

Styrene Block Copolymers

Commercial technologies & costs of production for styrene block copolymers: SBS - Poly(styrene-butadiene-styrene), SIS - Poly(styrene-isoprene-styrene), SEBS - Poly(styrene-ethylene/butylene-styrene), SEPS - and Poly(styrene-ethylene/propylene-styrene). Global and regional (North America, Europe, Japan, China, Rest of the World) supply/demand and plant capacity data are included, as well as a brief discussion on commercial formulations and additives.

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Report Abstract

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INTRODUCTION

Styrene block copolymers (SBCs), which combine the properties of a thermoplastic resin and those of an elastomer, are based on block copolymers having an elastomeric center segment and polystyrene end segments. It should be noted that there are many possible block configurations of SBCs. Common industry vernacular includes di-block (polystyrene-elastomer) materials, polystyrene-elastomeric center segment- polystyrene linear structures, as well as a variety of branched configurations. This report follows industry convention and includes di-block, linear as well as multi-block styrenic block copolymers which can be classified as thermoplastic elastomers. Of these different types of SBCs, linear materials remain the most common. However, this report does not include non-elastomeric di-block materials intended predominantly for packaging, such as “K-Resin” made by ChevronPhillips.

There are three possible center segment polymers in linear A-B-A (where A is polystyrene and B is the elastomeric segment) styrene block copolymers:

- Polybutadiene
- Polyisoprene
- Polyethylene-butylene

These center segments differentiate the three major styrene block copolymers (SBC):

- Poly(styrene-butadiene-styrene) (SBS)
- Poly(styrene-isoprene-styrene) (SIS)
- Poly(styrene-ethylene/butylene-styrene) (SEBS)

A fourth, much less common center segment, poly(ethylene/propylene), results in poly(styrene-ethylene/propylene-styrene) (SEPS). SEBS is produced by the hydrogenation of SBS; SEPS by the hydrogenation of SIS.

The structure of SBC renders an unusual combination of properties. The polystyrene end segments form regions or domains separate from the elastomeric center segments. At room temperature, the polystyrene segments act as physical cross-links to tie the elastomeric segments into a network similar to that of conventional vulcanized rubber. At higher temperatures, the end segments soften and the material can flow under stress.

Styrenic block copolymers are an important family of materials in the category of thermoplastic elastomers (TPEs). These materials have many of the properties of vulcanized rubbers but can be molded and extruded on conventional thermoplastic processing equipment. This gives them productivity advantages versus vulcanized rubbers which are thermosets and are processed using slow and costly curing processes.

In 1965, Shell (now Kraton Performance Polymers) developed the first commercially acceptable thermoplastic elastomer based on styrene-butadiene block copolymerization. Prior work on polyurethane systems had been carried out by other companies but Shell established a versatile material with an attractive cost base that has been the cornerstone of TPE market development ever since. Demand growth of SBCs was rapid in the early years as the new materials substituted for thermoset rubbers in molding/extrusion applications and for ethylene-vinyl acetate (EVA) in adhesives. Other applications have since been developed.

The unsaturated SBCs - SBS and SIS - are soft and flexible with excellent tack and adhesive properties. Hence, they tend to find use in adhesives (especially SIS), sealants and bitumen modification applications; footwear is also another important end-use for SBS on the basis of its softness and low cost. The hydrogenated materials, SEBS, and SEPS, have improved weatherability and UV resistance, and hence, find use in compounds for durable products, although they are sometimes used in adhesive formulations as well. Both the unsaturated and saturated materials find use as polymer modifiers or tie layers depending on final product requirements.

PROCESS TECHNOLOGY

This section of the report examines the regular production process for SBS, SIS, and subsequently, the hydrogenation step to SEBS or SEPS.

The technology is very flexible and enables plants to produce not only SBS, SIS, and SEBS/SEPS, but also, in some cases, SB Rubbers of the more conventional type. The plants are generally multi-stream in order to produce several grades in parallel. This reflects the fragmented and differentiated nature of the product and its markets.

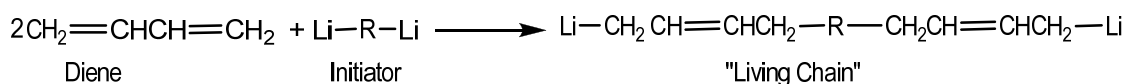
The operation is an interesting balance between batch (copolymerization) and continuous (polymer and solvent recovery) processes.

Chemistry

SBS and SIS polymers can be prepared by four different processes, each with unique characteristics:

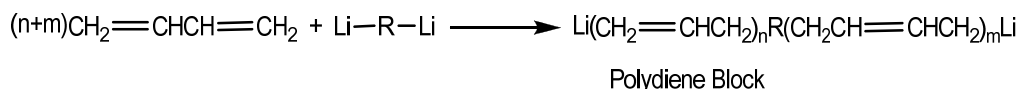
- Difunctional initiator process
- Three-stage sequential addition process
- Coupling process
- Tapered block process

Linear A-B-A block copolymers can be produced via the use of difunctional initiators (e.g., sodium naphthalene or dilithium compounds). The initiation reaction follows the pattern shown below:



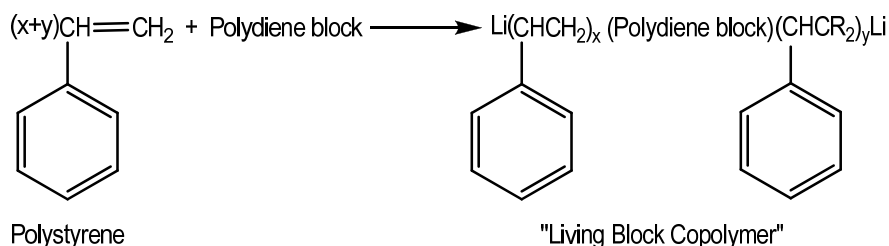
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Diene polymerization then proceeds as shown:



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Styrene polymerization onto the diene block then proceeds as follows:



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The resultant polymers can show a very narrow molecular weight distribution, but these initiators are generally only soluble in low polar solvents. As a result, the polydiene segment has a low 1,4 microstructure content which restricts the desirable property of low glass transition temperature.

