dazu kommen das sehr gute thermische und elektrische Isoliervermögen, die Beständigkeit gegen Wasser, Säuren und Laugen, sowie die hervorragende Strukturfestigkeit. Und was besonders wichtig ist: STYROPOR kann direkt in einfachen Arbeitsgängen zu porösen Formkörpern beliebiger Gestalt, wie z. B. Isolierbehältern, Platten, Schwimmern, Kugeln usw. verarbeitet werden.

Dieser neue BASF-Kunststoff wird als STYROPOR Blockmaterial, STYROPOR körnig und STYROPOR in Perlform in den Handel gebracht.

Badische Anilin- & Soda-Fabrik

LUDWIGSHAFEN A. RHEIN

Figure 1.9 A promotional photograph highlighting showcasing polystyrene foam for the BASF stand at the 1952 Kunststoffemesse show in Dusseldorf, Germany (courtesy of BASF, Ludwigshafen)

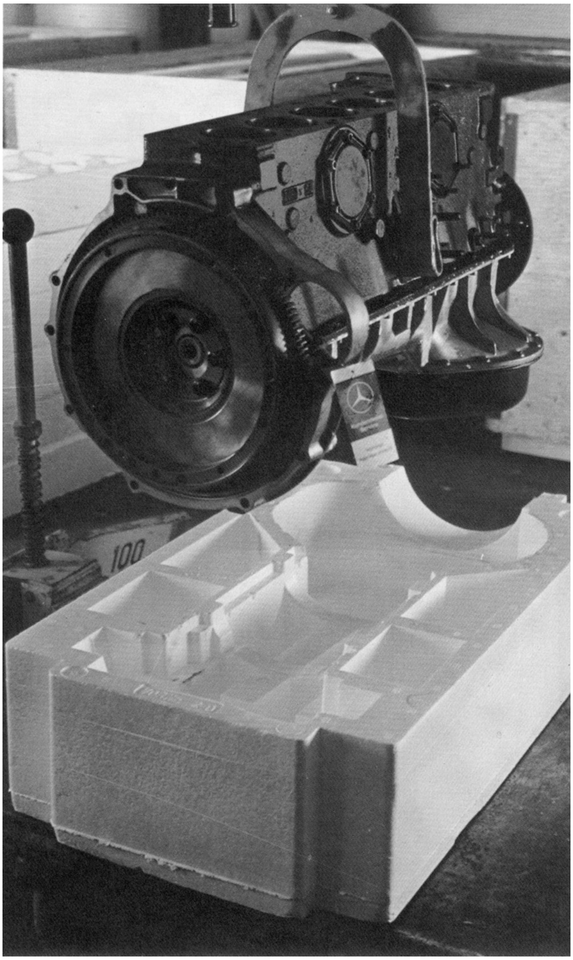

Figure 1.10 Polystyrene foam rapidly became the packaging material of choice for everything from medical instruments to engines (courtesy of BASF, Ludwigshafen)

In the late 1960s, demand for foamed PS increased dramatically owing to its increasing use in meat trays, fruit boxes and egg cartons. The expansion was stimulated by the design of extruders with provision for introducing the blowing agent into the barrel, thereby obviating the need to buy the more expensive expandable PS pellets as a raw material [11]. In 1969, the market for PS foam grew enormously especially for self-extinguishing grades. The main applications were for insulation board in cold-storage refrigeration, housing insulation and cut ceiling tiles.

4 RUBBER-MODIFIED POLYSTYRENE

Rubber-modified polystyrene was the next logical evolution after general-purpose polystyrene. Very early on it was apparent that the Achilles heel of polystyrene was its inherent brittleness. Rubber-modified polystyrene is a two-phase system consisting of a dispersed rubber phase and a continuous polystyrene phase (or matrix). Impact-modified polystyrene was invented as early as 1927 by Ostromislensky [15] by addition of natural rubber either polymerized with styrene or blended in polystyrene.

In the early 1940s, researchers at Dow produced interpolymer blends of styrene and butadiene by an emulsion process. The polymer, called Styralloy™ 22, was used as insulation for radar cables until it was displaced by low-density polyethylene produced by ICI. Later, Dow experimented with soluble GRS copolymerized with styrene to make high-impact polystyrene.

