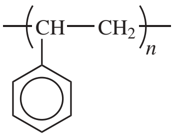
STYRENE PLASTICS

1. Introduction

Polystyrene [9003-53-6] (PS), the parent of the styrene plastics family, is a high molecular weight linear polymer which, for commercial uses, consists of ~1000 styrene units. Its chemical formula (**1**), where $n = \sim 1000$, tells little of its properties.



(**1**)

The main commercial form of PS is amorphous and hence PS is highly transparent. The polymer chain stiffening effect of the pendent phenyl groups raises the glass-transition temperature (T_g) to slightly over 100°C. Therefore, under ambient conditions, the polymer is a clear glass, whereas above the T_g it becomes a viscous liquid which can be easily fabricated, with only slight degradation, by extrusion or injection-molding techniques. This ease with which PS can be converted into useful articles accounts for the very high volume used in world commerce. Even though crude oil is the source of the polymer, the energy savings and environmental impact accrued during fabrication and use, compared to alternative materials, more than offset the short life of many PS articles (1).

Most PS is manufactured using continuous bulk polymerization plants. Generally, the key problems associated with manufacture of the polymer are removal of the heat of polymerization and pumping highly viscous solutions. Conversion of the monomer to the polymer is energetically very favorable and occurs spontaneously on heating without the addition of initiators. Because it is a continuous polymerization process, material-handling problems are minimized during manufacture. By almost any standard, the polymer produced is highly pure and is usually greater than 99 wt% PS; for particular applications, however, processing aids are often deliberately added to the polymer. Methods for improving the toughness, solvent resistance, and upper use temperature have been developed. Addition of butadiene-based rubbers increases impact resistance, and copolymerization of styrene with acrylonitrile produces heat- and solvent-resistant plastics (see ACRYLONITRILE POLYMERS, SURVEY AND STRYRENE-ACRYLONITRILE (SAN)). Uses for these plastics are extensive. Packaging applications, eg, disposable tumblers, television cabinets, meat and food trays, and egg cartons, are among the largest area of use for styrene plastics. Rigid foam insulation in various forms is being used increasingly in the construction industry, and modified styrene plastics are replacing steel or aluminum parts in automobiles; both applications result in energy savings beyond the initial investment in crude oil. The cost of achieving a given property, eg, impact strength, is among the lowest for styrene plastics as compared to other competitive materials.

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2. Properties

The general mechanical properties of styrene polymers are given in Table 1. Considerable differences in performance can be achieved by using the various styrene plastics. Within each group, additional variation is expected. In choosing an appropriate resin for a given application, other properties and polymer behavior during fabrication must be considered. These factors depend on the combination of inherent polymer properties, the fabrication technique, and the devices, eg, a mold, used for obtaining the final object. Accordingly, consideration must be given to such factors as the surface appearance of the part and the development of anisotropy, and the effect of anisotropy on mechanical strength, ie, long-term resistance of the molding to external strain.

2.1. Physical. An extensive compilation of physical properties of PS has been given (2,3). In general, a polymer must have a weight-average molecular weight (M_w) about 10 times higher than its chain entanglement molecular weight (M_e) to have optimal strength. Below M_e, the strength of a polymer changes rapidly with M_w. However, at about 10 times M_e, the strength reaches a plateau region (Fig. 1). For PS, the M_e is 18,100 (4). Thus PS having an $M_w < 180{,}000$ is generally too brittle to be useful. This indicates why no general-purpose molding and extrusion grades of PS are sold commercially that have $M_w < 190{,}000$.

2.2. Stress–Strain Properties. The strain energy, derived from the area under the stress–strain curve, is considered to indicate the level of toughness of a polymer. High impact PS (HIPS) has a higher strain energy than an acrylonitrile–butadiene–styrene (ABS) plastic, as shown in Figure 2. Based on different impact-testing techniques, ABS materials are generally tougher than HIPS materials (6,7). The failure of the stress–strain curve to reflect this ductility can be related to the fact that ABS polymers tend to show only localized flow or necking tendency at low rates of extension, and therefore fail at low elongation. HIPS extends uniformly during such tests, and the test specimen whitens over all of its length and extends well beyond the yield elongation. At higher testing speeds, ABS polymers also deform more uniformly and give high elongations (7).

Tensile strengths of styrene polymers vary with temperature. Increased temperature lowers the strength. However, tensile modulus in the temperature region of most tests (−40 to 50°C) is affected only slightly. The elongations of PS and styrene copolymers do not vary much with temperature (−40 to 50°C), but the elongation of rubber-modified polymers first increases with increasing temperature and ultimately decreases at high temperatures.

The molecular orientation of the polymer in a fabricated specimen can significantly alter the stress–strain data as compared with the data obtained for an isotropic specimen, eg, one obtained by compression molding. For example, tensile strengths as high as 120 MPa (18,000 psi) have been reported for PS films and fibers (8). PS tensile strengths below 14 MPa (2000 psi) have been obtained in the direction perpendicular to the flow.

Creep, Stress Relaxation, and Fatigue. The long-term engineering tests on plastics in intended-use environments and temperatures are required for predicting the overall performance of a polymer in a given application. Creep tests involve the measurement of deformation as a function of time at a constant

Table 1. **Mechanical Properties of Injection-Molded Specimens of Main Classes of Styrene-Based Plastics**[a]

Property	Polystyrene (PS)	Poly-(styrene-*co*-acrylonitrile) (SAN)[b]	Glass-filled PS[c]	High impact PS[d]	HIPS	Acrylonitrile–butadiene–styrene terpolymer (ABS)[d]		Standard ABS	Super ABS
						Type 1	Type 2		
CAS Registry Number	[9003-53-6]	[9003-54-7]			[9003-53-6]			[9003-56-9]	
specific gravity	1.05	1.08	1.20	1.05	1.05	1.05	1.05	1.04	1.04
Vicat softening point, °C	96	107	103	103	95	99	108	103	108
tensile yield, MPa[e]	42.0	68.9	131	39.6	29.6	31.0	53.8	41.4	34.5
elongation, rupture, %	1.8	3.5	1.5	15	58	55	10	20	60
modulus, MPa[e]	3170	3790	7580	2690	2140	2620	2620	2070	1790
impact strength (notched Izod), J/m[f]	21	21	80	96	134	193	187	267	428
dart-drop impact strength	very low	very low	medium high	low	medium high	medium high	high	very high	very high
relative ease of fabrication	excellent	excellent	poor	excellent	excellent	excellent	good	good	medium good

[a] Ref. 2.

[b] 24 wt% acrylonitrile.

[c] 20% glass fibers.

[d] Medium mol wt.

[e] To convert MPa to psi, multiply by 145.

[f] To convert J/m to ft·lbf/in., divide by 53.38.

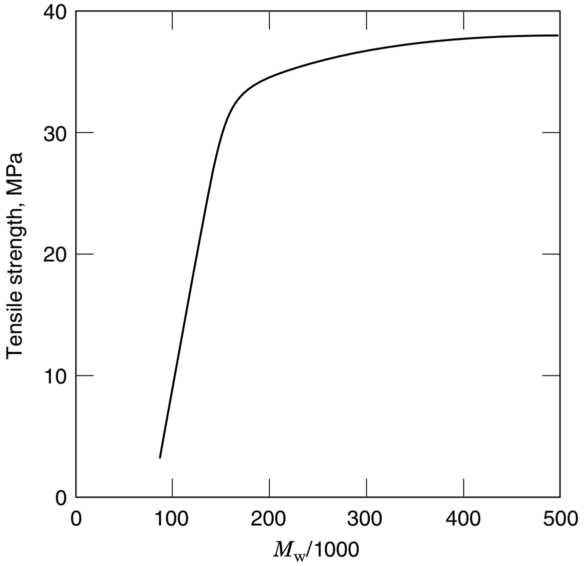


Fig. 1. PS tensile strength vs M_w (5). To convert MPa to psi, multiply by 145.

stress or load. For styrene-based plastics, many such studies have been carried out (9,10). Creep curves for styrene and its copolymers at room temperature show low elongation having only small variation with stress, whereas the rubber-modified polymers exhibit a low elongation region, followed by crazing and increasing elongation, usually to ca 20%, before failure (Fig. 3).

Creep tests are ideally suited for the measurement of long-term polymer properties in aggressive environments. Both the time to failure and the ultimate elongation in such creep tests tend to be reduced. Another test to determine plastic behavior in a corrosive atmosphere is a prestressed creep test in

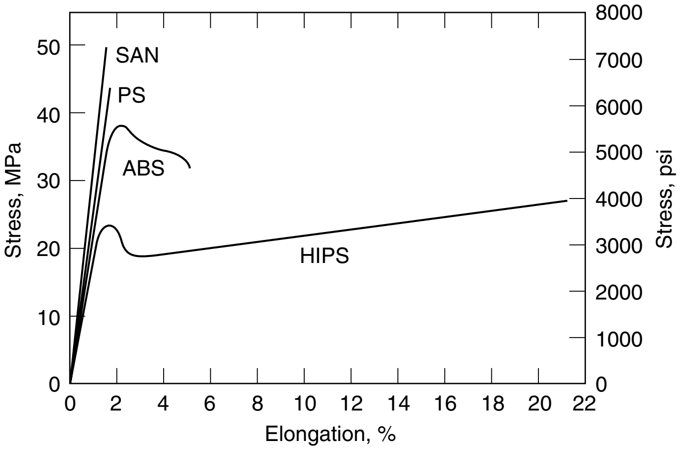


Fig. 2. Stress–strain curves for styrene-based plastics.

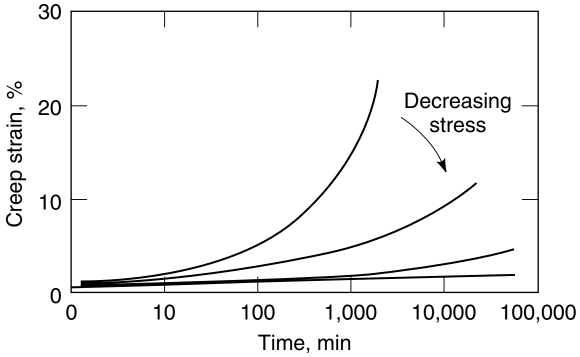


Fig. 3. Typical creep behavior for rubber-modified styrene polymers.

which the specimens are prestressed at different loads, which are lower than the creep load, before the final creep test (11).

Stress-relaxation measurements, where stress decay is measured as a function of time at a constant strain, have also been used extensively to predict the long-term behavior of styrene-based plastics (9,12). These tests have also been adapted to measurements in aggressive environments (13). Stress-relaxation measurements are further used to obtain modulus data over a wide temperature range (14).

Fatigue is another property of considerable interest to the design engineer. Cyclic deflections of a predetermined amplitude, short of giving immediate failure, are applied to the specimen, and the number of cycles to failure is recorded. In addition to mechanically induced periodic stresses, fatigue failure can be studied when developing cyclic stresses by fluctuating the temperature.

Fatigue in polymers has been reviewed (15); detailed theory and practice of fatigue testing are covered. Fatigue tests, conducted both in air and in aggressive environments (16), are carried out for two main reasons: to learn the inherent fatigue resistance of the material and to study the relationship between specimen design and fatigue failure.

2.3. Melt Properties. The melt properties of PS at temperatures between 120 and 260°C are important because it is in this temperature range that PS is extruded to make sheets, foams, and films, or molded into parts. Generally it is desirable to make parts having high strength from materials having low melt viscosity for easy melt processing. However, polymer molecular weight increases both strength and melt viscosity. The melt viscosity of PS can be decreased to improve its melt processibility by the addition of a plasticizer such as mineral oil. However, the addition of a plasticizer has a penalty, ie, the heat distortion temperature is lowered. In applications where heat resistance is important, melt processibility can be influenced, without a significant effect on heat resistance, by control of the polydispersity (17), by branching (18), or by the introduction of pendent ionic groups, eg, sodium sulfonate (19,20).

2.4. Impact Strength. PS and styrene copolymers are brittle polymers under normal use conditions. A high speed blow at temperatures below T_g causes catastrophic failure without significant deformation, crazing, or yielding in the polymer. Rubber-modified styrene polymers, however, are significantly more impact-resistant. These polymers are characterized by significant whitening of the specimen during the test as a result of craze formation, separation of the rubber phase from the matrix polymer, and cracks (21,22). The mechanism by which the dispersed rubber particles cause such increased toughness continues to be debated (23–25). Craze initiation and termination are controlled by the particles. Under tensile stress, crazes are initiated near the equators of the particles, ie, at the point of maximum stress, and propagate outward. The highly oriented PS fibrils with the surrounding voids constitute the craze (26). Because of the molecular orientation, such material is load-bearing and ductile. The large number of particles leads to a large number of small crazes, and on a microscopic scale the plastic is ductile instead of brittle. Creation of the craze matter absorbs energy and, so long as the stress does not cause the crazes to become true cracks, the plastic can recover after the stress is removed. Particle size sensitivity probably results from the ineffectiveness of very small particles in stopping craze growth. They may also be inefficient in producing the necessary stress level around the particle to initiate crazing. Although similar considerations apply to some ABS plastics, the observation of stress whitening or crazing and necking indicates shear yielding (27).

A brittle fracture of a styrene polymer can be brought about by producing uniaxially oriented moldings. Measuring the strength in these moldings across the flow direction or by biaxial loading, such as in a dart drop test, shows the embrittlement of an otherwise tough polymer. Injection moldings of HIPS produced at low temperatures have been shown to be particularly prone to brittle fracture, whereas the ABS polymers in general are less subject to fabrication-induced anisotropy and the consequent embrittlement (28). However, it has been shown that tough moldings of PS can be obtained through the introduction of balanced, multiaxial orientation (29). One way this orientation can be achieved is by molding objects with rotational symmetry at low molding temperatures and by rotating one half of the mold during and after filling, and until the polymer in the mold is cool enough to resist molecular relaxation. In addition to enhanced toughness, craze resistance is improved in such moldings.

Embrittlement of otherwise tough rubber-modified styrene polymers occurs through aging of these polymers (30). The effects of outdoor aging of rubber-modified thermoplastics have been studied (31). Outdoor aging was simulated by laminating a brittle film onto a virgin rubber-modified polymer molding. These experiments showed that aging reduces the energy of crack initiation, so that the final impact strength is determined by the inherent crack-propagation energy of the rubber-modified polymer.

2.5. Surface Appearance. HIPS materials can have a glossy or a dull surface appearance. This surface appearance is a function of surface roughness caused by rubber particles disrupting the surface regularity. The rubber particles near the surface can disrupt the surface by causing either depressions or elevations. These irregularities are caused not only by the nature of the rubber particles, eg, size and shape, but also by processing conditions. For example, during injection molding the surface of the polymer is pressed against a very smooth polished mold surface and quenched, locking in the smooth surface. However, when HIPS is extruded into sheets and thermoformed into parts, it is allowed to cool slowly, giving the rubber particles near the surface time to relax. Polybutadiene rubber particles shrink more upon cooling than the PS matrix, thus causing depressions (32).

3. Material Types

3.1. General-Purpose Polystyrene.

Polystyrene is a high molecular weight ($M_w = 2 - 3 \times 10^5$), crystal-clear thermoplastic that is hard, rigid, and free of odor and taste. Its ease of heat fabrication, thermal stability, low specific gravity, and low cost result in moldings, extrusions, and films of very low unit cost. In addition, PS materials have excellent thermal and electrical properties that make them useful as low cost insulating materials (see INSULATION, ELECTRIC; INSULATION, THERMAL).

Commercial polystyrenes are normally rather pure polymers. The amount of styrene, ethylbenzene, styrene dimers and trimers, and other hydrocarbons is minimized by effective devolatilization or by the use of chemical initiators (33). Polystyrenes with low overall volatiles content have relatively high heat-deformation temperatures. The very low content of monomer and other solvents, eg, ethylbenzene, in PS is desirable in the packaging of food. The negligible level of extraction of organic materials from PS is of crucial importance in this application.

When additional lubricants, eg, mineral oil and butyl stearate, are added to PS, easy-flow materials are produced. Improved flow is usually achieved at the cost of lowering the heat-deformation temperature. Stiff-flow PS has a high molecular weight and a low volatile level and is useful for extrusion applications. Typical levels of residuals in PS grades are listed in Table 2. Differences in molecular weight distribution are illustrated in Figure 4.

3.2. Specialty Polystyrenes.

These include ionomers and PS of specified tacticity, as well as stabilized PS.

Ionomers. PS ionomers are typically prepared by copolymerizing styrene with an acid functional monomer, eg, acrylic acid, or by sulfonation of PS followed by neutralization of the pendent acid groups with monovalent or divalent alkali metals. The introduction of ionic groups into PS leads to a significant modification of both solid-state and melt properties. The introduction of ionic interactions in PS leads to increasing T_g, rubbery modulus, and melt viscosity with increasing ion content (20). For the sodium salt of sulfonated PS, it has been

Table 2. **Residuals in Typical Polystyrene, wt%**

	Grade	
Polystyrene	Extrusion	Injection-molding
styrene	0.04	0.1
ethylbenzene	0.02	0.1
styrene dimer	0.04	0.1
styrene trimer	0.25	0.8

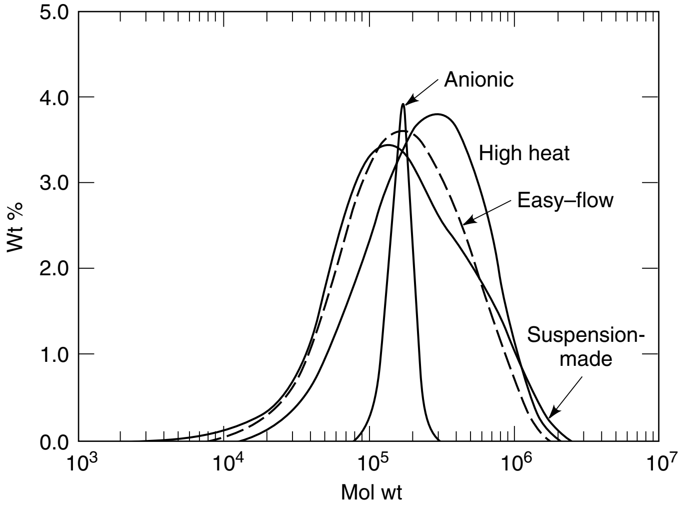
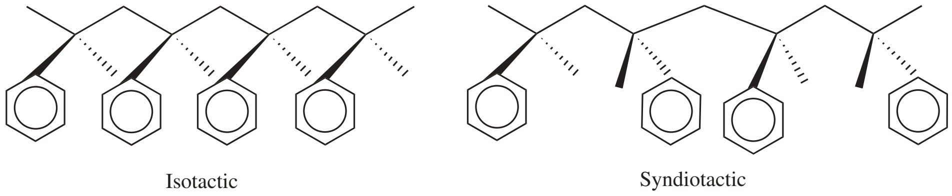


Fig. 4. Molecular weight distribution curves for representative polystyrenes.

shown that the mode of deformation changes from crazing to shear deformation as the ion content increases (34,35).

