

Polystyrene: Synthesis,
Production and Applications

Polystyrene

Synthesis, Production and Applications

J.R. Wunsch

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1 THE ECONOMIC SIGNIFICANCE OF POLYSTYRENE

1.1 Styrene: Production Capacities and Consumption

Styrene is an important feedstock in a variety of polymer products. Of the total amount of styrene produced, almost 50% is used to make polystyrene, 20% for elastomers, thermosetting resins and polymer dispersions, 15% in ABS and SAN copolymers, 10% in expanded polystyrene (EPS), and the remainder in a variety of copolymers and speciality materials.

Worldwide growth in styrene production capacity and plant utilization is largely determined by the demand for the polymers mentioned. Increased demand for styrenic polymers in the second half of the 1980s led to a big expansion of capacity in the three largest producer regions of North America, Western Europe and East Asia. Worldwide capacity grew by 25% between 1988 and 1992. Up to 1996, most of the new capacity was added in North America and Asia (see **Table 1**).

1.2 Polystyrene: Production Capacities and Consumption

The figures given in **Table 2** only relate to general-purpose and impact-modified polystyrene (EPS and

styrene copolymers are not included). Production stoppages due to product changes, breakdowns, maintenance etc. can reduce the effective annual capacity of a plant by up to 10%. Currently the top ten producers together hold around 50% of installed capacity. The world's major polystyrene producers also produce their own styrene.

Growth in polystyrene demand will vary greatly from region to region (see **Table 3**). Factors affecting demand include the general economic climate, government regulations, the price and performance of polystyrene against other types of polymer, environmental and recycling considerations, and the development potential for new applications.

In 1998 total plastics consumption stood at 158m tonnes. The five biggest polymers - polyethylene, polypropylene, polyvinyl chloride, polystyrene and nylon - together accounted for around 70% (111m) of this amount; polystyrene took a 9.7% share. **Figure 1** provides a breakdown of this consumption, by geographical region and polymer type. Total plastics consumption for the year 2000 is forecast to be around 175m tonnes.

Since the start of the 1980s, growth in regional consumption has shifted to Asian markets and continues to do so, being boosted by the huge potential of the Chinese market.

Table 1. Annual styrene production capacities (1,000 t)

	1988	1992	1996
Western Europe	3490	4025	4280
Eastern Europe	1295	1200	1230
North America ¹	4980	5910	6365
Latin America	370	430	560
Africa/West Asia	385	425	485
Japan	1710	2290	2970
China	100	270	635
Australasia	770	1870	2175
World	13100	16420	18700
¹ including Mexico			
Source: BASF ZZS/M			

Table 2. Annual polystyrene production capacities (1,000 t)

	Year			Change 1998–2000 in % p.a.
	1995	1998	2000	
Western Europe	2005	2190	2350	3.6
Eastern Europe	318	270	300	5.4
North America ¹	2503	2850	3150	5.1
Latin America	323	330	350	3.0
Africa/West Asia	124	170	200	8.5
Japan	1277	1162	1300	5.8
Australasia	2050	2678	2950	5.2
World	8600	9650	10600	4.8

¹ including Mexico
Source: BASF ZZS/M

Table 3. Polystyrene consumption up to the year 2000

	Per capita consumption in kg			Forecast change 1995–2000 in % p.a.
	1995	1998	2000 (forecast)	
Western Europe	4.87	5.43	5.78	3.5
Eastern Europe	0.62	0.59	0.60	-0.8
North America ¹	6.62	7.37	7.79	3.3
Latin America	0.97	1.04	1.11	2.7
Africa/West Asia	0.25	0.35	0.37	8.3
Japan	7.92	7.22	7.87	-0.1
Australasia	0.77	0.86	0.94	4.0
World	1.51	1.62	1.72	2.7

¹ including Mexico
Source: BASF ZZS/M

2 THE PRODUCTION AND PROPERTIES OF POLYSTYRENE

2.1 Historical Development

In 1839, the German chemist Eduard Simon coined the word Styrol for a colourless, mobile liquid he had obtained by distilling liquid storax (a.1), a medicinal

balsam found in certain tree species (a.2). Now known as styrene, the material had been isolated by distillation or pyrolysis before Simon's time. The early history of styrene is given in a classic monograph by Boundy and Boyer (a.3). Styrene was observed to convert itself relatively quickly into a resinous solid. Simon thought (wrongly) that the material had oxidized. Later researchers found that the composition of the solidified styrene had not changed and concluded that it was