In 1954, Haward of Shell obtained a patent for rubber-modified PS made by suspension polymerization [16]. This early product, however, contained 'fish-eyes' – small crosslinked gel particles – since each suspension particle was crosslinked by styrene–butadiene rubber. Researchers at Monsanto overcame this problem [17] by including a prepolymerization step with shearing agitation.

In 1954, Dow finally perfected a 'can' process to make high-impact polystyrene (HIPS). The secret was that the traditional 'can' process could not simply be used since the product would be full of gel particles of rubber ('fish-eyes'); instead, the styrene-rubber mixture was first carried out to 30 % conversion with shearing agitation. Then the mixture was transferred to 10 gallon cans where the reaction was completed. This process was documented in the now famous Amos patent [18].

In the late 1960s, Dow initiated patent infringement suits against its major competitors (Monsanto, Standard Oil, Amoco Chemical, Dart Industries) over the patent for high-impact polystyrene by Amos [6].

5 ABS

While Dow had experimented extensively with ABS-type polymers and even produced ABS in their commercial HIPS plant, they lost the lead in the development of commercial ABS resins. Dow sued Monsanto in 1969 for infringement of the ABS claim in the patent by Amos. The judge ruled in Monsanto's favour on the basis that Monsanto's product was outside the claimed composition. In another case, where Dow sued Dart Industries, the judge ruled that the Amos patent was invalid for reasons of obviousness [6].

As early as 1948 it was known that poly(styrene-co-acrylonitrile) or SAN could be blended with Buna-N (a copolymer of butadiene and acrylonitrile) or Buna-S (a copolymer of butadiene and styrene) to produce useful thermoplastics [19]. The commercial introduction of these polymers, however, was restricted by their poor low-temperature impact properties. Researchers at Marbon (a division of Marsene Corp., later renamed Borg Warner) knew that polybutadiene remained rubbery at temperatures lower than the earlier cited copolymers; however, polybutadiene and SAN were incompatible [20]. The trick was first to produce polybutadiene by emulsion polymerization and then to use this latex as the medium for the emulsion polymerization of styrene and acrylonitrile (Figure 1.11). In 1959, Borg Warner patented this ABS produced by grafting styrene plus acrylonitrile into polybutadiene. The Cyclolac™ brand of grafted ABS produced by Borg Warner rapidly became the market leader in ABS. In 1988, GE Plastics acquired Borg Warner Chemicals and its ABS technology. The chief researcher responsible for this discovery was Calvert [21,22]. The material he produced from the emulsion copolymerization had uniformly dispersed domains of rubber in a continuous phase of SAN. The rubber dispersion was stabilized by the SAN that was grafted to the polybutadiene emulsion particles [20].

It is interesting to note that Borg Warner conducted more than 10 000 laboratory trials before the optimum ABS composition was commercially produced in

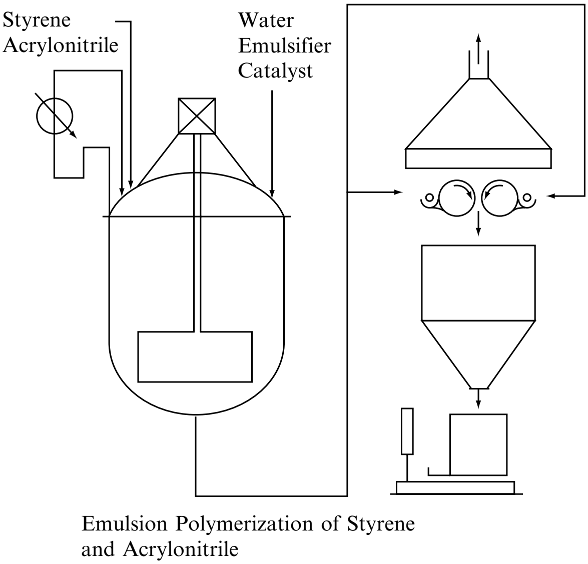

Figure 1.11 Schematic of BASF's stirred tank emulsion polymerization reactors (dated 1940) for the production of styrenic copolymers (courtesy of BASF, Ludwigshafen)

1954. In 1957, Cyclolac™ T was commercialized. The T designated toughness and later it was thought to stand for telephone as this grade of ABS became the industry standard for making telephone housings. The ability of ABS sheets to be thermoformed opened the door to a range of markets such as luggage (Samsonite™), machine housings, refrigerator liners and boat hulls.