Tactic Polystyrenes. Isotactic (IPS) and syndiotactic (SPS) polystyrenes can be obtained by the polymerization of styrene with stereospecific catalysts of the Ziegler-Natta type. Aluminum-activated $TiCl_3$ yields IPS, whereas soluble Ti complexes, eg, (η^5-C_5H_5)$TiCl_3$, in combination with a partially hydrolyzed alkylaluminum, eg, methylalumoxane, yield SPS. The discovery of the SPS catalyst system was first reported in 1986 (36). As a result of the regular tactic structure, both IPS (phenyl groups cis) and SPS (phenyl groups alternating trans) can be crystallized. Samples of IPS quenched from the melt are amorphous but become crystalline if annealed for some time at a temperature slightly below the crystalline melting point. The IPS rate of crystallization is relatively slow compared to that of SPS and those of other crystallizable polymers, eg, polyethylene or polypropylene. This slow rate of crystallization is what has kept IPS from becoming a commercially important polymer even though the material has been known for over 40 years. In the amorphous state, the properties of IPS and SPS are very similar to those of conventional atactic PS. Crystalline IPS has a melting temperature of around 240°C, whereas SPS melts at about 270°C (37). In the crystalline state, both IPS and SPS are opaque and insoluble in most common PS solvents.



Stabilized Polystyrenes. Stabilized polystyrenes are materials with added stabilizers, eg, uv-screening agents, antioxidants (qv), and synergistic agents. Early stabilization systems for PS included alkanolamines and methyl salicylate (38). Improved stabilizing systems have been developed; these involve a uv-radiation absorber, eg, Tinuvin P with a phenolic antioxidant. Iron as a contaminant, even at a very low concentration, can cause color formation during fabrication. However, this color formation can be appreciably retarded by using tridecyl phosphite as a costabilizer with the uv-radiation absorber and the antioxidant (39). Rubber-modified styrene polymers are heat-stabilized with nonstaining rubber antioxidants, eg, Irganox 1076. Typically stabilizer formulations for PS are designed by trial and error. However, more recently a predictive model was developed for PS photodegradation, which allows the prediction of weatherability of PS containing a certain concentration of a uv absorber (40).

Polymers containing flame retardants (qv) have been developed. The addition of flame retardants does not make a polymer noncombustible, but rather increases the polymer's resistance to ignition and reduces the rate of burning with minor fire sources. The primary commercial developments are in the areas of PS foams (see FOAMED PLASTICS) and television and computer housings. Both inorganic (hydrated aluminum oxide, antimony oxide) and organic (alkyl and aryl phosphates) additives have been used (41). Synergistic effects between halogen compounds and free-radical initiators have been reported (42). Several new halogenated compounds and corrosion inhibitors are effective additives (see CORROSION AND CORROSION CONTROL) (43). The polymer manufacturer's recommendations with regard to maximum fabrication temperature should be carefully observed to avoid discoloration of the molded part or corrosion of the mold or the machine.

Antistatic polystyrenes have been developed in terms of additives or coatings to minimize primarily dust collecting problems in storage (see ANTISTATIC AGENTS). Large lists of commercial antistatic additives have been published (41). For styrene-based polymers, alkyl and/or aryl amines, amides, quaternary ammonium compounds, anionics, etc, are all used.

3.3. Styrene Copolymers.

Acrylonitrile, butadiene, α-methylstyrene, acrylic acid, and maleic anhydride have been copolymerized with styrene to yield commercially significant copolymers. Acrylonitrile copolymer with styrene (SAN), the largest-volume styrenic copolymer, is used in applications requiring increased strength and chemical resistance over PS. Most of these polymers have been prepared at the cross-over or azeotropic composition, which is ca 24 wt% acrylonitrile (see ACRYLONITRILE POLYMERS, SURVEY AND STYRENE-ACRYLONITRILE (SAN); COPOLYMERS).

Copolymers are typically manufactured using well-mixed continuous-stirred tank reactor (CSTR) processes, where the lack of composition drift does not cause loss of transparency. SAN copolymers prepared in batch or continuous plug-flow processes, on the other hand, are typically hazy on account of composition drift. SAN copolymers with as little as 4% by wt difference in acrylonitrile composition are immiscible (44). SAN is extremely incompatible with PS; as little as 50 ppm of PS contamination in SAN causes haze. Copolymers with over 30 wt% acrylonitrile are available and have good barrier properties. If the acrylonitrile content of the copolymer is increased to >40 wt%, the copolymer becomes ductile. These copolymers also constitute the rigid matrix phase of the ABS engineering plastics.

Butadiene copolymers are mainly prepared to yield rubbers (see STYRENE-BUTADIENE RUBBER). Many commercially significant latex paints are based on styrene–butadiene copolymers (see COATINGS; PAINT). In latex paint the weight ratio S:B is usually 60:40 with high conversion. Most of the block copolymers prepared by anionic catalysts, eg, butyllithium, are also elastomers. However, some of these block copolymers are thermoplastic rubbers, which behave like cross-linked rubbers at room temperature but show regular thermoplastic flow at elevated temperatures (45,46). Diblock (styrene–butadiene (SB)) and triblock (styrene–butadiene–styrene (SBS)) copolymers are commercially available. Typically, they are blended with PS to achieve a desirable property, eg, improved clarity/flexibility (see POLYMER BLENDS) (46). These block copolymers represent a class of new and interesting polymeric materials (47,48). Of particular interest are their morphologies (49–52), solution properties (53,54), and mechanical behavior (55,56).

Maleic anhydride readily copolymerizes with styrene to form an alternating structure. Accordingly, equimolar copolymers are normally produced, corresponding to 48 wt% maleic anhydride. However, by means of CSTR processes, copolymers with random low maleic anhydride contents can be produced (57). Depending on their molecular weights, these can be used as chemically reactive resins, eg, epoxy systems and coating resins, for PS–foam nucleation, or as high heat-deformation molding materials (58).

It has been discovered that styrene forms a linear alternating copolymer with carbon monoxide using palladium II–phenanthroline complexes. The polymers are syndiotactic and have a crystalline melting point ~280°C (59,60).

3.4. Polymers of Styrene Derivatives.

Many styrene derivatives have been synthesized and the corresponding polymers and copolymers prepared (61). Glass-transition temperatures for a series of substituted styrene polymers are shown in Table 3. The highest T_g is that of poly(α-methylstyrene), which can be prepared by anionic polymerization. Because it has a low ceiling temperature (61°C), depolymerization can occur during fabrication with the formed monomer acting as a plasticizer and lowering the heat distortion to 110–125°C (62). The polymer, which is difficult to fabricate because of its high melt viscosity, is more brittle than PS but can be toughened with rubber.

Table 3. **Glass-Transition Temperatures of Substituted Polystyrene**

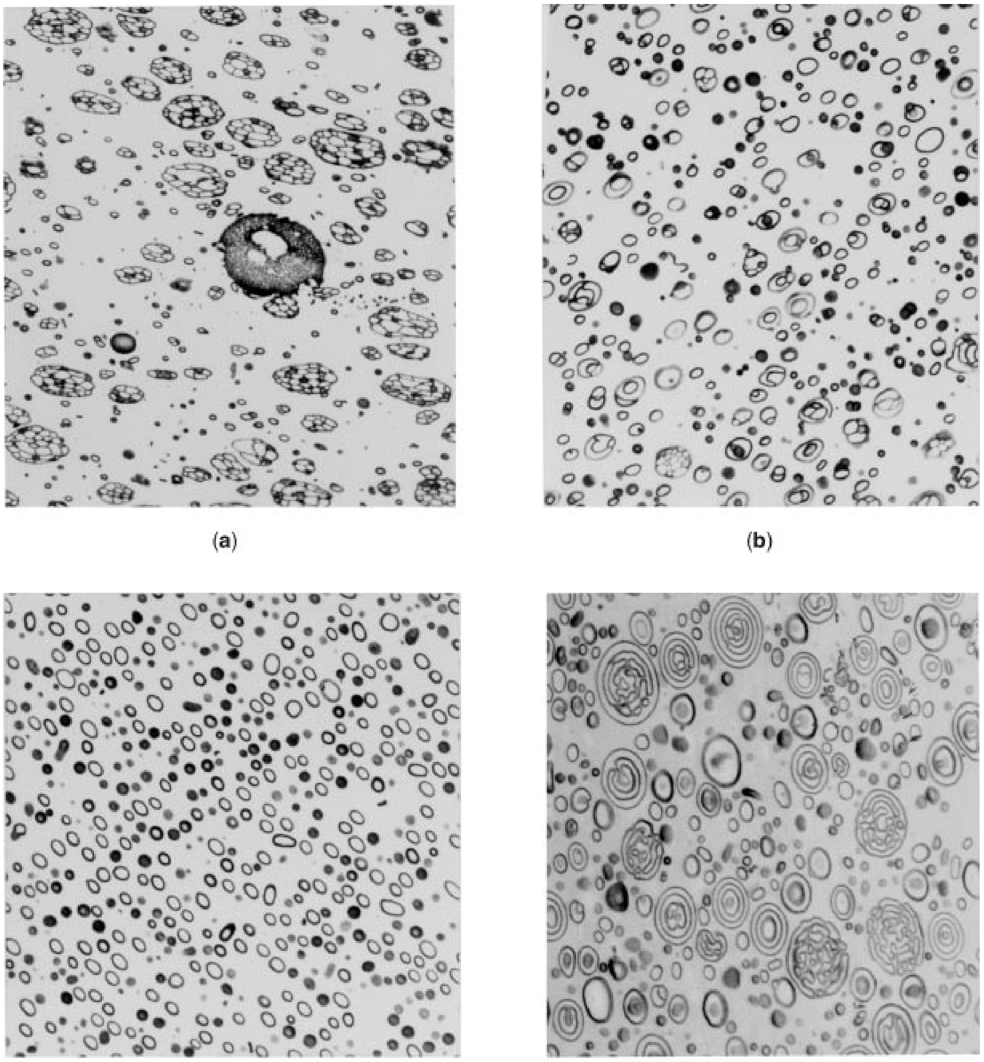
Polymer	CAS Registry Number	T_g, °C
polystyrene	[9003-53-6]	100
poly(*o*-methylstyrene)	[25087-21-2]	136
poly(*m*-methylstyrene)	[25037-62-1]	97
poly(*p*-methylstyrene)	[24936-41-2]	106
poly(2,4-dimethylstyrene)	[25990-16-3]	112
poly(2,5-dimethylstyrene)	[34031-72-6]	143
poly(*p*-*tert*-butylstyrene)	[26009-55-2]	130
poly(*p*-chlorostyrene)	[24991-47-7]	110
poly(α-methylstyrene)	[25014-31-7]	170

Some polymers from styrene derivatives seem to meet specific market demands and to have the potential to become commercially significant materials. For example, monomeric chlorostyrene is useful in glass-reinforced polyester recipes because it polymerizes several times as fast as styrene (61). Poly(sodium styrenesulfonate) [9003-59-2], a versatile water-soluble polymer, is used in water-pollution control and as a general flocculant (see WATER, TREATMENT; FLOCCULATING AGENTS) (63,64). Poly(vinylbenzyl ammonium chloride) [70504-37-9] has been useful as an electroconductive resin (see CONDUCTING POLYMERS) (65).

3.5. Rubber-Modified Polystyrene. Rubber is incorporated into PS primarily to impart toughness. The resulting materials, commonly called high impact polystyrene (HIPS), are available in many different varieties. In rubber-modified PS, the rubber is dispersed in the PS matrix in the form of discrete particles. The mechanism of rubber particle formation and rubber reinforcement, as well as several reviews of HIPS and other heterogeneous polymers, have been published (21,22,66–70). The photomicrographs in Figure 5 show the different morphologies possible in HIPS materials prepared using various types of rubbers (71,72). If the particles are much larger than 5–10 micrometers, poor surface appearance of moldings, extrusions, and vacuum-formed parts are usually noted. Although most commercial HIPSs contain ca 3–10 wt% polybutadiene or styrene–butadiene copolymer rubber, the presence of PS occlusions within the rubber particles gives rise to a 10–40% volume fraction of the reinforcing rubber phase (22,73). Accordingly, a significant portion of the PS matrix is filled with rubber particles. Techniques have been published for evaluating the morphology of HIPS (72,74,75).

For effective toughening of otherwise brittle PS with rubbers, the following generalizations can be made. In order to have good impact strength over a wide temperature range, the T_g of the rubber must be below -50°C, as measured, eg, by torsion pendulum at 1 Hz. The use of butadiene rubbers is particularly effective when the rubber is present during the polymerization of styrene. Grafting of some styrene to rubber takes place, and occlusion of PS extends the volume fraction of the dispersed, reinforcing rubber phase. The rubber phase in the final product is cross-linked to some degree for the most effective reinforcement. Because the rubber phase exists in the form of discrete rubber particles, the degree of cross-linking does not significantly influence the melt flow, which is that of a linear, ie, uncross-linked, thermoplastic polymer. A variation in the degree of cross-linking may be needed to optimize product properties for different applications. Depending on the process and rubber concentration used, there is some latitude in the size of the rubber particles that results in a good balance of properties. This range may extend from <1 to >5 μm.

Rubber-Modified Copolymers. Acrylonitrile–butadiene–styrene polymers have become important commercial products since the mid-1950s. The development and properties of ABS polymers have been discussed in detail (76) (see ACRYLONITRILE POLYMERS, SURVEY AND STYRENE-ACRYLONITRILE (SAN)). ABS polymers, like HIPS, are two-phase systems in which the elastomer component is dispersed in the rigid SAN copolymer matrix. The electron photomicrographs in Figure 6 show the difference in morphology of mass vs emulsion ABS polymers. The differences in structure of the dispersed phases are primarily a result



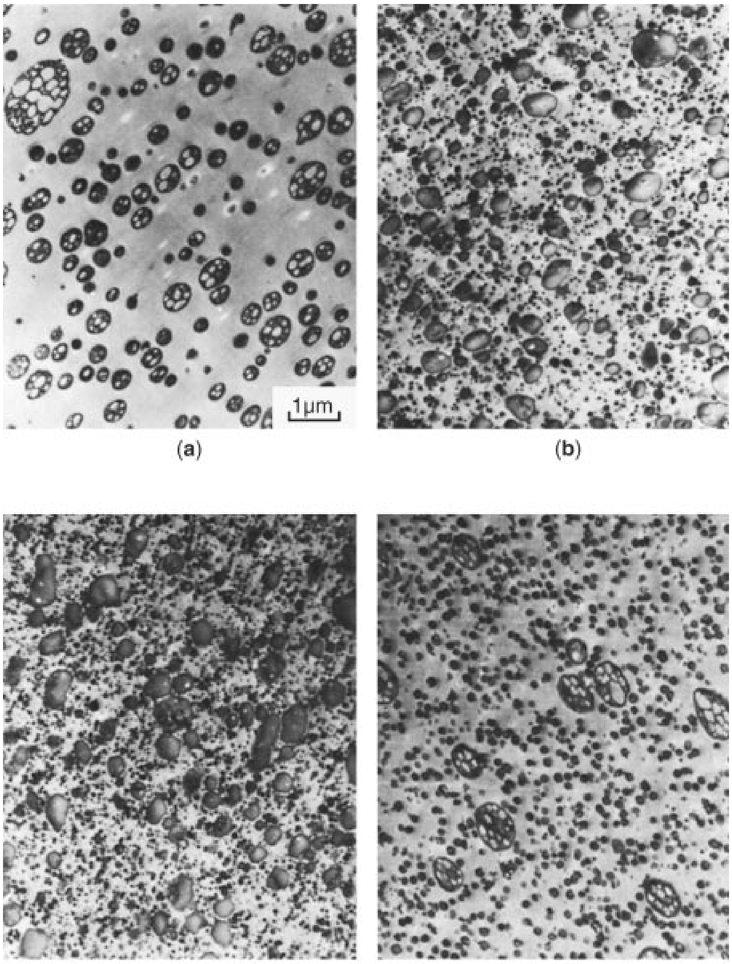
(a) (b)

(c) (d)

Fig. 5. Electron photomicrographs of several HIPS resins prepared using different types of rubbers.

of differences in production processes, types of rubber used, and variation in rubber concentrations.

Because of the possible changes in the nature and concentration of the rubber phase, a wide range of ABS polymers is available. Generally, they are rigid, showing a modulus at room temperature of 1.8–2.6 GPa $((2.6-3.8)\times 10^5\,\text{psi})$, and have excellent notched impact strength at room temperature, ca 135–4.00 J/m (2.5–7.5 ft lb/in.), and at lower (eg, −40°C) temperatures, 50–140 J/m (0.94–2.6 ft lb/in.). This combination of stiffness, impact strength, and solvent resistance makes ABS polymers particularly suitable for demanding applications. Another important attribute of several ABS polymers is their minimum



(a) (b) (c) (d)

Fig. 6. Electron photomicrographs of some commercial ABS resins produced by bulk, emulsion, or a mixture of the two: (**a**) Dow ABS 340; (**b**) Borg-Warner Cycolac T-1000; (**c**) United States Steel Kralastic 606ED, ACFXS53972; and (**d**) Monsanto Lustrex I-448. Scale in (**a**) applies to all photomicrographs.

tendency to orient or develop mechanical anisotropy during molding (28,77). Accordingly, uniform tough moldings are obtained. In addition, ABS polymers exhibit good ease of fabrication and produce moldings and extrusions with excellent gloss, which can be decorated by many techniques, eg, lacquer painting, vacuum metallizing, and electroplating (78–81). In the case of electroplating, the strength of the molded piece is significantly improved (77). When an appropriate decorative coating or a laminated film is applied, ABS polymers can be used outdoors (82).