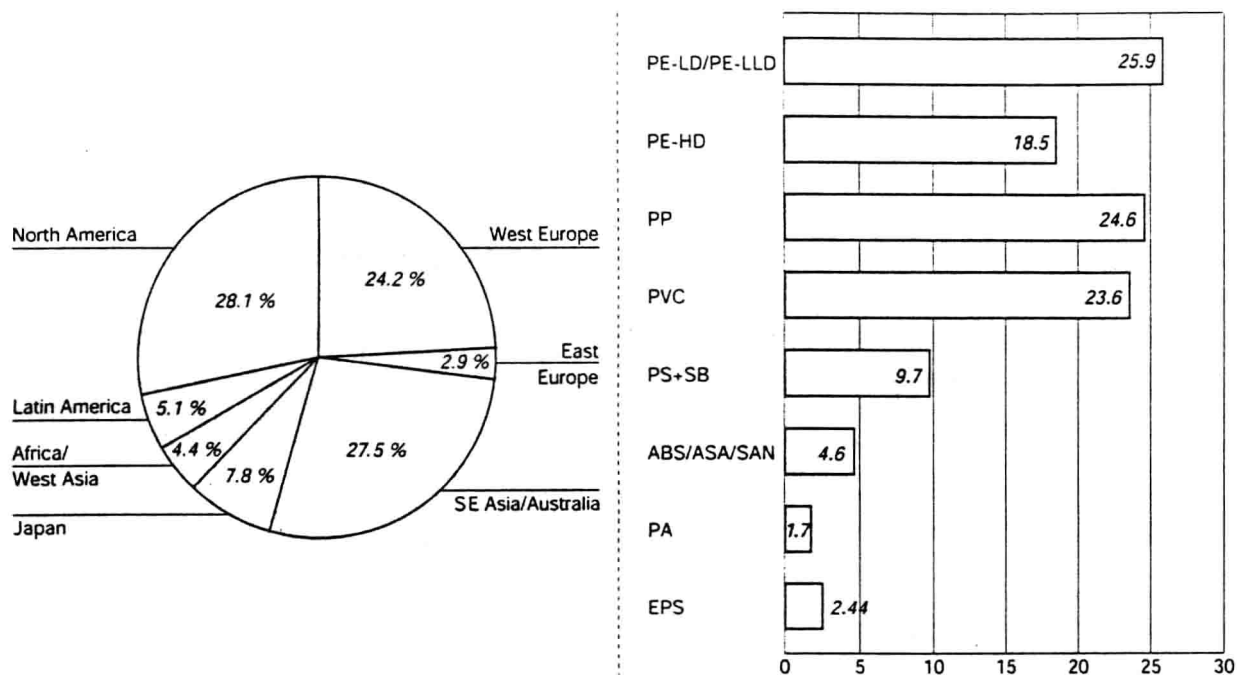


Figure 1

Consumption of the five major plastics (1998)

simply another form of styrene, which they referred to as 'meta-styrene'. It was nearly a century later that Herman Staudinger was able to describe what had really happened. The individual molecules of styrene had polymerized, forming into chain-like molecules that Staudinger called macromolecules. Staudinger called the material polystyrol - we now know it as polystyrene.

Styrene was first produced on an industrial scale in 1931 by IG Farbenindustrie in Germany, and a little later by the Dow Chemical Company in the USA. Both companies employed the catalytic dehydrogenation of ethylbenzene, still the main process used today. Styrene production was boosted by the need for synthetic styrene butadiene rubber during the war, and later by the rapid growth in demand for plastics. Today styrene production is a major branch of the petrochemicals industry (a.4).

2.2 Preparation of Ethylbenzene

Ethylbenzene can be prepared in the laboratory by the Wolff-Kizner reduction of acetophenone (methyl phenyl ketone) by the action of hydrazine and a strong base like potassium hydroxide. Another method is by the catalytic hydrogenation of styrene (a.5).

On an industrial scale, the catalytic alkylation of benzene with ethylene is currently the most common method for producing ethylbenzene commercially (497, 522, a.6-9). The following have been used as catalysts (a.5): AlBr_3 , AlCl_3 , FeCl_3 , ZrCl_4 , TaCl_5 , BF_3 , UCl_3 , TiCl_3 , WCl_6 , ZnCl_2 , SnCl_4 , TiCl_4 , BeCl_2 , SbCl_5 , HgCl_2 , CuCl_2 , BiCl_3 , AsF_3 . The alkylation of aromatic compounds in the presence of AlCl_3 was first practised by M. Bahlsohn in 1879, but much of the early work on alkylation and aluminium chloride catalysis is due to Friedel and Crafts (a.6). The method has been used commercially since 1932. In the past decades very many plants employing Friedel-Craft reaction chemistry were built. Newer plants have turned to synthetic zeolite catalysts because of the corrosive properties of AlCl_3 .