The report illustrates the differences in process chemistry between the above difunctional initiator process and the three other processes mentioned above.

Technology Trends

Introduced over 40 years ago, SBC products can be described as mature, with well-established compositions, well-known properties and relatively mature applications. However, research continues into the SBCs focused mainly on improving various physical properties through molecular tailoring, and on developing materials and compositions which better meet specific end-use application requirements. Lesser areas of research include ways to functionalize the SBC molecule, alternative coupling agents, various additives, and on improving the SBC manufacturing process. Technology trends are briefly reviewed.

ECONOMICS

Cost of production estimates were developed for producing:

- SBS (Oil Free, Minimal Additive Package) via Basic Living Polymerization
- SIS (Oil Free, Minimal Additive Package) via Basic Living Polymerization
- SEBS via SBS Hydrogenation (Incremental Basis)
- SEPS via SIS Hydrogenation (Incremental Basis)

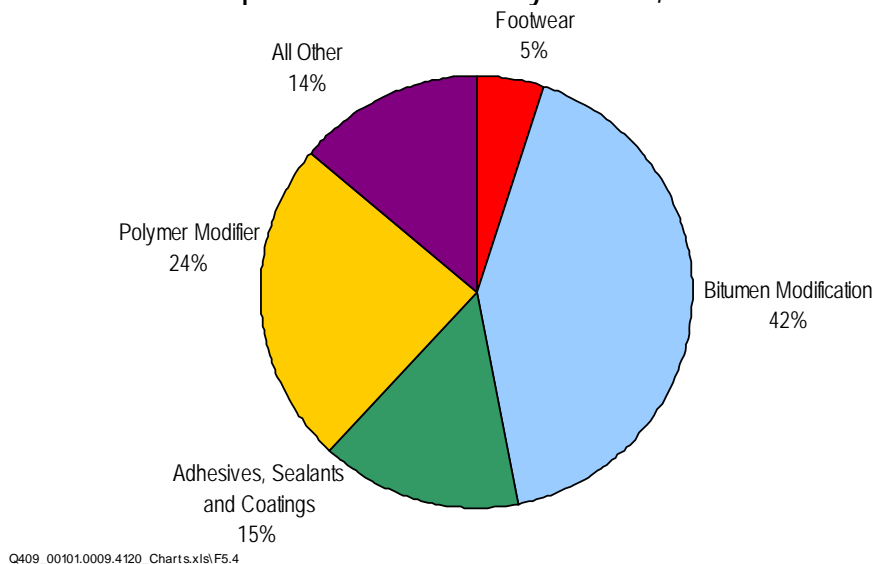
To test the effect of raw material prices on SBS and SIS production cash costs, a sensitivity analysis for a range of butadiene and isoprene raw material prices was carried out.

COMMERCIAL ANALYSIS

The styrenic block copolymers are somewhat different than other thermoplastic elastomers in that they are seldom used as pure materials. Instead, they are commonly used with a host of additives and other polymers so as to specifically formulate the final compound to meet required physical properties, hardness, and processing characteristics. The other additives and ingredients can include conventional elastomers, fillers, extender oils, processing aids, other polymers, resins, colorants and antidegradants. Reportedly, SBC content in some formulations can be as low as 25 percent by weight. Common SBC additive categories are discussed in the report.

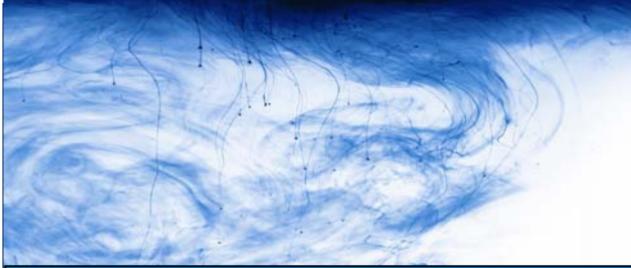
The wide range of physical properties which can be incorporated into the SBC polymer backbone, together with the great latitude in incorporating fillers, extenders, modifiers, or other additives into SBCs has enabled these materials to be used in a wide range of end-use applications. These end-use applications make use of several of the key, inherent properties as offered by SBCs. Specific end-use applications for SBCs are exemplified in the Figure below. End-use analysis is discussed further in the report.

Japanese SBC Demand by End Use, 2009



Styrene block copolymers are often produced in multipurpose facilities, which manufacture other rubber products as well, such as SBR and polybutadiene rubber. This ability to “swing” production assets complicates the allocation of capacity between SBC and the production of other rubber products. Nevertheless, in the event of the ability to swing capacity, the intent of the capacity tables contained in this section is to show the proportion of total capacity typically used to produce SBCs.

- Supply, demand and trade data is given and discussed in the report for the following regions: North America (includes US, Canada and Mexico), Europe (includes Eastern and Western Europe), Japan, China and the Rest Of the World (predominantly other Asian countries, but also includes South America, Africa and the Middle East); a global overview is also given.
- Tables giving production capacity according to plant location, plant owner and products synthesized for the regions listed above are also included in the report.



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