ABS can be blended with bisphenol A polycarbonate resins to make a material having excellent low temperature toughness. The most important application of this blend is for automotive body panels.

When inherent outdoor weatherability is important, acrylonitrile–ethylene–styrene (AES) or acrylonitrile–styrene–acrylate (ASA) materials are typically used. These materials utilize ethylene–propylene (EP) copolymers and poly(butyl acrylate), respectively, as the rubber phase. EP and poly(butyl acrylate) rubbers are inherently more weatherable than polybutadiene because they are more saturated, leaving fewer labile sites for oxidation (83). Even though AES and ASA polymers are more weatherable than ABS, additives are needed to stabilize the materials against outdoor photochemical degradation for prolonged periods. Additive packages for AES and ASA weatherable materials generally contain both uv absorbers and hindered amine light stabilizers. Typical outdoor applications for weatherable polymers include recreational vehicles, camper tops, and swimming pool accessories. The extremely hostile environments where these stabilized AES materials are utilized still take their toll on the materials. Over prolonged periods of use, the surface gains a chalky appearance as the polymer degrades. Serious discoloration can also result and has been found to be caused by degradation of the additives (84).

High heat ABS resins are produced by adding a third monomer to the styrene and acrylonitrile to stiffen the polymer backbone, thus raising the T_g. Two monomers used commercially for this purpose are α-methylstyrene (85) and *N*-phenylmaleimide (86).

Not only are ABS polymers useful engineering plastics, but some of the high rubber compositions are excellent impact modifiers for poly(vinyl chloride) (PVC). Styrene–acrylonitrile-grafted butadiene rubbers have been used as modifiers for PVC since 1957 (87).

Rubber modification of styrene copolymers other than HIPS and ABS has been useful for specialty purposes. Transparency has been achieved with the use of methyl methacrylate as a comonomer; styrene–methyl methacrylate copolymers have been successfully modified with rubber. Improved weatherability is achieved by modifying SAN copolymers with saturated, aging-resistant elastomers (88).

3.6. Glass-Reinforced Styrene Polymers. Glass reinforcement of PS and SAN markedly improves mechanical properties. The strength, stiffness, and fracture toughness are generally doubled at least. Creep and relaxation rates are significantly reduced and creep rupture times are increased. The coefficient of thermal expansion is reduced by more than one half, and generally response to temperature changes is minimized (89). Normally, ca 20 wt% glass fibers, eg, 6-mm long, 0.009-mm dia E glass, can be used to achieve these improvements. PS, SAN, HIPS, and ABS have been used with glass reinforcement.

Four approaches are available for producing glass-reinforced parts: use of preblended, reinforced molding compound; blending of reinforced concentrates with virgin resin; a direct process, in which the glass is cut and weighed automatically and blended with the polymer at the molding machine; and general inplant compounding (77). The choice of any of these processes depends primarily on the size of the operation and the corresponding economics. The use of concentrates, eg, 80 wt% glass–20 wt% PS, for the subsequent blending to ca 20 wt% glass in the final product has many attractive features and seems to be appropriate for a medium-sized operation, whereas the direct process is emphasized in very large-scale operations.

4. Degradation

Like almost all synthetic polymers, styrene plastics are susceptible to degradation by heat, oxidation, uv radiation, high energy radiation, and shear, although in normal use only uv radiation imposes any real limit on the general usefulness of these plastics (90,91). Thus, it is generally recommended that the use of styrene plastics in outdoor applications be avoided.

Typically, PS loses about 10% of its M_w when it is fabricated. A significant amount of research has been carried out to determine the nature of the weak links in PS (92–95). Various modes of initiation of degradation mechanisms have been proposed: (*1*) chain-end initiation, (*2*) random scission initiation, and (*3*) scission of weak links in the polymer backbone. It has been suggested that chain-end initiation is the predominant mechanism at 310°C, whereas random scission produces stable molecules. Evidence for weak-link scissions comes mainly from studies showing loss of molecular weight vs degradation time. These plots usually show a rapid initial drop in molecular weight indicating initial rapid weak-link scission. However, the picture is also complicated by the fact that the mechanism of degradation is temperature-dependent. It appears that weak-link scissions taking place at high temperatures initiate depolymerization whereas at lower temperatures scissions simply cause a decrease in molecular weight. In any case, a clear difference in thermal stability has been shown between PS produced using free-radical (FRPS) and anionic (APS) polymerization (Fig. 7). This difference is due mainly to the initiator-derived fragments that remain in the polymer after isolation.

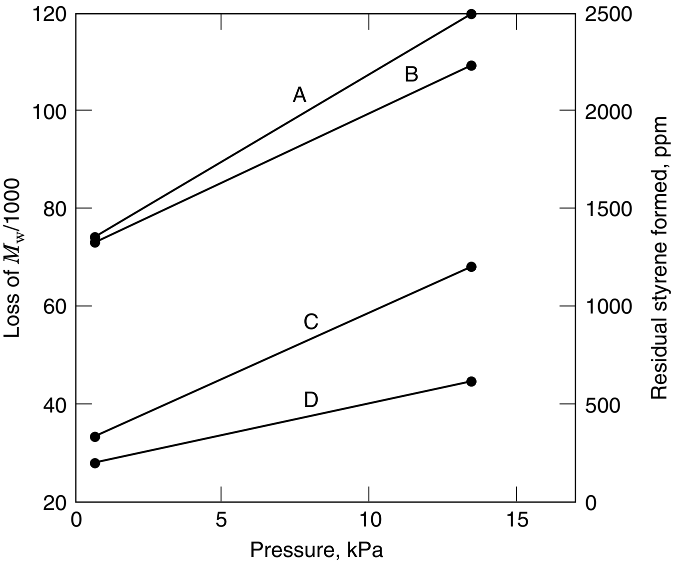


Fig. 7. Comparison of the thermal stability, ie, formation of monomer and loss of M_w, of FRPS and APS upon heating for 2.5 h at 285°C in glass tubes sealed at 0.67 or 13.3 kPa. A is FRPS residual styrene formed; B, FRPS M_w loss; C, APS M_w loss; and D, APS residual styrene formed. To convert kPa to mm Hg, multiply by 7.5.

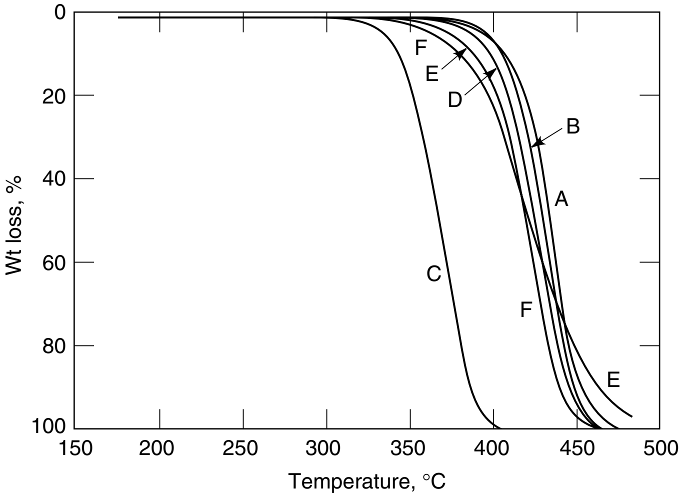


Fig. 8. Thermogravimetric analysis of polymers and copolymers of styrene in nitrogen at 10°C/min: A represents PS; B, poly(vinyltoluene); C, poly(α-methylstyrene); D, poly(styrene-*co*-acrylonitrile), with 71.5% styrene; E, poly(styrene-*co*-butadiene), with 80% styrene; and F, poly(styrene-*co*-methylstyrene), with 75% styrene.

Poly(α-methylstyrene) unzips to monomer exclusively. Figure 8 is a comparison of the thermal stability of several copolymers. Thermal oxidative degradation of PS occurs much faster, leading to additional volatile components consisting of aldehydes and ketones, yellowing of the polymer with a very dramatic drop in molecular weight, and some cross-linking. Rates and yields are highly oxygen- and temperature-sensitive. Figure 9 shows the magnitude of oxidative attack on PS and the extent to which an antioxidant can protect the polymer.

5. Environmental Considerations

Polystyrene has received much public and media attention and has been described as being nondegradable, nonrecyclable, toxic when burned, landfill-choking, ozone-depleting, wildlife-killing, and even carcinogenic. These misconceptions regarding PS have resulted in boycotts and bans across North America. In 2003, total generation (before recycling) was 26×10^6 t. Plastics represented 11.3% of this volume, PS represents less than 0.5% of the solid waste going to landfills (96,97).

The approach that the plastics industry has taken in managing plastics waste is an integrated one of source reduction, recycling, incineration for energy recovery, reduction of litter, development of photodegradable plastics for specific litter-prone applications, the development of biodegradable plastics, and increasing public awareness of the recyclability and value of PS. The balance of these approaches varies from year to year depending on public concerns, political pressures, legislation, technological advancement, and the development of an understanding of the actual contribution of plastics to total solid-waste generation.

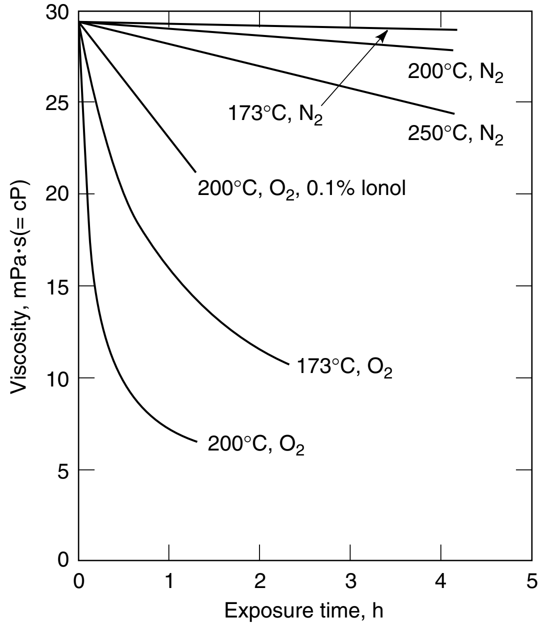


Fig. 9. Thermal and thermooxidative degradation of PS. Viscosity is for a 10% solution in toluene at 25°C.

5.1. How Plastics are Recycled.

According to the American Plastics Council (APC), more than 1,800 U.S. businesses handle or reclaim post-consumer plastics. Plastics from MSW are usually collected from curbside recycling bins or drop-off sites. Then, they go to a material recovery facility, where they are sorted either mechanically or manually from other recyclables. The resulting mixed plastics are sorted by plastic type, baled, and sent to a reclaimer. At the reclaiming facility, the scrap plastic is passed across a shaker screen to remove trash and dirt, and then washed and ground into small flakes. A flotation tank then further separates contaminants, based on their different densities. Flakes are then dried, melted, filtered, and formed into pellets. The pellets are shipped to product manufacturing plants, where they are made into new plastic products (97).

The patent literature contains information on reclamation of polystyrene from waste (98,99).

5.2. Environmental Degradation.

Natural sunlight emits energy only in wavelengths above 290 nm. Therefore any polymer that does not absorb light energy at wavelengths above 290 nm should not be photodegradable. The activation spectrum of PS vs the intensity of the solar spectrum is shown in Figure 10. Polystyrene, the degradation of which can be activated by radiation at wavelengths above 290 nm, is quite photodegradable and must be stabilized by the addition of uv-absorbing additives if it is to be used in outdoor applications where durability is important.

Even though PS is naturally quite photodegradable, there have been considerable efforts to accelerate the process to produce so-called photodegradable PS (100–103). The approach is to add photosensitizers, typically ketone

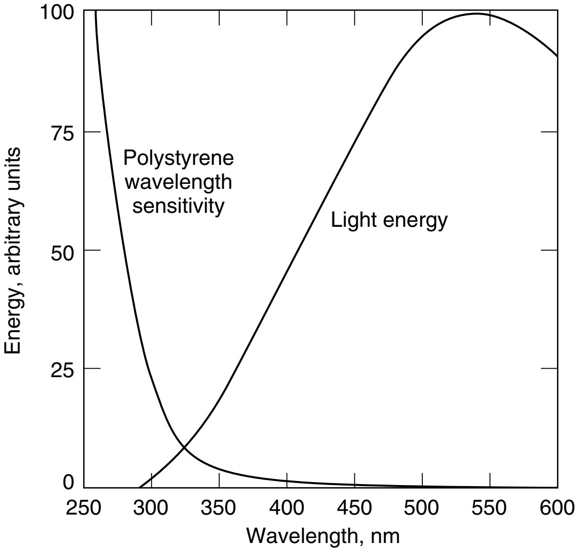
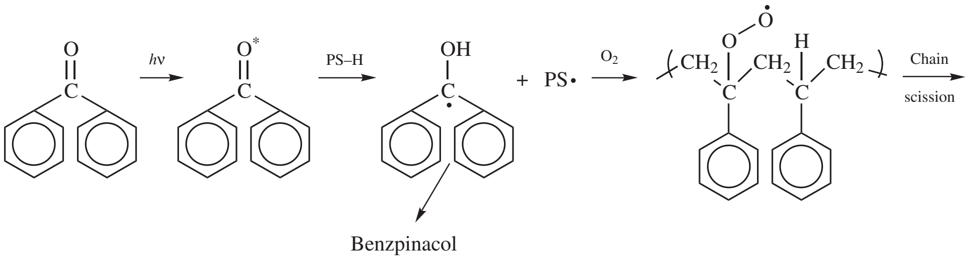


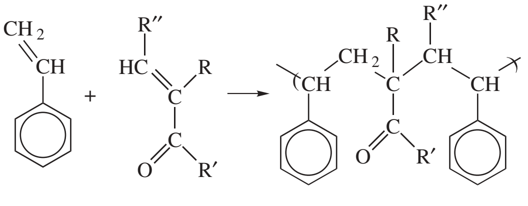
Fig. 10. Energy of the solar spectrum vs the wavelength sensitivity of PS.

containing molecules, that absorb sunlight, eg, benzophenone. The absorbed light energy is then transferred to the polymer to cause backbone scission via an oxidation mechanism:



Photodegradable PS is useful in litter-prone applications, eg, fast food packaging.

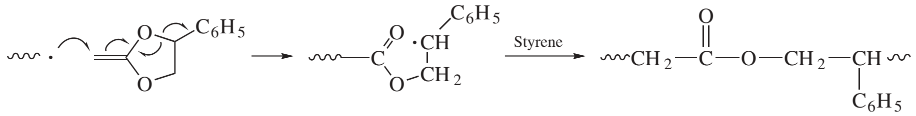
A more effective approach to enhancing the rate of photodegradation of PS is to copolymerize styrene with a small amount of a ketone-containing monomer. Thus the ketone groups are attached to the polymer during its manufacture (100,102).



Attaching the ketone groups to the polymer backbone is more efficient on a chain scission/ketone basis because some of the light energy that the pendent ketone absorbs leads directly to chain scission via the Norrish type II mechanism, as well as photooxidation via the Norrish type I mechanism (see POLYMERS, ENVIRONMENTALLY DEGRADABLE).

A key problem with the manufacture of photodegradable PS containing low levels of methyl vinyl ketone and methyl isopropenyl ketone is their human toxicity. This problem has been solved by adding the β-ketoalcohol intermediate, formed during vinyl ketone manufacture, to the styrene polymerization and generating the α,β-unsaturated ketone *in situ* (103). A concern in the use of photodegradable PS is the environmental impact of the products of photooxidation. However, photodegraded PS is expected to be more susceptible to biodegradation because the molecular weight has been reduced, the PS chains have oxidized end groups, the incorporation of oxygen as alcohol and ketone groups has increased the hydrophilicity of the PS fragments, and the surface area has increased (104–106).

5.3. Biodegradation. PS is inherently resistant to biodegradation mainly on account of its hydrophobicity. Efforts have been made to enhance the biodegradability of PS by inserting hydrolyzable linkages, eg, ester and amide, into its backbone. This was accomplished by adding monomers to the polymerization which are capable of undergoing ring-opening copolymerization (107).



5.4. Blowing Agents. Until the mid-1980s, the most common blowing agents for extruded PS foams were chlorofluorocarbons (CFCs) (see FLUORINATED AROMATIC COMPOUNDS). However, when these materials were shown to contribute to the ozone depletion problem, a considerable effort to find alternative blowing agents for the manufacture of extruded PS foam emerged. Most of the research has focused on the development of carbon dioxide foaming technology for PS (108). By contrast, PS bead foam uses hydrocarbon blowing agents, eg, pentane. Hydrocarbon blowing agents are extremely flammable and add volatile organic compounds to the atmosphere.

6. Polymerization

Styrene [100-42-5] and most of its derivatives are among the few monomers that can be polymerized by all four distinct mechanisms, ie, anionic, cationic, free-radical, and Ziegler-Natta. These include processes dependent on electromagnetic radiation, which is usually a free-radical mechanism, or high energy radiation, which is either a cationic or free-radical mechanism, depending on the water content of the system. All mechanisms, other than Ziegler-Natta, generally yield polymers with a high degree of random placement of the phenyl group relative to the backbone, ie, the polymers are classified as atactic and amorphous. Anionically made PS is usually atactic and amorphous, but in some cases, eg, at low temperatures, isotactic PS has been prepared.

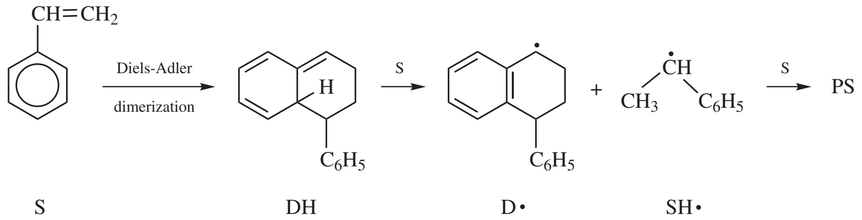
Each of the mechanisms used to polymerize styrene has its own unique advantages and disadvantages. In the anionic mechanism, initiation, propagation, and termination steps are sequential, resulting in the formation of narrow polydispersity ($M_w/M_n < 1.1$). The termination step is controlled, allowing control of end-group structure. However, the polymerization feed must be purified. High molecular weight polymers are difficult to make by the cationic mechanism on account of instability of the polystyryl carbocation giving fast termination. In addition, polymerization feed must be purified. Free-radical initiation, propagation, and termination steps are simultaneous, resulting in the formation of broad polydispersity ($M_w/M_n > 2$). Multiple termination paths lead to a variety of end groups. However, the polymerization feed need not be purified. In the Ziegler-Natta method, metal complexes allow stereospecific polymerization, resulting in the formation of high melting crystalline tactic PS. The polymerization feed must be purified.