The industrial synthesis of ethylbenzene from benzene and ethanol became possible relatively recently, following the development of appropriate metallo-silicate zeolite catalysts (a.10, a.11). In the reaction, which takes place at over 450°C , rather than reacting directly with the benzene, most of the ethanol is dehydrated to ethylene, which then reacts with the benzene to form ethylbenzene. The process has never caught on commercially because of poor conversion rates and low selectivity to ethylbenzene.

2.2.1 Raw Materials

Around half of all benzene produced is used for synthesizing ethylbenzene (a.12). The main source of benzene used to be coal. Nowadays, this source accounts for less than 10%. About 20% of benzene is made by the hydroalkylation of other aromatic compounds and from the BTX fraction of reformat (4%) and pyrolysis gasoline (8%). Additionally the aromatic fraction in the pyrolysis gasoline which is obtained by cracking naphtha consists of about one third benzene. Benzene with a high level of purity (at least 99.8%) is necessary for manufacturing ethylbenzene. Contaminants cause undesirable side reactions and lower yields, and can deactivate the catalyst. A typical specification for benzene for ethylbenzene synthesis is given in Table 4.

Table 4. Benzene specification

Density at 20 °C	0.878 - 0.881 g/cm ³
Freezing point	> 5.4 °C
Purity	min. 99.85%
Toluene	max. 0.05%
Non-aromatics	max. 0.15%
Water content	max. 0.02%
Platinum-cobalt number	max. 10
Sulfur compounds	max. 2 ppm

Table 5. Ethylene specification

Ethylene	min. 99.9%
Hydrogen	max. 10 ppm
Methane	max. 1000 ppm
Ethane	max. 500 ppm
Acetylene	max. 10 ppm
C ₁ and higher	max. 10 ppm
CO	max. 2 ppm
CO ₂	max. 5 ppm
Water	max. 10 ppm
Oxygen	max. 5 ppm
Nitrogen	max. 100 ppm

Most ethylene (a.13) is produced by the pyrolysis (or steam cracking) of aliphatic hydrocarbons and naphthas. Like benzene, the ethylene feedstock must also have high purity. The specification in Table 5 shows the maximum content of the other stream cracker by-products.

2.2.2 Friedel-Crafts AlCl₃ Catalysis by the Badger Process

The Badger process is the main route to ethylbenzene. The process comprises three stages: alkylation, isolation and separation. Aluminium chloride catalyst is metered continuously into a stirred reactor containing polyalkylbenzenes, in which it forms a suspension. Hydrogen chloride or ethyl chloride is added as a catalyst promoter and the suspension pumped into an acid-resistant pressure reactor, where it is made to react at 140-160 °C and 3-6 bar to form a reddish-brown aluminium chloride catalyst complex. The ligands of this complex consist of benzene, ethylbenzene and polyethylbenzenes (PEB).

In the continuous process, dry benzene is fed in from the top of the reactor, where it reacts spontaneously with ethylene fed from below. The reaction takes place in the presence of excess benzene (about 2.5 mols of benzene to 1 mol of ethylene) to minimize the formation of polyalkylated benzenes.

The reaction is strongly exothermic: 114 kJ/mol of ethylbenzene. The PEB that does form is separated by distillation and returned to the reactor, where it is converted to ethylbenzene in the presence of excess benzene. This transalkylation reaction reaches equilibrium after one hour for a ratio of hydrocarbon to complex of 10:1 (a.14).

In an initial treatment step, the organic phase is washed with water to remove dissolved catalyst. In a second step, the crude ethylbenzene is neutralized with sodium hydroxide solution. Residual water is removed from the crude ethylbenzene in an electrostatic separator and the ethylbenzene then transferred to a buffer tank to await distillation.

The ethylbenzene is purified in a series of (usually) five distillation columns: four pressure columns, operating at 1.5-8.0 bar, and a vacuum column.

Dry benzene (< 30 ppm water) is required for the alkylation reaction as water decreases the activity of the AlCl₃ catalyst. Benzene dehydration is carried out in a separate column, which processes fresh benzene and residual material from the benzene recovery column.