When ABS was first commercialized, there was much confusion in the plastics industry referring to it as a terpolymer. The system is not a terpolymer as butadiene is added to the reactor as a polymer along with styrene and acrylonitrile monomers. Polymerization causes SAN to be grafted to the rubber to produce a dispersible domain. It is indeed a requirement that the polybutadiene regions exist as a separate phase of a specified size. Since the domain size is critical to its impact properties, it is important that it is stable through compounding and processing steps [20].

High-heat versions of ABS were subsequently introduced by using α-methylstyrene as a partial replacement of styrene, in both the graft and the matrix. This resulted in an ABS polymer with a higher heat deflection temperature. The heat deflection temperature could be tailored by varying the level of α-methylstyrene. These new high-heat versions of Cyclolac™ ABS were introduced to the automotive market in 1958 and won widespread acceptance [20]. The high heat resistance grades, however, had higher melt viscosities, making them more difficult to process owing to the stiffer molecule that results from the addition of methyl groups to the backbone.

The next evolution in ABS technology was the need to produce a transparent ABS. Existing ABS was opaque owing to the scattering of light by the rubber domains. While producing smaller domains would make the system clear, it led to a loss of impact strength. The answer was to modify the refractive index of the components so that the various phases were less optically different. A fourth 'monomer', methyl methacrylate, was used to minimize the refractive index variation in the ABS and a clear impact-resistant thermoplastic named Cyclolac™ CIT was achieved [20].

6 ASA

Acrylonitrile–styrene–acrylate (ASA) polymers share obvious similarities with ABS but ASA was only developed in the 1960s. ASA polymers are essentially SAN polymers impact modified with an acrylate rubber. The earliest attempt to make ASA was by Herbig and Salyer of Monsanto [23] using butyl acrylate as the rubber phase. This work was then refined by Otto [24] and Siebel [25], both of BASF, who copolymerized butyl acrylate with butadiene to prepare the rubber phase.

7 EARLY STYRENE COPOLYMERS

The first styrene copolymer was reported in 1930 by Wagner-Juaregg and was a copolymer of styrene and maleic anhydride [26]. This copolymer (SMA), which was called a heteropolymer by its inventor, has excellent resistance to continuous exposure in boiling water.

Koppers produced SMA moulding powders under the tradename Dylark™. Arco has since acquired this business and continues to produce these SMA resins today under the Dylark tradename. Another styrene copolymer with better heat resistance than regular polystyrene is the copolymer of styrene and fumaronitrile which was reported in 1948 [27]. Both of these styrene copolymers are based on nonpolymerizable monomers – that is, fumaronitrile, like its corresponding anhydride (maleic anhydride), does not form homopolymers but readily copolymerizes with styrene at levels of up to 40 %. Monsanto attempted to commercialize the styrene–fumaronitrile copolymer under the tradename Cerex™, but residual fumaronitrile was a powerful vesicant (an irritant which causes blisters) and the project was shelved [28].

8 STYRENIC BLOCK COPOLYMERS

The advent of alkyllithium-initiated anionic polymerization based on the fundamental work by Szwarc in 1956 [29,30] opened the door to the commercial development of styrene–butadiene copolymers. Styrenic block copolymers were first produced in the late 1950s after the discovery by Szwarc of living anionic polymerization [31]. In the late 1950s, Shell, Phillips and Firestone manufactured styrene–butadiene copolymers produced by anionic polymerization also referred to as ‘living polymerization’. The styrene–butadiene copolymer named K-resin with a high styrene content was invented in the early 1960s at Phillips Petroleum by Alonzo Kitchen and is purportedly named after his surname initial. The alkyllithium initiators such as n-butyllithium allowed the production of copolymers with tightly defined and controlled polymer microstructures with highly regular block structures. To this day, living anionic polymerization continues to be the main commercial route for the production of styrenic block copolymers [31]. Most of these polymers are made using butyllithium catalysts. Today the following styrene–butadiene copolymers are well known under the tradenames Kraton™, K-Resin™, Styroflex™ and Styrolux™.