Free-radical polymerization is the preferred industrial route both because monomer purification is not required (109) and because initiator residues need not be removed from polymer for they have minimal effect on polymer properties.

Styrene–butadiene block copolymers are made with anionic chain carriers, and low molecular weight PS is made by a cationic mechanism (110). Analytical standards are available for PS prepared by all four mechanisms (see INITIATORS, ANIONIC).

6.1. Free-Radical Polymerization. The styrene family of monomers are almost unique in their ability to undergo spontaneous or thermal polymerization merely by heating to >100°C. Styrene in essence acts as its own initiator. The mechanism by which this spontaneous polymerization occurs has challenged researchers since the 1940s. Two mechanisms explaining spontaneous styrene polymerization have been proposed and supported by considerable circumstantial evidence. The oldest mechanism, first postulated by Flory (111), involves a bond-forming reaction between two molecules of styrene (S) to form a 1,4-diradical. However, experiments to test the mechanism showed that there was no significant difference in the molecular weight of PS initiated by monoradicals compared with the spontaneously initiated polymerizations taken to the same monomer conversion (112). It thus became clear that the initiating species was not a diradical. Evidences favoring this mechanism include the identification of *cis*- and *trans*-1,2-diphenylcyclobutanes as principal dimers (113,114), and the large differences between spontaneous and chemically initiated (azobisisobutyronitrile) styrene polymerizations in the presence of the free-radical scavenger 1, 1′-diphenyl-2-picrylhydrazyl (DPPH). The rate of consumption of DPPH is 25 times faster than that expected from polymerization rate measurements. This difference was explained by the spontaneous formation of diradicals, many of which become self-terminated before initiating polymer radicals (115).

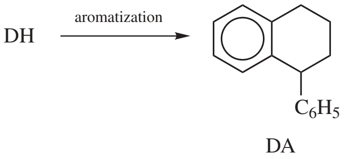
The second mechanism, proposed by Mayo (116), involves the Diels-Alder reaction of two styrene molecules to form a reactive dimer (DH) followed by a molecular assisted homolysis between DH and another styrene molecule.



The Mayo mechanism has been generally preferred even though critical reviews (113,117) have pointed out that the mechanism is only partially consistent with the available data. Also, the postulated intermediate DH has never been isolated. Evidences supporting the mechanism include kinetic investigations (118,119), isotope effects (117), and isolation/structure determination of oligomers (117,120). Even though the reactive dimer intermediate DH has never been isolated, the aromatized derivative DA has been detected in PS (120). Also, D has been indicated as an end-group in PS using ^{1}H-nmr and uv spectroscopy (121).

The Flory and Mayo proposals can be combined by the common diradical ·D·, which collapses to either DH or 1,2-diphenylcyclobutane. Nonconcerted Diels-Alder reactions are permissible for two nonpolar reactants (122).

The spontaneous polymerization of styrene was studied in the presence of various acid catalysts (123) to see if the postulated reactive intermediate DH could be intentionally aromatized to form inactive DA. The results showed that the rate of polymerization of styrene is significantly retarded by acids, eg, camphorsulfonic acid, accompanied by increases in the formation of DA. This finding gave further confirmation of the intermediacy of DH because acids would have little effect on the cyclobutane dimer intermediate in the Flory mechanism.



A potentially important commercial benefit of adding an acid catalyst to the spontaneous free-radical polymerization of styrene is that a significant shift results in the rate–molecular weight curve for PS. This shift (Fig. 11) is most pronounced at high molecular weights, thus allowing formation of high molecular weight PS at much faster polymerization rates. An explanation for this phenomenon is that the rate of formation of initiating radicals is reduced in the presence of acid. To return the rate of initiating free-radical formation back to a higher level, the temperature must be increased. The increased temperature increases the rate of propagation. The main mechanism of termination is radical coupling (124), the rate of which is most affected by radical concentration. Because the polymerization temperature can be raised in the presence of acid

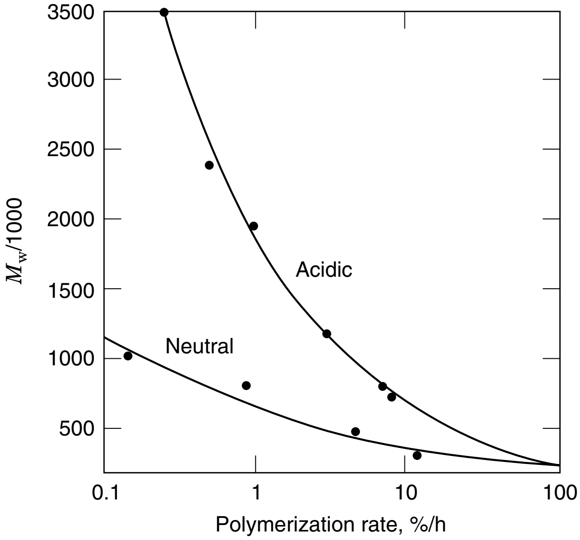


Fig. 11. Polymerization rate vs molecular weight relationship for spontaneous bulk styrene polymerization under neutral and acidic conditions.

without increasing free-radical concentration, the propagation rate is increased relative to termination rate, thereby raising the molecular weight. Other mechanisms of termination include chain-transfer with solvent and with the Diels-Alder dimer (DH), and disproportionation between two polystyryl radicals.

PS produced by the spontaneous initiation mechanism is typically contaminated by dimers and trimers (1–2 wt/wt). These oligomers are somewhat volatile and cause problems during extrusion (vapors) and molding (mold sweat) operations. The use of chemicals to generate initiating free radicals significantly reduces the formation of the oligomers. Oligomer production is reduced because the polymerization temperature can be lowered to slow down the Diels-Alder dimerization reaction. A wide range of free-radical initiators are available. They differ mainly in the temperature at which each generate free radicals at a useful rate. Typically, it is best to polymerize styrene at about the 1-h half-life temperature of the initiator it contains.

Initiators (qv) that have been utilized to initiate styrene polymerization can be generally categorized into three types: peroxides, azo, and carbon–carbon (125). Peroxides are thermally unstable, decomposing by homolysis of the O–O bond and resulting in the formation of two oxy radicals. Azo compounds decompose by concerted homolysis of the N–C bonds on either side of the azo linkage, resulting in extrusion of nitrogen gas and the formation of two carbon-centered radicals. Carbon–carbon initiators decompose by homolysis of a sterically strained C–C bond, resulting in the formation of two carbon-centered radicals. The radicals that initiate styrene polymerization end up attached to the chain ends and may have an effect on polymer stability (126–129).

Because most of the bulk PS reactors were originally designed to produce spontaneously initiated PS in the 100–170°C temperature range, the peroxide initiators used generally have 1-h half-lives in the range of 90–140°C. If the

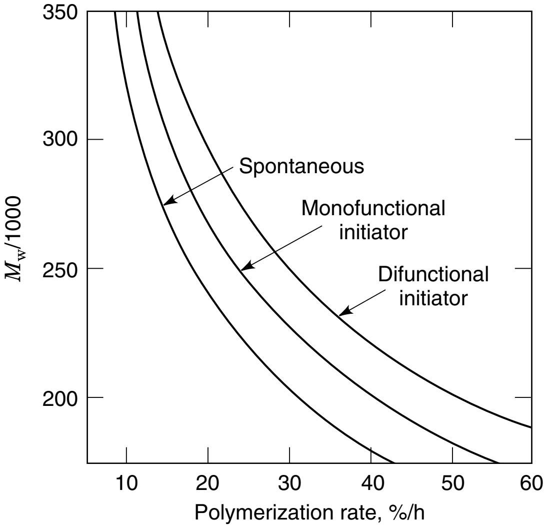


Fig. 12. Polymerization rate advantage of difunctional initiator.

peroxide decomposes too rapidly, a runaway polymerization could result; if it decomposes too slowly, peroxide exits the reactor. Because organic peroxides are significantly more expensive than styrene monomer (5–20 times), it is economically prudent to choose an initiator that is highly efficient and entirely consumed during the polymerization.

Another economically driven objective is to utilize initiators that increase the rate of styrene polymerization to form PS having the desired molecular weight. The commercial weight average molecular weight (M_w) range for general-purpose PS is 200,000–400,000. For spontaneous polymerization, the M_w is inversely proportional to polymerization rate (Fig. 12).

The main reason that the M_w decreases as the polymerization temperature increases is the increase in the initiation and termination reactions, which leads to a decrease in the kinetic chain length (Fig. 13). At low temperature, the main termination mechanism is polystyryl radical coupling, but as the temperature increases, radical disproportionation becomes increasingly important. Termination by coupling results in higher M_w PS than any of the other termination modes.

There are typically several different product grades produced in a single polymerization reactor; transition between these products in the minimum time maximizes production yield. Most PS producers rely on the use of kinetic modeling and computer simulation to aid in the manufacture of PS to minimize transition time between product grades. Kinetic models have been developed for styrene polymerization without added initiators (130–132), using one (133–137) or two (138) monofunctional initiators with different half-lives; and using symmetrical difunctional (Fig. 14**a**, **b** and **c**) or unsymmetrical difunctional initiators (Fig. 14**d** and **e**). These models clearly show the polymerization rate advantage of using initiators for the manufacture of PS using continuous bulk polymerization processes (see Fig. 12).

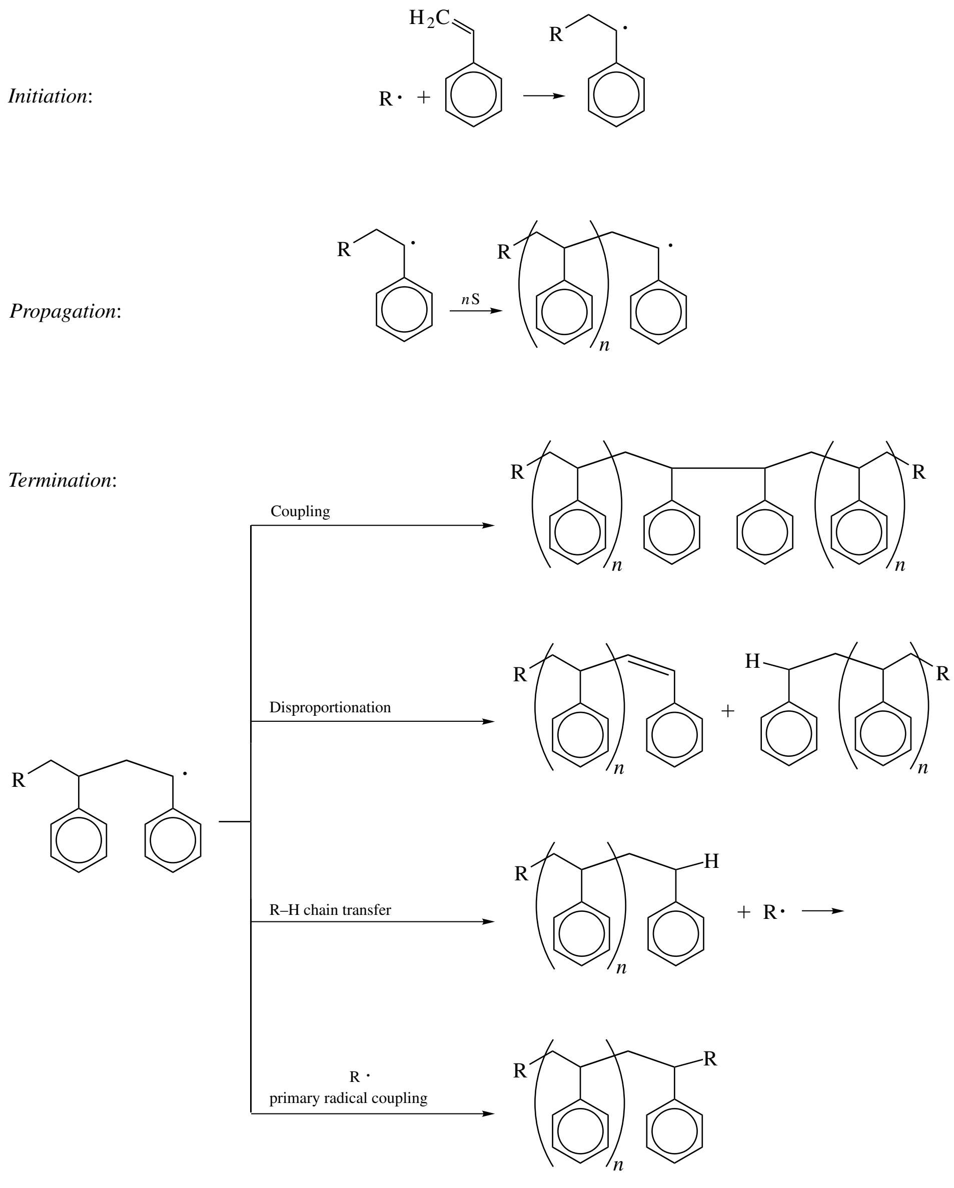


Fig. 13. General chemistry of free-radical styrene polymerization.

One of the key reasons for the polymerization rate advantage using difunctional initiators is their theoretical ability to form initiator fragments, which can initiate polymer growth from two different sites within the same fragment and ultimately lead to double-ended PS. If double-ended PS chains are produced, provided that the main mechanism of termination is chain coupling, higher M_w PS can be produced at faster rates using difunctional initiators (145).

Below 80°C, radical combination is the primary termination mechanism (146); above it, both disproportionation and chain transfer with the Diels-Alder

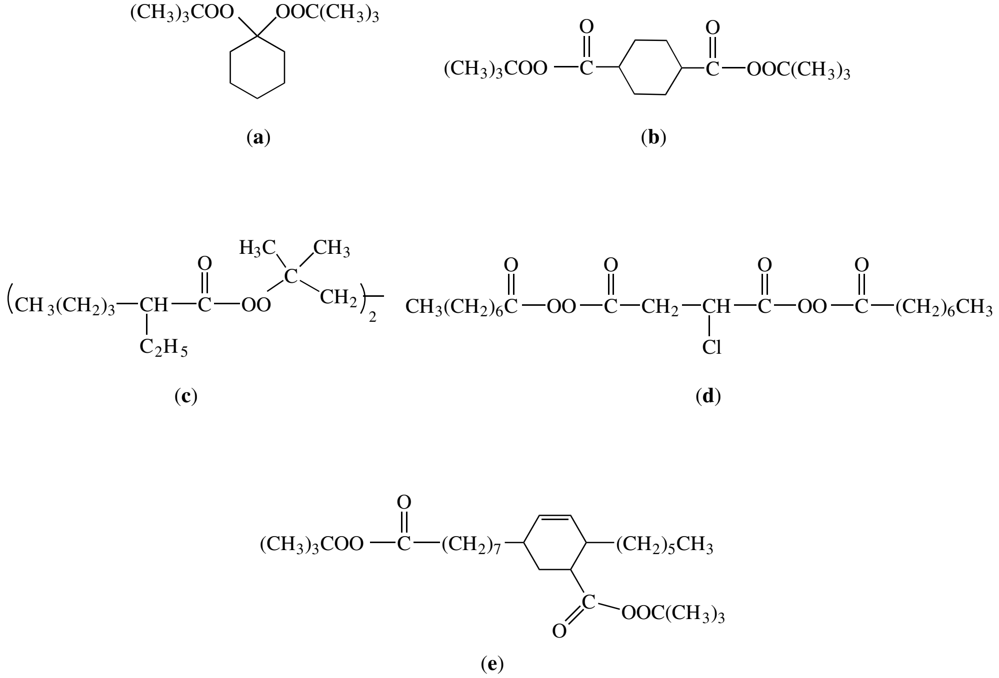


Fig. 14. Difunctional initiators for styrene polymerization: (**a**) (139), (**b**) (139), and (**c**) (140) are symmetrical difunctional; (**d**) (141,142) and (**e**) (143,144) are unsymmetrical difunctional initiators.

dimer are increasingly important. The gel or Trommsdorff effects, as manifested by a period of accelerating rate concomitant with increasing molecular weight, is apparent at below 80°C in styrene polymerization, although subtle changes during the polymerization at higher temperature may be attributed to variation of the specific rate constants with viscosity (146,147).

In some cases, inhibition of polymerization can be regarded as a special type of chain transfer. This is of importance in commercial-scale operations involving styrene storage for extended periods. The majority of inhibitors are of the phenolic/quinone family. All of these species function as inhibitors only in the presence of oxygen. 4-*tert*-Butylcatechol (TBC) at 12–50 ppm is the most universally used inhibitor for protecting styrene. At ambient conditions and with a continuous supply of air, TBC has a half-life of 6–10 weeks (148). The requirement of oxygen causes complex side reactions, resulting in significant oxidation of the monomer, which causes yellow coloration, especially in the vapor phase. An inert gas blanket reduces this problem as well as flammability hazards, but precautions must be taken to ensure an adequate level of dissolved oxygen in the liquid phase. Another family of inhibitors is that characterized by the N–O bond, which does not seem to require oxygen for effectiveness. This family includes a variety of nitrophenol compounds, hydroxylamine derivatives, and nitrogen oxides (149,150). Nitric oxide is particularly useful. Presumably, the function of this family depends on the unpaired electron associated with the N–O bond.

Other miscellaneous compounds that have been used as inhibitors are sulfur and certain sulfur compounds (qv), picrylhydrazyl derivatives, carbon black, and a number of soluble transition-metal salts (151). Both inhibition and acceleration have been reported for styrene polymerized in the presence of oxygen. The complexity of this system has been clearly demonstrated (152). The key reaction is the alternating copolymerization of styrene with oxygen to produce a polyperoxide, which at above 100°C decomposes to initiating alkoxy radicals. Therefore, depending on the temperature, oxygen can inhibit or accelerate the rate of polymerization.

Chain Transfer. Chain-transfer (CT) agents are occasionally added to styrene to reduce the molecular weight of the polymer, although for many applications this is unnecessary. Polymerization temperature alone is generally sufficient to achieve molecular weight control. Diluents, ie, materials with little or no chain-transfer activity, are sometimes used to reduce engineering problems. Some typical chain-transfer agents for styrene polymerization are listed in Table 4. The CT agents of commercial significance are α-methylstyrene dimer, terpinolene, dodecane-1-thiol, and 1,1-dimethyldecane-1-thiol. Chain transfer to styrene monomer has been reported, but some work strongly suggests that this reaction is negligible and transfer with the Diels-Alder dimer is the actual inherent transfer reaction (153,154). Chain transfer to PS has received some attention, but experiments indicate that it is minimal (155,156). If it did occur at a significant extent, then the polymer would be branched. The CT constants of several common solvents and CT agents are also shown in Table 4.

High levels of CT agents can be used to control the termination process. If the CT agent has a functional group attached to it, the functional group ends up becoming attached to the end of the PS chain. If the functionalized CT agent operates by donating an H atom to the polystyryl radical, the functional group ends up becoming attached to only one end of the PS chain. However, this technique does not quantitatively functionalize the polymer chains because not all chains get initiated by the functionalized CT agent fragment formed by loss of the H atom. However, if both the initiator and the CT agent contain the functional group, high purity one-end functional PS can be produced (157).

Another approach to control end-group structure is the use of CT agents that operate by an addition-fragmentation mechanism. This approach can lead to the formation of PS having functional groups at both ends if both the initiating

Table 4. **Chain-Transfer Constants (K_{ct}) in Free-Radical Styrene Polymerization**

Compound	K_{ct}	Temperature, °C
benzene	0.00002	100
toluene	0.00005	100
ethylbenzene	0.0002	100
isopropylbenzene	0.0002	100
α-methylstyrene dimer	0.3	120
1-dodecanethiol	13	130
1,1-dimethyl-1-decanethiol	1.1	120
1-hexanethiol	15	100

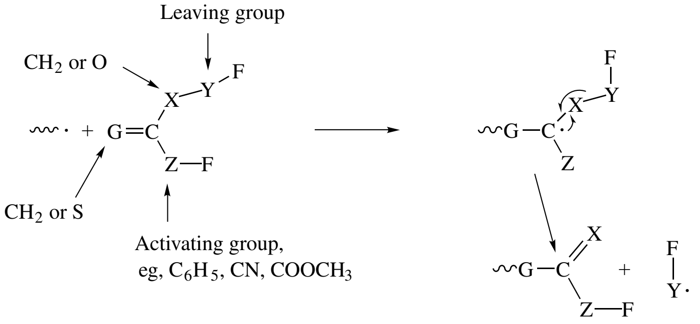


Fig. 15. Generic addition fragmentation CT structure and the mechanism of action, where F = functional group.

and terminating fragments contain functional groups (Fig. 15). It has been found that the common CT agent α-methylstyrene dimer operates by an addition-fragmentation mechanism (158). The use of addition-fragmentation CT agents also places a reactive double bond on one end of the polymer chain and thus yields a macromonomer. Copolymerization of the chain-end double bond with more styrene leads to branched PS.

6.2. Ionic Polymerization. Instead of a neutral unpaired electron, styrene polymerization can proceed with great facility through a positively charged species (cationic polymerization) or a negatively charged species (anionic polymerization). The polymerization reaction is more sensitive to impurities than the free-radical system, and pretreatment of the monomer is generally required (159). *n*-Butyllithium (NBL) is the most widely used initiator for anionic polymerization of styrene. In solution, it exists as six-membered aggregates, and a key step in the initiation sequence is dissociation yielding at least one isolated molecule.

If the initiation reaction is much faster than the propagation reaction, then all chains start to grow at the same time. Because there is no inherent termination step, the statistical distribution of chain lengths is very narrow. The average molecular weight is calculated from the mole ratio of monomer-to-initiator sites. Chain termination is usually accomplished by adding proton donors, eg, water or alcohols, or electrophiles such as carbon dioxide.

Anionic polymerization, if carried out properly, can be truly a living polymerization (160). Addition of a second monomer to polystyryl anion results in the formation of a block polymer with no detectable free PS. This technique is of considerable importance in the commercial preparation of styrene–butadiene block copolymers, which are used either alone or blended with PS as thermoplastics.

Anionic polymerization offers fast polymerization rates on account of the long life-time of polystyryl carbanions. Early studies have focused on this attribute, most of which were conducted at short reactor residence times (<1 h), at relatively low temperatures (10–50°C), and in low chain-transfer solvents (typically benzene) to ensure that premature termination did not take place. Also, relatively low degrees of polymerization (DP) were typically studied. Continuous commercial free-radical solution polymerization processes to make PS,

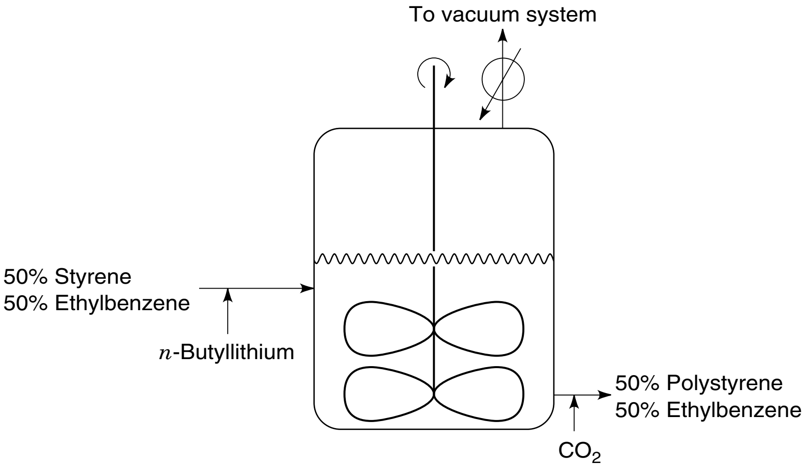


Fig. 16. Dow ebullient cstr anionic polymerization process.

on the other hand, operate at relatively high temperatures (>100°C), at long residence times (>1.5 h), utilize a chain-transfer solvent (ethylbenzene), and produce polymer in the range of 1000–1500 DP.

Two companies, Dow and BASF, have devoted significant research efforts to develop continuous anionic polymerization processes for PS. However, no PS is produced commercially using these processes. The Dow Chemical Company researchers utilized conventional free-radical polymerization reactors of the cstr type (161–165) to study the anionic polymerization of styrene, whereas BASF focused on continuous reactors of the linear flow type (166). In an anionic CSTR process, initiation, propagation, and termination are occurring simultaneously and thus the polydispersity of the resulting PS is ~2. A CT solvent (ethylbenzene) and relatively high temperatures (80–140°C) were also used. Under these conditions, chain transfer to solvent (CTS) is extremely high because the high monomer conversions (>99%) achieved under steady-state operation result in a large ratio (typically 500:1) of solvent to monomer. Figure 16 depicts the ebullient CSTR anionic process investigated by Dow researchers.

The result of high CTS is that very high yields of PS based on NBL (the most costly raw material) and PS having high clarity (low color) are produced (Fig. 17). Under stringent feed purification conditions, as high as 8000% yield based on NBL initiator (109) can be achieved. According to Figure 17, without high levels of CTS, it would be impossible to make a PS having sufficient clarity to meet the color requirements to be sold as prime resin. However, with no CTS, 640 ppm of NBL is required to produce a PS of 1000 DP.

One of the key benefits of anionic PS is that it contains much lower levels of residual styrene monomer than free-radical PS (167). This is because free-radical polymerization processes only operate at 60–80% styrene conversion, whereas anionic processes operate at >99% styrene conversion. Removal of unreacted styrene monomer from free-radical PS is accomplished using continuous devolatilization at high temperature (220–260°C) and vacuum. This process leaves about 200–800 ppm of styrene monomer in the product. Taking the

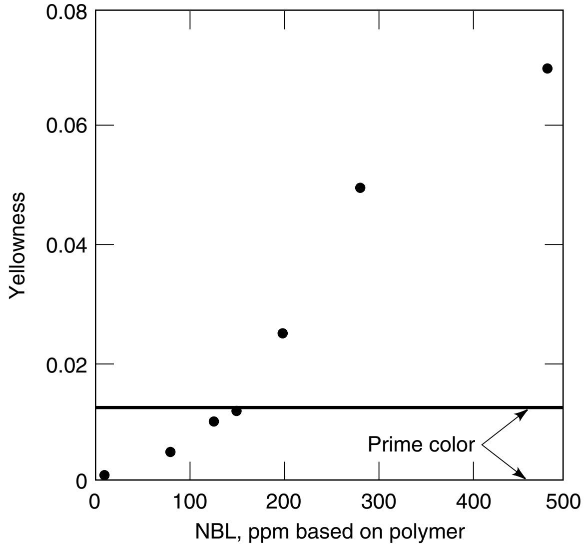


Fig. 17. PS color vs amount of *n*-butyllithium consumed for its production in a CSTR.

styrene to a lower level requires special devolatilization procedures such as steam stripping (168).

The BASF process utilizes continuous linear-flow reactors (LFR) with no back-mixing to make narrow polydispersity resins aimed at producing anionic PS. This process consists of a series alternating reactors and heat exchangers (Fig. 18). Inside the reactors, the polymerization exotherm carries the temperature from 30°C at the inlet to 90°C at the outlet. The heat exchangers then take the temperature back down to 30°C. This process, which requires no solvent, results in the formation of narrow polydispersity PS.

Continuous anionic polymerization conducted above the ceiling temperature (61°C) is also useful for making thermally stable styrene-co-α-methylstyrene (SAMS) having high α-methylstyrene (AMS) content. Preparation of SAMS having >20 wt% of AMS units using bulk free-radical polymerization leads to very slow polymerization rates, low molecular weight polymer, and the formation of high levels of oligomers. The preparation of SAMS using an anionic CSTR polymerizer operating at 90–100°C allows the production of SAMS having up to about 70 wt% AMS units (Fig. 19) (169). By conducting the polymerization above the ceiling temperature, no AMS polyads of more than two units are possible. SAMS copolymers having polyads of greater than two units in length are thermally unstable (170).

Cationic polymerization of styrene can be initiated either by strong acids, eg, perchloric acid, or by Friedel-Crafts reagents with a proton-donating activator, eg, boron trifluoride or aluminum trichloride with a trace of a protonic acid or water. The solvent again plays an important role, and chain-transfer reactions are very common where the reactants are polymer, monomer, solvent, and counterion. As a result, high molecular weights are more difficult to achieve and molecular weight distributions are often comparable to those obtained

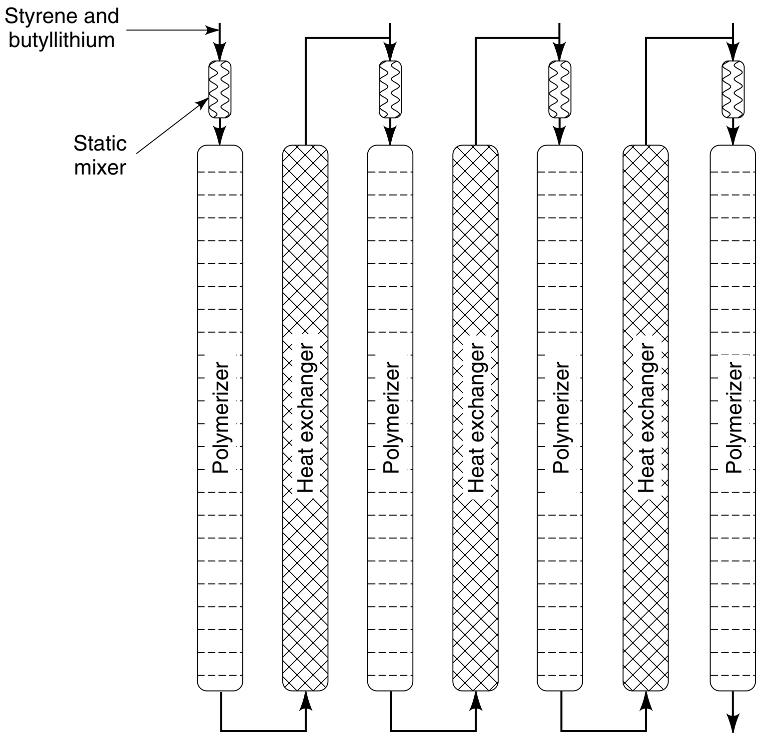


Fig. 18. BASF continuous anionic process.

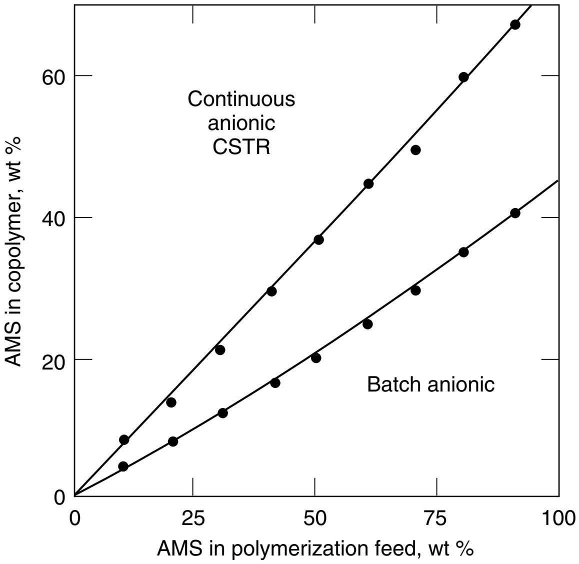


Fig. 19. Comparison of continuous (cstr) and batch anionic production of SAMS.

from free-radical polymerizations. Commercial use of cationic styrene polymerization is reported only where low molecular weight polymers are desired (110).

Considerable advances have taken place with regard to cationic polymerization of styrene. Its uses to make block copolymers and even living cationic polymerization have been reported (171).

Ziegler-Natta. Ziegler-Natta-initiated styrene polymerization yields stereoregular tactic PS. The tacticity can be isotactic (phenyl rings cis to each other) or syndiotactic (phenyl rings trans to each other), depending on the initiator structure. All commercially important styrenic plastics in the 1990s are amorphous because the vast excess of these polymers is made by a free-radical mechanism. However, Dow Chemical and Idemitsu Petrochemical Companies were working together to commercialize crystalline syndiotactic PS. SPS is produced using a bulk polymerization process. Because the SPS crystallizes as it forms, the polymerization process is challenging, requiring mixing and removal of the heat of polymerization from a sticky solid. Proper reactor design is required to keep the sticky mass from solidifying.

6.3. Living Styrene Polymerization. The requirements for a polymerization to be truly living are that the propagating chain ends must not terminate during polymerization. If the initiation, propagation, and termination steps are sequential, ie, all of the chains are initiated and then propagate at the same time without any termination, then monodisperse (ie, $M_w/M_n = 1.0$) polymer is produced. In general, anionic polymerization is the only mechanism that yields truly living styrene polymerization and thus monodisperse PS. However, significant research has been conducted to achieve living styrene polymerization using cationic, free-radical, and Ziegler-Natta mechanisms.

Since living free-radical polymerization (LFRP) was first proposed in 1982 (172,173), there has emerged a multitude of examples (174–182). However, significant controversy exist over the nature of the living chain-end and whether the process can really be called living. Instead, terms such as pseudo-living, quasi-living, resuscitatable, and dormant have been used to better describe the process. The process generally involves the addition of relatively stable free radicals to the polymerization. The growing polystyryl radicals are intercepted and terminated by coupling with the stable radicals, thereby minimizing termination by chain transfer and the coupling of polystyryl radicals with themselves. Prior to the discovery of LFRP, stable free radicals were only added to styrene as polymerization inhibitors. They acted as radical scavengers to stop the propagation process. However, the bond formed between the polystyryl radical and the stable free radical is somewhat labile and styrene can insert into the bond once it is activated by heat or photolysis. The main evidences used to support the living nature of the polymerization are the increase of molecular weight with monomer conversion, the formation of narrow-polydispersity PS, and the ability to prepare block copolymers. Normally free-radical polymerizations show relatively flat molecular weight vs conversion plots. Although the preparation of truly monodisperse ($M_w/M_n = 1.0$) PS using LFRP has yet been demonstrated, polydispersities approaching 1.1 have been reported for very low molecular weight PS prepared in the presence of stable nitroxyl radicals, ie, $M_w = 20,000$.

Most of the LFRP research in the 1990s was focused on the use of nitroxides as the stable free radical. The main problems associated with nitroxide-mediated styrene polymerizations are slow polymerization rate and the inability to make high molecular weight narrow-polydispersity PS. This inability is likely to be the result of side reactions of the living end leading to termination rather than propagation (183). The polymerization rate can be accelerated by the addition of acids to the process (184). The mechanism of the accelerative effect of the acid is not certain.

6.4. Copolymerization. Styrene readily copolymerizes with many other monomers spontaneously. The styrene double bond is electronegative on account of the donating effect of the phenyl ring. Monomers that have electron-withdrawing substituents, eg, acrylonitrile and maleic anhydride, tend to copolymerize most readily with styrene because their electropositive double bonds are attached to the electronegative styrene double bond. Spontaneous copolymerization experiments of many different monomer pair combinations indicate that the mechanism of initiation changes with the relative electronegativity difference between the monomer pairs (185).

Copolymerization makes possible dramatic improvements in one or more properties. There is a vast amount of literature on styrene-containing copolymers (186). The reactivity ratios for the monomer pairs are listed in Table 5. Styrene–acrylonitrile (SAN) copolymers are large-volume thermoplastics having improved mechanical properties and heat and solvent resistance with some loss of color stability (see ACRYLONITRILE POLYMERS, SURVEY AND STYRENE-ACRYLONITRILE (SAN)). The disparity of reactivity ratios shown in Table 5 implies an unequal insertion rate of the monomers into the copolymer. Figure 20 illustrates manifestations of this effect. Most SAN copolymers are manufactured at or near the azeotrope or cross-over point (A in Fig. 20) to avoid significant drift in composition (Fig. 21) (187,188). SAN copolymers having as little as a difference of 4 wt% in AN content are not miscible (44). Therefore the preparation of SAN under conditions where composition drift can occur leads to haze. Reactors have been designed to overcome composition drift problems on a commercial scale (189). All SAN copolymers produced in the United States are made in a mass or solution continuous process. The greater tendency of these copolymers to develop yellow coloration requires more attention to techniques of polymerization and devolatilization (190–193). The discoloration mechanism has been linked to both AN sequence distribution in the polymer backbone (194) and the thermal decomposition of oligomers (195–198).