9 SYNDIOTACTIC POLYSTYRENE

Syndiotactic polystyrene (SPS) with its melting point of 270 °C has been claimed as the first styrenic engineering plastic. Syndiotactic polystyrene was first synthesized in 1985 by Ishihara of Idemitsu Kosan by using titanium complexes/methylaluminoxane catalyst [32–34]. SPS displays entirely different properties to conventional polystyrene such as high chemical resistance and excellent environmental stress crack resistance. SPS does share one major property with conventional PS, however, namely inherent brittleness. For this reason, SPS is generally modified with rubber tougheners or glass fibre reinforcement. When SPS is reinforced with glass fibres it has comparable toughness to glass-filled PBT and glass-filled nylon 66. Blending of SPS with other polymers is another strategy for improving performance properties (see Chapter 20). Dow and the Idemitsu Petrochemical entered into a cooperation in 1988 and are now commercially producing SPS under the tradenames Questra™ and Xarec™, respectively.

10 MODERN POLYSTYRENE PRODUCTION

In the late 1970s, Dow undertook a major programme to change the way polystyrene was commercially produced. The conversion involved moving from thermally initiated polystyrene polymerization to polymerization initiated by a bifunctional initiator (Dow calls the initiator DP275, named after its inventor Duane Priddy). Today the majority of general-purpose polystyrene is produced by solution polymerization in a continuous process. The solution process allows for the easy removal of heat from the polymerization medium. This technique, however, necessitates the use of exhaustive post-polymerization devolatilization equipment employing high temperatures and high vacuum to ensure the removal of volatiles and oligomers.

11 THE FUTURE

Figure 1.12 shows the timeline of discovery of various styrenic polymers and copolymers. It would be naive to suggest that the rate of invention and innovation will level off in this century. Rather, the pace of discovery of new styrenic polymers will probably increase. Advances in new catalyst technology and 'controlled radical polymerisation' technology will undoubtedly yield new styrenic polymers with well-defined architecture, as we have recently seen with the introduction of syndiotactic PS and ethylene–styrene interpolymers.

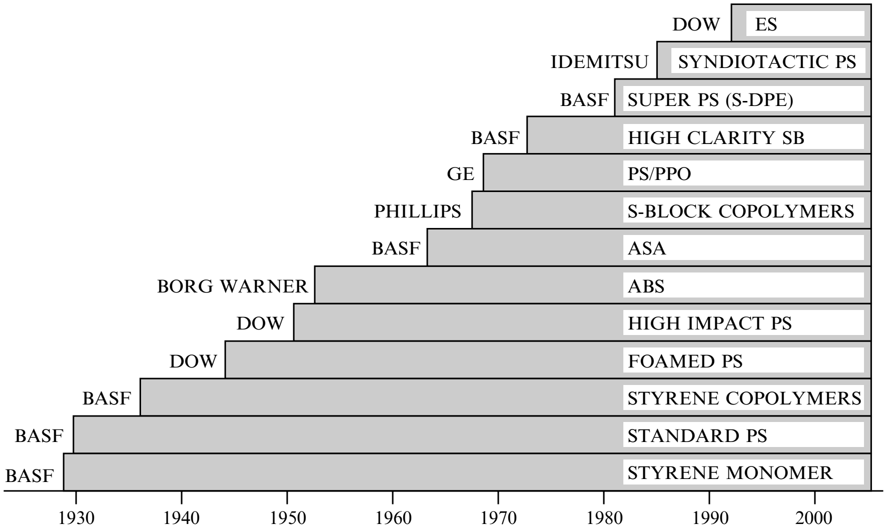

Figure 1.12 Timeline of the development of styrenic polymers (adapted from a BASF document by Franz Haaf, entitled '50 Jahre Polystyrol – Entwicklung', BASF, Ludwigshafen)

Advances in the synthesis of dendritic and hyperbranched styrenic polymers will also contribute to the slate of new products. Hitherto uncommerciallized are a range of polymers in which styrene is copolymerized with three or more other monomers. This is because styrene readily copolymerizes with other monomers, even nonpolymerizable monomers such as anhydrides and nitriles. As far as process technology is concerned, all commercial polystyrene has until now been produced using free radical chemistry. BASF and Asahi have recently been aggressively developing 'retarded' anionic polymerization process technology which will allow them to manufacture polystyrene (both general-purpose polystyrene and high-impact polystyrene) in continuous bulk polymerization processes. The advantage of these new anionic processes will be the production of highly pure PS virtually free of traces of volatile impurities such as unreacted styrene monomer. Also, anionic polymerization processes allow the production of PS having a more narrow polydispersity, resulting in an improved flow/strength property balance.

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