Copolymers with butadiene, ie, those containing at least 60 wt% butadiene, are an important family of rubbers. In addition to synthetic rubber,

Table 5. **Free-Radical Copolymerization Reactivity Ratios, r^a**

Monomer 2	r_1	r_2	Temperature, °C
acrylonitrile	0.4	0.04	60
butadiene	0.5	1.40	50
methyl methacrylate	0.54	0.49	60
m-divinylbenzene	0.65	0.60	60

[a] Styrene = monomer 1.

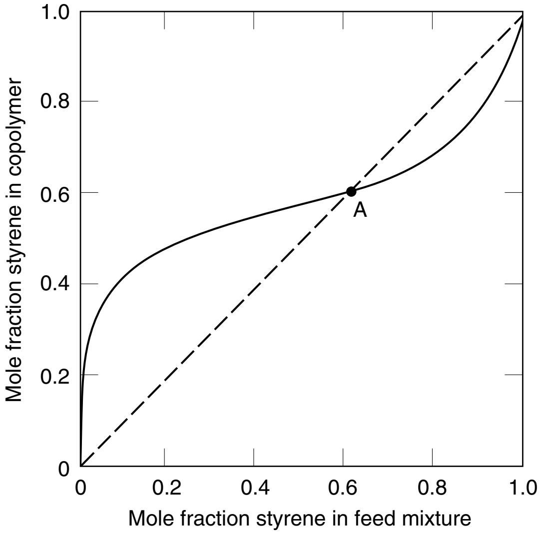


Fig. 20. Relationship between feed composition and copolymer composition of styrene–acrylonitrile copolymerization. See text.

these compositions have extensive uses as paper coatings, water-based paints, and carpet backing. Because of unfavorable reaction kinetics in a mass system, these copolymers are made in an emulsion polymerization system, which favors chain propagation but not termination (199). The result is economically acceptable rates with desirable chain lengths. Usually such processes are run batchwise in order to achieve satisfactory particle size distribution.

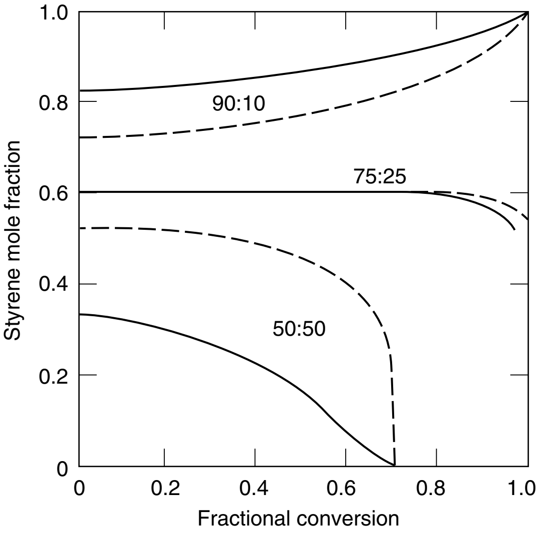


Fig. 21. Drift in monomer composition (—) and copolymer composition (– – –) with conversion for three initial monomer mixtures. Ratios are based on wt%.

Styrene–maleic anhydride (SMA) copolymers are used where improved resistance to heat is required. Processes similar to those used for SAN copolymers are used. Because of the tendency of maleic anhydride to form alternating copolymers with styrene, composition drift is extremely severe unless the polymerization is carried out in CSTR reactors having high degrees of back-mixing.

Divinylbenzene copolymers with styrene are produced extensively as supports for the active sites of ion-exchange resins and in biochemical synthesis. About 1–10 wt% divinylbenzene is used, depending on the required rigidity of the cross-linked gel, and the polymerization is carried out as a suspension of the monomer-phase droplets in water, usually as a batch process. Several studies have been reported on the reaction kinetics (200,201).

Polymerization of styrene in the presence of polybutadiene rubber yields a much tougher material than PS. Although the material is usually opaque and has a somewhat lower modulus, the gain in impact resistance has placed this plastic in wide commercial usage. The polymerization is complex because the rubber has sufficient reactivity, ie, at the allylic hydrogen and 1:2 addition units, to graft and cross-link, and the polymerization system is comprised of two phases. The graft copolymer of PS on polybutadiene acts as an emulsifier, stabilizing the dispersion against coalescence. Events taking place during this polymerization can be followed with the ternary phase diagram shown in Figure 22. For example, for a feed mixture made up of 8 wt% rubber in styrene (point A) on an increment of conversion to PS (to D), phase separation occurs. Small droplets of styrene–PS, which are stabilized by the graft copolymer, are dispersed in the styrene–polybutadiene solution. The composition of the two

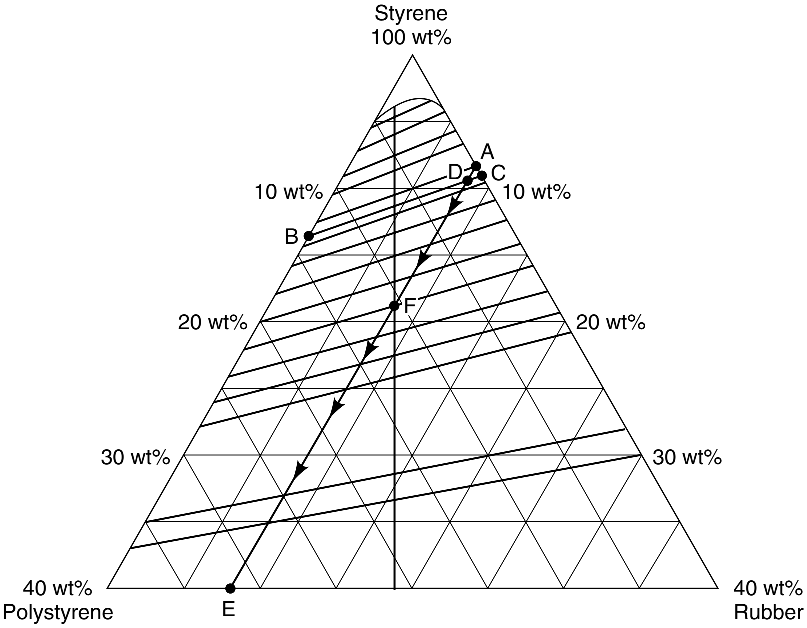


Fig. 22. Ternary-phase diagram for the system styrene–PS–polybutadiene rubber.

phases is given by points B and C for the PS-rich phase and polybutadiene-rich phase, respectively. The phase–volume ratio, ie, rubber phase/PS phase, is given by the ratio DB/DC. As the reaction proceeds along the line AE, the phase composition and phase–volume ratio can be read from the tie lines. Larger droplets of PS solution form and the small, original ones remain. When the phase–volume ratio is about unity (point F), provided that there is sufficient shearing agitation, the larger PS-containing droplets, which have mostly coalesced into large pools, become the continuous phase and polybutadiene-containing droplets are dispersed therein (202,203). However, the latter contain the small, original PS particles as occlusions.

The particle size and size distribution are largely controlled by the applied shear rate during and after phase inversion, the viscosity of the continuous phase, the viscosity ratio of the two phases, and the interfacial tension between the phases (51,202). The viscosity parameters depend on phase compositions, polymer molecular weights, and temperatures; the interfacial tension is largely controlled by the amount and structure of the graft copolymer available at the particle surface. Phase-contrast micrographs of this phase-inversion sequence, wherein the PS phase is dark, are shown in Figure 23. If shearing agitation is insufficient, then phase inversion does not occur and the product obtained is a network of cross-linked rubber with PS and its properties are much inferior. The morphology of the dispersed rubber phase remains much as formed after phase inversion, unless there is a step change in phase concentration, eg, by blending streams. Rubber-phase volume, including the occlusions, largely controls performance. Izod impact strength depends on rubber particle size and varies from 48 J/m (0.9 ft·lbf/in.) at an average particle diameter of 0.6 μm to ∼100 J/m (1.9 ftbf/in.) at 3.5 μm diameter (204).

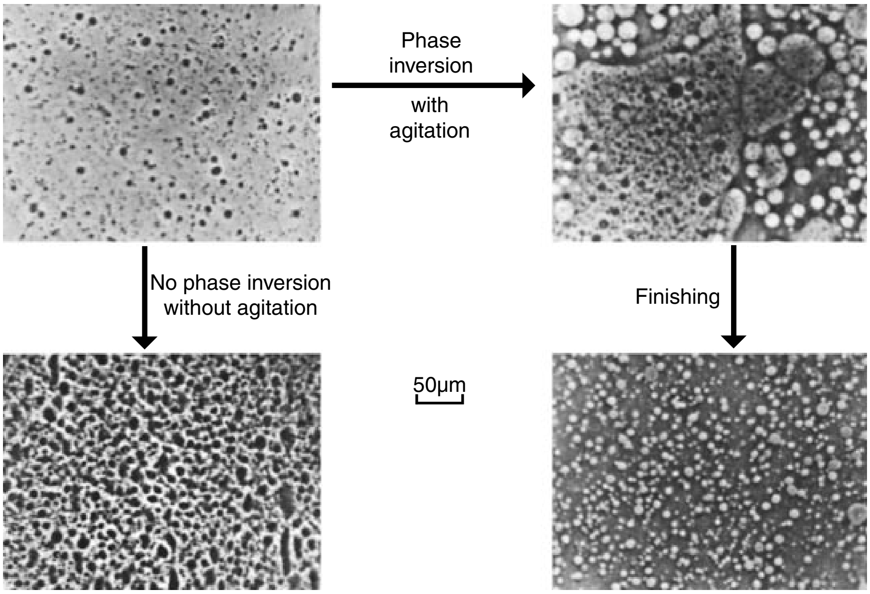


Fig. 23. Phase contrast photomicrographs showing particle formation via phase inversion.

Once the desired particle size and morphology with sufficient graft to provide adequate adhesion between the rubber particles and the PS phase have been achieved, the integrity of the particle must be protected against deformation or destruction during fabrication by cross-linking of the polybutadiene chains. These chemical changes taking place on the rubber begin with polymerization. Either anionic or Ziegler-Natta-polymerized polybutadiene is used at 5–10 wt% styrene. If peroxide initiators are used, about one half of the rubber is grafted by the time phase inversion occurs; less is grafted in the absence of peroxides (205).

Hydrogen abstraction by alkoxy radicals at any of the allylic sites yields a site for styrene polymerization, resulting in a graft (205,206). Model studies based on styrene–butadiene block copolymers show a strong influence of graft structure on particle morphology (51,52). The double bonds in polybutadiene are much less reactive than those in styrene but as conversion exceeds ca 80% and temperature approaches or exceeds 200°C, copolymerization through the polybutadiene (1,2 units) chain seems to occur and leads to cross-linking and hence gel formation (207).

7. Commercial Processes

There are two problems in the manufacture of PS: removal of the heat of polymerization (ca 700 kJ/kg (300 Btu/lb)) of styrene polymerized and the simultaneous handling of a partially converted polymer syrup with a viscosity of ca 10^5 mPa(=cP). The latter problem strongly aggravates the former. A wide variety of solutions to these problems have been reported; for the four mechanisms described earlier, ie, free radical, anionic, cationic, and Ziegler, several processes can be used. Table 6 summarizes the processes which have been used to implement each mechanism for liquid-phase systems. Free-radical polymerization of styrenic systems, primarily in solution, is of principal commercial interest. Details of suspension processes, which are declining in importance, are available

Table 6. **Process vs Mechanism for Styrene Polymerization**

	Mechanism			
Process	Free radical	Anionic	Cationic	Ziegler
mass/bulk	used for all styrene plastics	yes	yes	
solution	used for all styrene plastics	styrene–butadiene block copolymers	yes	yes
suspension	used for all styrene plastics			
precipitation	yes			
emulsion	used for styrene–butadiene latices and ABS plastics			

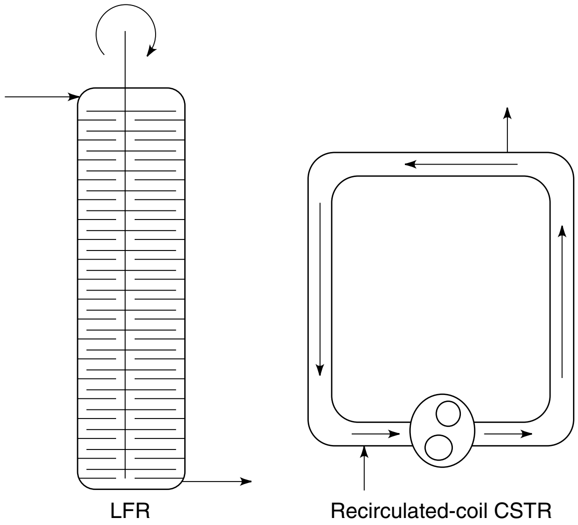


Fig. 24. Linear and CSTR reactor configuration used commercially for PS manufacture (see also Fig. 16).

(208,209), as are descriptions of emulsion processes (210) and summaries of the historical development of styrene polymerization processes (208,211,212).

Two types of reactors are used for continuous solution polymerization: the linear-flow reactor (lfr), approximating in the ideal case a plug-flow reactor, and the continuous-stirred tank reactor (CSTR), which ideally is isotropic in composition and temperature (Fig. 24) (see REACTOR TECHNOLOGY). LFR usually involve conductive heat transfer to many tubes through which a heat-transfer fluid flows. Multiple temperature zones can easily be achieved in a single reactor; agitation is provided by a rotating shaft with arms down the central axis of the tubular vessel. Reactors of this type operate for long periods and handle very high viscosity partial polymers with reliable heat-transfer coefficients. CSTRs are either of the recirculated coil configuration and rely on conduction to the cooled jacket for heat removal, or ebullient and makes use primarily of evaporative cooling to achieve temperature control. The limitation of this reactor occurs at high viscosity, when the rate of vapor disengagement is exceeded by the rate of vapor generation and the ability to mix in the condensed vapor. Typically, this limit occurs at 60–70 wt% solids. Figures 25 and 26 illustrate typical processes based on these two types of reactors. Most general-purpose, ie, unmodified PS is manufactured in the United States in such facilities. The LFR process (see Fig. 26) typically uses up to 20 wt% ethylbenzene mainly to reduce viscosity. The three reactors may each be subdivided into three temperature-control zones, which allow for flexible control of the molecular weight distribution of the polymer as well as optimum output per reactor volume. Temperatures are 100–170°C. At ca 80 wt% solids, the partial polymer is heated from 180 to 240°C before being devolatilized upon entering a vacuum tank. The recovered solvent and monomer are continuously recycled to the feed. The molten polymer leaves the vacuum tank and is stranded, cooled, and chopped into pellets for shipping. The CSTR process (see Fig. 25) differs in that it is typically a single

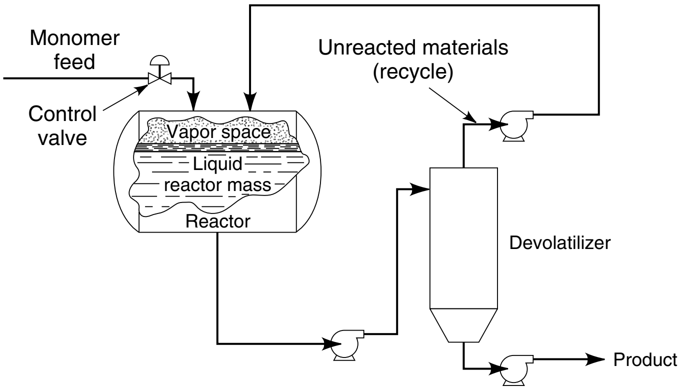


Fig. 25. Typical CSTR polymerization process.

reactor and, therefore, involves a single temperature zone, although more can be added, and operates at ca 60 wt% solids, requiring a large polymer heater to achieve adequate devolatilization (213,214).

There has been some research aimed at continuously converting monomer completely to polymer using reactive extrusion (215).

Rubber-modified PS manufacture places several additional demands: dissolving ca 5–10 wt% polybutadiene in styrene, often a 10–20-h process; shear conditions to achieve phase inversion and the desired particle size for a given product; control of phase compositions to produce the desired particle morphology; and sufficient time and temperature at the end of the process to achieve the necessary cross-linking, gel formation, and swelling index. Graft copolymer formation occurs throughout the polymerization, and sufficient amount of graft copolymer for phase stability is necessary at phase inversion. In the case of an

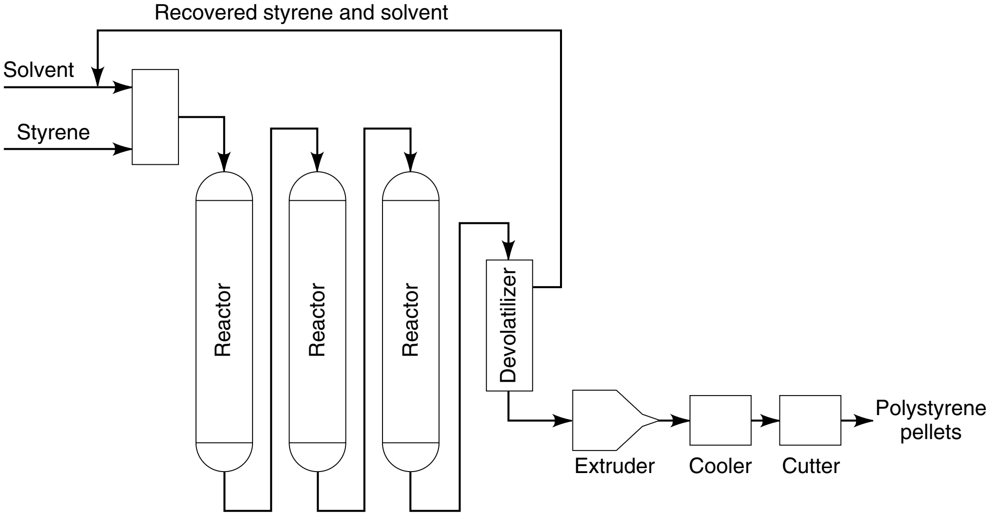


Fig. 26. Typical LFR polymerization process.

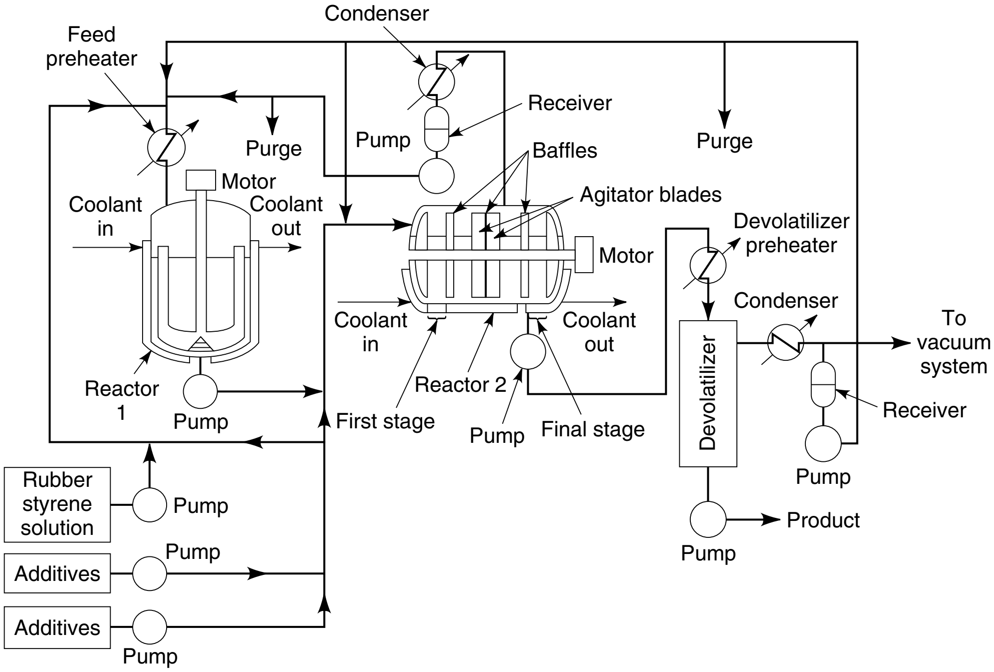


Fig. 27. Typical staged CSTR process for HIPS.

LFR system, only addition of a rubber dissolver is needed to meet the above requirements. For a CSTR-based system, multiple reactors in series are required to avoid rapid shifts in phase compositions on mixing of one reactor effluent with the next reaction contents with loss of desirable morphology (216,217). Figure 27 shows a multizone CSTR reactor system. Phase inversion and particle sizing are accomplished in the first-stage reactor with the effluent entering a single-tank, baffled reactor operating as five stages with a common vapor space. An alternative is three CSTR reactors in series, followed by an adiabatic reactor to achieve high solids content (216). Multiple stages are necessary to achieve favorable rubber particle morphology with CSTRs; LFR systems inherently avoid sudden phase composition changes, unless severe internal backmixing is allowed to occur.

Generally, phase inversion and particle sizing occur in the first reactor. Grafting rate is highest initially, and the amount formed is adequate to stabilize the particles. The shear field in the reactor is critical to control of particle size as well as to meet the minimum shear rate for phase inversion, without which the product consists of a continuous cross-linked rubber network with markedly inferior properties (202,203). After the particles are formed and sized, only gentle agitation is applied to aid heat transfer without disturbing the particle structure. Conditions that produce the desired PS-phase molecular weight are used. Prior to devolatilization, the partial polymer is heated to ca 200°C to cross-link the rubber chain in order to protect the rubber particles from the very high shear fields during fabrication. Stranding, cooling, and chopping into pellets follow.

Polybutadiene rubbers are used almost exclusively as reinforcing agents for styrenic plastics. The very low glass-transition temperature (−80°C or lower) gives good low temperature properties, and the allylic hydrogen atom and weakly active double bonds can provide the desired degree of grafting and cross-linking. Other rubbers have been used; acrylates, ethylene–propylene–diene rubbers, polyisoprene, and polyethylene have been reported, but with limited commercial success because of their low chemical reactivity, not withstanding their acceptable glass-transition temperature (218).

8. Fabrication

8.1. Injection Molding. There are two basic types of injection-molding machines in use: the reciprocating screw and the screw preplasticator (219). Their simple design, uniform melting temperature, and excellent mixing characteristics make them the preferred choice for injection molding. Machines with shot capacities up to 25 kg for solid injection-molded parts and 65 kg for structural foam parts are available (220,221). Large solid moldings include automotive dash panels, television cabinets, and furniture components. One-piece structural foam parts weighing 35 kg or more are molded for increased rigidity, strength, and part weight reduction (222) (see PLASTICS PROCESSING).

The injection-molding process is basically the forcing of melted polymer into a relatively cool mold where it freezes and is removed in a minimum time. The shape of a molding is defined by the cavity of the mold. Quick entry of the material into the mold followed by quick setup results in a significant amount of orientation in the molded part. The polymer molecules and, in the case of heterogeneous rubber-modified polymers, the rubber particles tend to be highly oriented at the surface of the molding. Orientation at the center of the molding tends to be significantly less because of the relaxation of the molten polymer.

The anisotropy that develops during the molding operation is detrimental to the performance of the fabricated part in several ways. First, highly oriented moldings, which form particularly if low melt temperatures are used, exhibit good gloss, have an abnormally narrow use-temperature range that causes early warping, and, perhaps most importantly, tend to be brittle even though the material is inherently capable of producing tough parts (223). However, this development of polymer orientation during molding can also be used to advantage, as in the case of rotational orientation during the molding operation (224).

The achievement of isotropic moldings is also important when the molded part is to be decorated, eg, painted or metallized. Highly oriented parts that have a high frozen-in internal stress memory tend to give rise to rough or distorted surfaces as a result of the relaxing effect of the solvents and/or heat. For electroplating ABS moldings, it is particularly important to obtain isotropic moldings. Isotropy can be achieved by the use of a high melt temperature, a slow fill speed, a low injection pressure, and a high mold temperature (80,81,225,226).

Injection molding of styrene-based plastics is usually carried out at 200–300°C. For ABS polymers, the upper limit may be somewhat less, because these polymers tend to yellow somewhat if too high a temperature and/or too long a residence time are imposed.

To obtain satisfactory moldings with good surface appearance, contamination, including that by moisture, must be avoided. For good molding practice, particularly with the more polar styrene copolymers, drying must be part of the molding operation. A maximum of 0.1 wt% moisture can be tolerated before surface imperfections appear.

For achieving appropriate economics, injection-molding operations are highly automated and require few operating personnel (219). Loading of the hopper is usually done by an air-conveying system; the pieces are automatically ejected, and the rejects and sprues are ground and reused with the virgin polymer. Also, hot probes or manifold dies are used to eliminate sprues and runners.

8.2. Extrusion. Extrusion of styrene polymers is one of the most convenient and least expensive fabrication methods, particularly for obtaining sheet, pipe, irregular profiles, and films. Relatively small extruders, eg, 11.5-cm dia, can produce well over 675 kg/h of polymer sheet (227). Extrusion is also the method for plasticizing the polymer in screw injection-molding machines and is used to develop the parison for blow molding. Extrusion of plastics is one of the most economical methods of fabrication because it is a continuous method involving relatively inexpensive equipment. The extrusion process has been studied in great detail (228,229). Single-screw extruders work extremely well with styrene-based plastics. Machines are available with length-to-diameter (L/D) ratios of 36:1 or more. Some of the longer L/D extruders are used with as many as three vent zones for removal of volatiles, often eliminating the necessity for predrying as is practiced with hygroscopic materials, eg, SAN and ABS. Where venting is inadequate, these polymers must be predried to a maximum moisture content of 0.03–0.05 wt% to obtain high quality sheet (see FILM AND SHEETING MATERIALS).

Many rubber-modified styrene plastics are fabricated into sheet by extrusion primarily for subsequent thermoforming operations. Much consideration has been given to the problem of achieving good surface quality in extruded sheet (230,231). Excellent surface gloss and sheet uniformity can be obtained with styrene-based polymers.

Considerable work has been done on mathematic models of the extrusion process, with particular emphasis on screw design. Good results are claimed for extrusion of styrene-based resins using these mathematical methods (229,232). With the advent of low cost computers, closed-loop control of the extrusion system has become commonplace. More uniform gauge control at higher output rates is achievable with many commercial systems (233,234).

Lamination of polymer films, both styrene-based and other polymer types, to styrene-based materials can be carried out during the extrusion process for protection or decorative purposes. For example, an acrylic film can be laminated to ABS sheet during extrusion for protection in outdoor applications. Multiple extrusion of styrene-based plastics with one or more other plastics has grown rapidly from the mid-1980s to the mid-1990s.

8.3. Thermoforming and Orientation. Thermoforming of HIPS and ABS extruded sheet is of considerable importance in several industries. In the refrigeration industry, large parts are obtained by vacuum-forming extruded sheet. Vacuum forming of HIPS sheet for refrigerator-door liners was one of the most significant early developments promoting the rapid growth of the whole family of HIPS. When a thermoplastic polymer film or sheet is heated above its glass-transition temperature, it can be formed or stretched. Under controlled conditions, new shapes can be controlled; also, various amounts of orientation can be imparted to the polymer film or sheet for altering its mechanical behavior.

Thermoforming is usually accomplished by heating a plastic sheet above its softening point and forcing it against a mold by applying vacuum, air, or mechanical pressure. On cooling, the contour of the mold is reproduced in detail. In order to obtain the best reproduction of the mold surface, carefully determined conditions for the plastic-sheet temperature, ie, heating time and mold temperature, must be maintained.

Several modifications of thermoforming plastic sheet have been developed. In addition to straight vacuum forming, there are vacuum snapback forming, drape forming, and plug-assisted-pressure-and-vacuum forming. Some combinations of these techniques are also practiced. Such modifications are usually necessary to achieve more uniform wall thickness in the finished deep-draw sections. Vacuum forming can also be continuous by using the sheet as it is extruded. An example of this technology is practiced with several high speed European lines in operation in the United States. Precise temperature conditioning allows carefully controlled levels or orientation in the finished part (235).

Thermoforming is perhaps the process with the lowest unit cost. Examples of thermoformed articles are refrigerator-door and food-container liners, containers for dairy products, and luggage. Some of the largest formed parts are camper/trailer covers and liners for refrigerated-railroad-car doors (236).

Orientation of styrene-based copolymers is usually carried out at temperatures just above T_g. Biaxially oriented films and sheet are of particular interest. Such orientation increases tensile properties, flexibility, toughness, and shrinkability. PS produces particularly clear and sparkling film after being oriented biaxially for envelope windows, decoration tapes, etc. Oriented films and sheet of styrene-based polymers are made by the bubble process and by the flat-sheet or tentering process. Fibers and films can be produced by uniaxial orientation (237) (see FILM AND SHEETING MATERIALS).

8.4. Blow Molding. Blow molding is a multistep fabrication process for manufacturing hollow symmetrical objects. The granules are melted and a parison is obtained by extrusion or by injection molding. The parison is then enclosed by the mold, and pressure or vacuum is applied to force the material to assume the contour of the mold. After sufficient cooling, the object is ejected.

Styrene-based plastics are used somewhat in blow molding but not as much as linear polyethylene and PVC. HIPS and ABS are used in specialty bottles, containers, and furniture parts. ABS is also used as one of the impact modifiers for PVC. Clear, tough bottles with good barrier properties are blow-molded from these formulations.

PS or copolymers are used extensively in injection blow molding. Tough and craze-resistant PS containers have been made by multiaxially oriented injection-molded parisons (238). This process permits the design of blow-molded objects with a high degree of controlled orientation, independent of blow ratio or shape.

Table 7. **Additives Used in Styrene Plastics**

Type	Compounds	Examples	Amount, wt%	Comments
plasticizers (qv)	mineral oil phthalate esters adipate esters		<4	all cause loss of heat distortion temperature
mold-release agents	steric acid metal sterates sterate esters silicones amide waxes		0.13	many mold-release agents cause yellowness of haze
antioxidants (qv)	alkylated phenols phosphite esters thioesters	ionol tris(nonylphenyl) phosphite dilaurylthiodipropionate	1 1 1	synergism some-times achieved with multiple use
antistatic agents (qv)	quaternary ammonium compounds		2	
uv stabilizers	benzotriazoles benzophenones	Tinuvin P	0.25	
ignition suppression agents	halogenated compounds, antimony oxide, aluminum oxide, phosphate esters			synergism some-times achieved with multiple use

8.5. Additives. Processing aids, eg, plasticizers and mold-release agents, are often added to PS (see RELEASE AGENTS). Even though PS is an inherently stable polymer, other compounds are sometimes added to give extra protection for a particular application. Rubber-modified polymers containing unreacted allylic groups are very susceptible to oxidation and require carefully considered antioxidant packages for optimum long-term performance. Ziegler-Natta-initiated polybutadiene rubbers are especially sensitive in this respect, for they often contain organocobalt residues from the catalyst complex. For food contact applications, the additives must be FDA-approved. Important additives used in styrene plastics are listed in Table 7.

9. Economic Aspects

Table 8 lists the United States producers of polystyrene and their capacities. Most capacity is for polystyrene resins supplied as crystal, impact, and expandable beads. Demand was strong for polystyrene and other styrene plastics in 2004 and was expected to continue. However, the surge in benzene prices from which styrene is made putting pressure on styrene producers. Some producers fear that the rising costs will lead converters to seek alternative plastics.

Table 8. **U.S. Producers of Polystyrene and their Capacities**[a]

Producer	Location	Capacity, $\times 10^3$ t
Alcoa Kam	Hazelton, Pa.	34
American Polymers	Oxford, Mass.	41
American Polystyrene	Torrance, Calif.	14
BASF	Joliet, Ill.	344
Chevron Phillips Chemical	Marietta, Ohio	363
Dart Polymers	Owensboro, Ky.	48
Dow Chemical	Gales Ferry, Conn.	73
	Hanging Rock, Ohio	86
	Joliet, Ill.	127
	Midland, Mich.	136
	Pevely, Mo.	77
	Torrance, Calif.	113
GE Plastics	Selkirk, N.Y.	45
Huntsman	Peru, Ill.	118
Nova Chemicals	Beaver Valley, Pa.	127
	Belpre, Ohio	217
	Decatur, Ala.	179
	Painesville, Ohio	39
	Springfield, Mass.	141
	Chesapeake, Va.	200
StyroChem	Fort Worth, Tex.	54
Total Petrochemicals USA	Carville, La.	771
Total		*3,347*

[a] Ref. 239.

However, polystyrene demand was up 7–8% in 2004 and the trend was expected to continue at the rate of 5–6%. Demand in 2004 was 3,057 × 10^3 t in 2004 and is projected to be 3,506 × 10^3 t in 2008 (239).

Styrene-acrylonitrile (SAN) resins are optically clear resins used in a variety of end uses including housewares, packaging, appliances, industrial batteries, and automotive and medical applications. Among the plastics with which SAN competes are acrylics, general-purpose polystyrene and polycarbonate.

Global SAN consumption reached almost 700 × 10^3 t in 2004 and is forecast to reach over 800 × 10^3 t in 2009, at an average annual growth rate of around 3% from 2004 to 2009. Growth will be driven by applications in housewares, compounding, medical and industrial uses.

During 2004–2009, SAN consumption is expected to grow in the United States and Western Europe at 2.7% per year and 2.2% per year, respectively. Demand in Japan is expected to decrease by 1.6% per year during this period, while the Asian region is expected to observe a 3.6% increase per year (240).

10. Characterization

Four modes of characterization are of interest: chemical analyses, ie, qualitative and quantitative analyses of all components; mechanical characterization, ie, tensile and impact testing; morphology of the rubber phase; and rheology at a

Table 9. **Chemical Characterization Techniques**

High mol wt component		Additives		Residuals	
Variable	Method[a]	Variable	Method[a]	Variable	Method[a]
mol wt	solution viscometry	mineral oil	gc/hplc	styrene	gc
mol wt distribution	gpc	phthalate esters	gc	solvents	gc
copolymer composition	ir	stearates	ir	oligomers	gc
rubber content	ir	other	hplc		
graft yield	solubility				

[a] gpc = gel-permeation chromatography; gc = gas chromatography; hplc = high performance liquid chromatography; ir = infrared analysis.

range of shear rates. Other properties measured are stress crack resistance, heat distortion temperatures, flammability, creep, etc, depending on the particular application (241).

Because plastics are almost invariably modified with one or more additives, there are three components of chemical analysis: the high molecular weight portion, ie, the polymer; the additives, ie, plasticizer and mold-release agent; and the residuals remaining from the polymerization process. The high molecular weight portion is best characterized using gpc, which gives molecular weight and polydispersity information. If the gpc is equipped with a diode array detector, chromophores responsible for polymer discoloration can be located (125). The additives in the polymer are best characterized by extracting them from the polymer and analyzing the extract using high performance liquid chromatography (242). The relevant characterization methods are listed in Table 9. Figure 4 illustrates typical molecular weight distribution curves from gpc. Capillary gas chromatogry is used to determine residuals. Mechanical testing is carried out according to standard ASTM methods.

Rubber particle size distribution is usually measured with a Coulter counter or directly from electron photomicrographs (72); the latter also gives details of particle morphology. Rheological studies are made using a modified tensile tester with capillary rheometer (ASTM D1238-79) or with the powerful Rheometrics mechanical spectrometer (243). For product specifications, a simple melt-flow test is used (ASTM D1238 condition G) with a measurement of the heat distortion temperature (ASTM D1525). These two tests, with solution viscosity as a measure of molecular weight, have been used historically to characterize PS. However, molecular weight distribution and residuals analyses, in general, have replaced them.

11. Health and Safety Factors

In pellet form, styrene-based plastics have a very low degree of toxicity (244). Under normal conditions of handling and use, they should pose no unusual problems from ingestion, inhalation, or eye and skin contact. Heating of these

Table 10. **Ignition Temperatures and Burning Rates of Styrene-Based Polymers**[a]

Polymer	Minimum flash-ignition temperature, °C	Minimum self-ignition temperature, °C	Burning rate,[b] cm/s
polystyrene			
general-purpose	345–360	488–496	<0.06
rubber-modified	385–399	435–474	<0.06
styrene–acrylonitrile copolymer	366	454	<0.06
acrylonitrile–butadiene–styrene	404	>404	<0.06

[a] Test specimens for burning rate data were $1.27 \times 15.24 \times 0.318\ \text{cm}^3$. Descriptions of burning rate and other flammability characteristics developed from small-scale laboratory testing do not reflect hazards presented by these or any other materials under actual fire conditions.
[b] In a horizontal position.

polymers usually results in the release of some vapors. The vapors contain some styrene (ACGIH TLV TWA 20 ppm, STE L, 40 ppm; human detection, 5–10 ppm) and, in the case of styrene–acrylonitrile copolymers, some acrylonitrile (TLV = 2 ppm) as well as very low levels of degraded and oxidized hydrocarbons and additives (245). The warning properties of styrene and any oxidized organics are such that the vapors normally can be detected by humans at very low levels, and hazardous concentrations are usually irritating and obnoxious. Nevertheless, adequate ventilation should be provided.

Styrene polymers burn under the right conditions of heat and oxygen supply. This can occur even when they are modified by addition of ignition suppression chemicals. Once ignited, these polymers may burn rapidly and produce a dense black smoke. Combustion products from any burning organic material should be considered toxic. Ignition temperatures of several styrenic polymers are listed in Table 10. Fires can be extinguished by conventional means, ie, water and water fog.

12. Uses

12.1. PS Foams.

The early history of foamed PS is available (246), as are discussions of the theory of plastic foams (247). Foamable PS beads were developed in the 1950s by BASF under the trademark of STYROPOR (248). These beads, made by suspension polymerization in the presence of blowing agents such as pentane or hexane, or by post-pressurization with the same blowing agents, have had an almost explosive growth, with 200,000 metric tons used in 1980. Some typical physical properties of PS foams are listed in Table 11 (see FOAMED PLASTICS). Some believe there are unlimited opportunities for the development of new foam materials.

The following are commercially significant foamed PSs. Extruded planks and boards that are largely flame-retardant and in the density range of 29 kg/m^3 are used for low temperature thermal insulation, buoyancy, floral display, novelty, packaging (qv), and construction purposes. Foamed boards and shapes from

Table 11. **Characteristic Properties of Some Polystyrene Foams**

Property	Styrofoam,[a] extruded	Bead, board-molded	Foam sheet	ASTM
density, kg/m^3[b]	35	32	96	
compressive strength, kPa[c]	310	207–276	290	D1621
tensile strength, kPa[c]	517	310–379	2070–3450	D1623
flexural strength, MPa[d]	1138	379–517		D790
thermal conductivity, W/(m·K)[e]	0.030	0.035	0.035	C177
heat distortion, °C	80	85	85	

[a] Registered trademark of The Dow Chemical Company.

[b] To convert kg/m^3 to lb/ft^3, multiply by 0.0624.

[c] To convert kPa to psi, multiply by 0.145.

[d] To convert MPa to psi, multiply by 145.

[e] To convert W/(m·K) to (Btu·in.)/(h·ft^2·°F), multiply by 6.933.

foaming-in-place (FIP) beads (density 16–32 kg/m^3) are used for packaging, buoyancy, insulation, and numerous other applications. Batch molding of boards and shapes as well as automated molding of continuous planks are used. Extruded foamed PS sheet 17-mm thick with densities of 64–160 kg/m^3 are used largely in packaging applications. Extremely fine cell size is required for texture and strength. Special nucleating agents are employed for this purpose, eg, polymers of styrene and maleic anhydride, citric acid–sodium bicarbonate mixtures, and talc (249). High density extruded planks (density 35–64 kg/m^3), are used for heavy-duty structural applications. Styrene copolymer foams containing, eg, acrylonitrile for gasoline resistance, are made either by extrusion or from beads. High density (480–800 kg/m^3) injection-molded objects are made from mixtures of FIP beads and PS granules or more commonly HIPS or ABS with a chemical blowing agent, eg, azodicarbonamide. These moldings have a high density skin of essentially PS and a foamed core. Foamable ABS systems, eg, laminates with ABS skins and a heat-foamable core, are used for structural applications, as in car body parts (250). Of growing commercial significance is coextruded, foam-core ABS pipe (251,252). Reducing the density of the foam core by up to one half and using a chemical blowing agent result in a ~20% overall pipe weight and raw material usage reduction. Syntactic foams are combinations of foamable beads, eg, expandable PS or styrene–acrylonitrile copolymers. These are mixed with a resin, usually thermosetting, which has a large exotherm during curing, eg, epoxy or phenolic resins (253). The mixture is then placed in a mold and the exotherm from the resin cure causes the expandable particles to foam and forces the resin to the surface of the mold. A typical example is expandable PS in a flexible polyurethane foam matrix used in cushioning applications (254). Sandwich panels are made either by foaming beads between the skin materials or by adhering skins to planks cut to precise dimensions. Foamed PS beads are admixed with concrete for lightweight masonry structures (255).

Extruded Rigid Foam. In addition to low temperature thermal insulation, foamed PSs are used for insulation against ambient temperatures in the form of perimeter insulation and insulation under floors and in walls and roofs. The upside-down roof system has been patented (256), in which foamed plastic such as Styrofoam (Dow) plastic foam is applied above the tar-paper vapor seal, thereby protecting the tar paper from extreme thermal stresses that cause cracking. The foam is covered with gravel or some other wear-resistant topping (see ROOFING MATERIALS).

In addition to such thermal insulation uses in buildings, there is a potentially tremendous new area in the form of highway underlayment to prevent frost damage. Damage to roadways, roadbeds, and airfields because of frost action is a costly and aggravating problem. Conventional treatments to prevent such damage are expensive and unreliable. During the 1960s, an improved and more economical solution to the problem was developed (257). It is based on the use of thermal insulation to reduce the heat loss in the frost-susceptible subgrade soil so that no freezing occurs. Many miles of insulated pavements have been built in the United States, Canada, Europe, and Japan. The concept has proved valid, and the performance of extruded PS foam has been completely satisfactory. It is expected that the use of this concept will continue to grow as natural road-building materials continue to become more scarce and expensive and as the weight and speed of land and airborne vehicles continue to increase.

A 2.54-cm Styrofoam plastic foam with thermal conductivity of ca 0.03 W/(m·K) (0.21 (Btu·in.)/(ft·h·°F)) is equivalent to 61 cm of gravel. Any synthetic foam having compressive strength sufficiently high and thermal conductivity sufficiently low is effective. However, the resistance of PS-type foams to water, frost damage, and microorganisms in the soil makes them especially desirable. An interesting and important application of this concept was the use of Styrofoam in the construction of the Alaska pipeline. In this case, the foam was used to protect the permafrost.

Rigid Foam from Foaming-in-Place Beads. Expandable PS (EPS) has been in wide use in packaging since its introduction. Applications range from pallet shipping containers for computer terminals, material-handling stacking trays, to packages for fresh fruits and vegetables. Expandable PS serves as a cushioning material, a package insert for blocking and bracing, a flotation item, or as insulation.

The basic resin for EPS is in the form of beads that are expanded to a desired density before molding. Densities for packaging parts are typically 20–40 kg/m^3. Once expanded, the beads are fused in a steam-heated mold to form a specific shape. Most parts are molded of standard-white resins, although several pastel colors are available.

Converters who manufacture EPS parts and components for packaging are called shape molders. Others who mold large billets, eg, measuring $0.6 \times 1.2 \times 2.4\,m^3$, are called block molders. The package user can obtain EPS parts without the benefits of a mold; parts can be fabricated from billets by hot-wire cutting. Whether molded or fabricated, EPS packages and their components are typically designed by careful consideration of the compression and cushioning properties of expanded PS (258).

A large number of factors that influence the foaming of foamable PS beads, eg, the molecular weight of the polymer, polymer type, blowing agent type and content, and bead size, have been analyzed (259). It is suggested that at least part of the pentane blowing agent is present in microvoids in the glassy PS.

Table 12. **Loss of Isopentane from Foaming-in-Place Chlorostyrene Beads**[a] **in Open Storage, wt%**[b]

	After 20 h		After 300 h	
Temperature, °C	Polystyrene	Poly-chlorostyrene	Polystyrene	Poly-chlorostyrene
25	18	1.3	40	10
50	38	12	72	33
80	48	24	80	54

[a] 420-mm beads.

[b] Initial concentration of isopentane = 6 wt%.

Thus, the density of beads containing 5.7 wt% n-pentane is 1080 kg/m^3, compared to a value of 1050 kg/m^3 for pure PS beads and a calculated density of 1020 kg/m^3 for a simple mixture in which n-pentane is dissolved in the PS. If all of the pentane were in voids, the calculated density would be 1120 kg/m^3. About 60% of the pentane is held in voids, with the balance presumably dissolved. n-Pentane present in voids has a reduced vapor pressure, which depends on the effective microcapillary diameter. Dissolved n-pentane in PS also has a reduced vapor pressure, by an amount determined by the thermodynamic interaction between solvent and polymer.

An unspecified experimental styrene copolymer, possibly with acrylonitrile, shows a greatly reduced tendency to lose blowing agent on aging at 23°C (259). FIP beads from chlorostyrene likewise have a greatly enhanced ability to retain blowing agent, as indicated in Table 12. The higher heat distortion of this polymer requires steam pressures of 210–340 kPa (30–50 psi) for blowing.

Various other factors that influence the foaming of PS, especially cross-linking, have been described (255). Reference 255 discusses foaming as a viscoelastic process in which there is competition between the blowing pressure, which increases with temperature, and the thinning and rupture of cell walls with consequent collapse of the foam. The presence of cross-links reduces the tendency for cell wall rupture. Figure 27 shows foam volumes attained as a function of temperature for various amounts of divinylbenzene. The effects of temperature and cross-linking on the kinetics of foaming have also been discussed (255).

Another important factor affecting the foaming of PS beads is the differential rate of diffusion of n-pentane compared to steam and air. It is estimated that the quantity of n-pentane normally used is sufficient to produce a foaming volume of 30-fold and hence a foam density of no more than 32 kg/m^3. However, the steam and/or air that diffuse into the beads contribute to further expansion, so that foaming volumes of 60-fold or more are commonly achieved. This aspect of diffusion has been discussed in some detail (260). In cycle foaming in air, beads are allowed to equilibrate with air after each heat-foaming step through a series of stages. Foaming volumes of 200:1 have been achieved in this manner, with densities down to 3.2–4.8 kg/m^3.

Lightweight concrete is made from prefoamed EPS beads, Portland cement, and organic binders. Precast shapes are being used to provide structural strength, thermal insulation, and sound deadening.

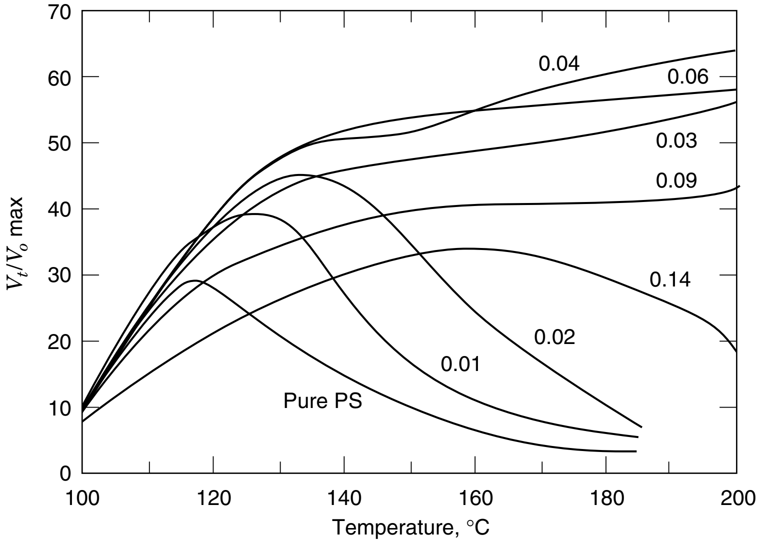


Fig. 28. Maximum foaming volume of styrene divinylbenzene copolymers containing 8.8 wt% CO_2 as a function of divinylbenzene content and temperature. Numbers beside curves indicate wt% divinylbenzene, V_t/V_o is the ratio of final volume to initial volume at temperature t (258).

PS as a Raw Material for Rigid Thermoplastic Foams. The low cost of PS and its high thermal stability, which provides good recycle efficiency, as well as the possibility of using low cost blowing agents, are important to its use in rigid thermoplastic foams. The heat distortion point of ca 80°C, in contrast to 65°C for PVC foam, permits its use in most construction applications. The low sensitivity of the polymer to moisture is another important factor. Because of the above and possibly for other reasons, PS has been the dominant material used in rigid thermoplastic foams. Poly(vinyl chloride) is economical, has good physical properties, and is flame-retarding, but it has marginal heat distortion properties for some uses and does not readily lend itself to the continuous extrusion process used for PS foam. No FIP beads system based on PVC has been perfected as of this writing. This could well be a result of its high vapor barrier compared to PS. Polyethylene is too permeable to retain a blowing agent and hence is ruled out as an FIP bead material, but it is commercially significant as extruded foam.

Flame Retardants. The growing use of PS foams in the construction industry has provided impetus for continuing research on flame-retardant additives (see FLAME RETARDANTS FOR TEXTILES). Organic bromine compounds, eg, pentabromomonochlorocyclohexane, have long been used for this purpose in extruded PS foam. Use of injection-molded structural foams, based on HIPS and ABS and containing flame-retardant additives, has grown rapidly since the late 1970s. A typical additive system to impart the required flame-retardant properties is bis(pentabromophenyl) oxide and a synergist, eg, antimony trioxide. Because of environmental concerns over the use of halogenated flame-retardant chemicals, research is focusing on the development of halogen-free

Table 13. **Gas and Water-Vapor Permeabilities[a] of PS Films**

Composition	Oxygen	Carbon dioxide	Water
unmodified polystyrene	1,560	6,240	714,000
72:28 styrene-*stat*-acrylonitrile	40	2,060	1,290,000

[a] Gas permeability units = nmol/m·s·GPa.

systems. Phosphorus-containing compounds are the most heavily researched alternative.

Foamed Sheet. PS foamed sheet is used for foamed trays, egg cartons, disposable dinnerware, and packaging. Foam sheet manufacturing techniques, manufacturers' logistics, and markets have been described (261). Choice of the correct blowing agent for foam sheet is critical in determining ultimate density and physical properties. The choice of blowing agent may also be dictated by safety considerations, eg, flammability of hydrocarbons, or environmental concerns, eg, chlorofluorocarbons.

12.2. Oriented PS Film and Sheet. Oriented PS film, in addition to being heat-shrinkable and having the lowest cost of any of the rigid plastic materials, offers a high degree of optical clarity, high surface gloss, and excellent dimensional stability, particularly with regard to relative humidity. It is not a barrier film; in fact, one of its largest uses, that of packaging field-fresh produce, depends on its being highly permeable to oxygen and water vapor (Table 13). A review of PS film as part of a larger study on films of all types is available (263,264). Other relevant reviews have also been published (265,266).

Although PS is normally considered a rather brittle material, biaxial orientation imparts some extremely desirable properties, particularly in regard to an increase in elongation. Thus, the 1.5–2% of elongation normally associated with unoriented PS can become as high as 10%, depending on the exact conditions of preparation (267,268).

Several methods utilized for preparing biaxially oriented PS film. The bubble process is used commercially. The high softening point, coupled with the tendency of oriented film to shrink above 85°C, makes heat sealing difficult. Solvent, adhesive, and ultrasonic sealing are used in most applications. Scratch resistance, impact strength, and crease resistance are low. Although the bubble process superficially resembles the common bubble process for making polyethylene, polypropylene, and Saran film, there are a number of substantive differences; the PS process is considerably more difficult to achieve. In the case of polyethylene, for example, crystallinity stabilizes the blown bubble, whereas with a true thermoplastic, eg, PS, the blown film must be stabilized by cooling below the T_g. This involves extremely careful control of temperature in the blowing process.

As a general rule, there is an economic break-even point at ca 0.08 mm, which coincides with the defined difference between film and sheet. Film is made more economically by the bubble method and sheet by the tenter-frame method. The exact thickness for break-even depends on technological improvements, which can be made in both processes, in the degree of control used in regulating them and in quality requirements.

PS film contains no plasticizers, absorbs negligible moisture, and exhibits exceptionally good dimensional stability. It does not become brittle with age nor distort when exposed to low or high humidity. Excellent clarity, stability, and machinability, ie, ability to pass through packaging machinery at high speeds and be cut and sealed, etc, are central factors in the use of oriented PS in window envelopes. These same characteristics have also led to applications of film for window cartons. An antifog film 0.025–0.032-mm thick has been used extensively for the windows of cartons for bacon. Substantial amounts of film are also employed as sheet protectors and as inserts in wallets. A thickness of 0.060–0.130 mm is customary for these applications. PS film can be printed by means of flexographic, rotogravure, and silkscreen methods. A lamination of reverse-printed film and paper has been used for an attractive, high sparkle package for hand soap. The film is an excellent base for metallizing because of the almost complete absence of volatiles. Oriented PS film is also widely used for lamination to PS foamed sheet for preprinted decoration and/or property enhancement (269).

For PS sheet, the use responsible for its rapid growth is in meat trays, where the merchandising value is important, ie, the transparency of the package, as well as its dimensional stability and resistance to moisture. A smaller but growing use is as a photographic film base where dimensional stability at all humidities and low gel count are both important. The thermoplastic nature of PS and the memory effects built into it through biaxial orientation make it especially suitable for packaging applications. It must be processed under pressure rather than by vacuum-forming equipment to avoid the shrinkage that would otherwise result from the high level of orientation.

Important uses of PS are as windows in envelopes and as produce overwrap. High optical clarity is required for mechanized reading of characters through envelope windows, a significant technological trend that is certain to enhance the use of PS film. In regard to produce overwrap, the transmission characteristics of PS for water vapor and oxygen coincide more or less with the metabolic requirements of the produce being packaged, eg, lettuce, so that in addition to giving mechanical protection, the overwrap allows the produce to metabolize in a normal manner (270). Low cost and high optical clarity are important. Furthermore, the feel of PS film gives an impression of crispness to the product. PS film also has potential use as a type of synthetic paper (see Pulp). Whereas HIPS is reasonably opaque, general-purpose PS must be treated so that it is opaque; this can take the form of pigmentation, mechanical abrasion, or surface treatment, eg, chemical etch. PS film can be given a suitable coating, eg, a latex-clay coating, of the kind that is used on ordinary paper for the purpose of achieving a good printable surface. General discussions of gas permeabilities in plastic films are available (6,8,9,271,272) (see Barrier polymers).

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