ACRYLONITRILE POLYMERS, SURVEY AND STYRENE-ACRYLONITRILE (SAN)

1. Introduction

Acrylonitrile (AN), C_3H_3N, is a versatile and reactive monomer (1) that can be polymerized under a wide variety of conditions (2) and copolymerized with an extensive range of other vinyl monomers (3). It first became an important polymeric building block in the 1940s. Although acrylonitrile had been discovered in 1893, its unique properties were not realized until the development of nitrile rubbers during World War II (see ELASTOMERS, SYNTHETIC, NITRILE RUBBER) and the discovery of solvents for the homopolymer with resultant fiber applications (see FIBERS, ACRYLIC) for textiles and carbon fibers. Because of the difficulty of melt processing the homopolymer, acrylonitrile is usually copolymerized to achieve a desirable thermal stability, melt flow, and physical properties. As a comonomer, acrylonitrile (qv) contributes hardness, rigidity, solvent and light resistance, gas impermeability, and the ability to orient. These properties have led to many copolymer application developments since 1950.

The utility of acrylonitrile [107-13-1] in thermoplastics was first realized in its copolymer with styrene, C_8H_8 [100-42-5], in the late 1950s. Styrene is the largest volume of comonomer for acrylonitrile in thermoplastic applications. Styrene–acrylonitrile (SAN) copolymers [9003-54-7] are inherently transparent plastics with high heat resistance and excellent gloss and chemical resistance (4). They are also characterized by good hardness, rigidity, dimensional stability, and load-bearing strength (due to relatively high tensile and flexual strengths). Because of their inherent transparency, SAN copolymers are most frequently used in clear application. These optically clear materials can be readily processed by extrusion and injection molding, but they lack real impact resistance.

The subsequent development of acrylonitrile–butadiene–styrene (ABS) resins [9003-56-9], which contain an elastomeric component within a SAN matrix to provide toughness and impact strength, further boosted commercial application of the basic SAN copolymer as a portion of these rubber-toughened thermoplastics (see ACRYLONITRILE POLYMERS, ABS RESINS). When SAN is grafted onto a butadiene-based rubber, and optionally blended with additional SAN, the two-phase thermoplastic ABS is produced. ABS has the useful SAN properties of rigidity and resistance to chemicals and solvents, while the elastomeric component contributes real impact resistance. Because ABS is a two-phase system and each phase has a different refractive index, the final ABS is normally opaque. A clear ABS can be made by adjusting the refractive indexes through the inclusion of another monomer such as methyl methacrylate. ABS is a versatile material and modifications have brought out many specialty grades such as clear ABS and high-temperature and flame-retardant grades. Saturated hydrocarbon elastomers or acrylic elastomers (5,6) can be used instead of those based on butadiene, C_4H_6 [106-99-0] as weatherable-grade ABS.

In the late 1960s a new class of AN copolymers and multipolymers was introduced that contain more than 60% acrylonitrile. These are commonly known as barrier resins and have found their greatest acceptance where excellent barrier properties toward gases (7), chemicals, and solvents are needed. They may be processed into bottles, sheets, films, and various laminates, and have found wide usage in the packaging industry (see BARRIER POLYMERS).

Acrylonitrile has found its way into a great variety of other polymeric compositions based on its polar nature and reactivity, imparting to other systems some or all of the properties noted above. Some of these areas include adhesives and binders, antioxidants, medicines, dyes, electrical insulations, emulsifying agents, graphic arts, insecticides, leather, paper, plasticizers, soil-modifying agents, solvents, surface coatings, textile treatments, viscosity modifiers, azeotropic distillations, artificial organs, lubricants, asphalt additives, water-soluble polymers, hollow spheres, cross-linking agents, and catalyst treatments (8).

2. SAN Physical Properties and Test Methods

SAN resins possess many physical properties desired for thermoplastic applications. They are characteristically hard, rigid, and dimensionally stable with load-bearing capabilities. They are also transparent, have high heat distortion temperatures, possess excellent gloss and chemical resistance, and adapt easily to conventional thermoplastic fabrication techniques (9).

SAN polymers are random linear amorphous copolymers. Physical properties are dependent on molecular weight and the percentage of acrylonitrile. An increase of either generally improves physical properties, but may cause a loss of processability or an increase in yellowness. Various processing aids and

Table 1. **Physical/Mechanical Properties of Commercial Injection-Molded SAN Resins**[a]

	Bayer Lustran 31-2060	Dow Tyril 100	ASTM Method
specific gravity (23/23°C)	1.07	1.07	D 792
Vicat softening point (°C)	110	108	D 1525
tensile strength, MPa[b]	72.4	71.7	D 638
ultimate elongation @ breakage (%)	3.0	2.5	D 638
flexural modulus, GPa[c]	3.45	3.87	D 790
impact strength, notched Izod (J/m[d])	21.4 @ 0.125 in.	16.0 @ 0.125 in.	D 256
melt flow rate (g/10 min)	8.0	8.0	D 1238, cond. 1
refractive index, n_D	1.570	1.570	D 542
mold shrinkage (in./in.)	0.003–0.004	0.004–0.005	D 955
transmittance at 0.125-in. thickness (%)	89.0	89.0	D 1003
haze at 0.125-in. thickness (%)	0.8	0.6	D 1003

[a] Product literature.

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

[c] To convert GPa to psi, multiply by 145,000.

[d] To convert J/m to ft lb/in., divide by 53.39.

Table 2. **Compositional Effects on SAN Physical Properties**[a]

AN, wt %	Tensile strength, MPa[b]	Elongation, %	Impact strength, J/m notch[c]	Heat distortion, temp., °C	Solution viscosity, mPa (=cP)
5.5	42.27	1.6	26.6	72	11.1
9.8	54.61	2.1	26.0	82	10.7
14.0	57.37	2.2	27.1	84	13.0
21.0	63.85	2.5	27.1	88	16.5
27.0	72.47	3.2	27.1	88	25.7

[a] Ref. 15.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to ft lb/in., divide by 53.39.

modifiers can be used to achieve a specific set of properties. Modifiers may include mold release agents, UV stabilizers, antistatic aids, elastomers, flow and processing aids, and reinforcing agents such as fillers and fibers (9). Methods for testing and some typical physical properties are listed in Table 1.

The properties of SAN resins depend on their acrylonitrile content. Both melt viscosity and hardness increase with increasing acrylonitrile level. Unnotched impact and flexural strengths depict dramatic maxima at ca 87.5 mol % (78 wt %) acrylonitrile (10). With increasing acrylonitrile content, copolymers show continuous improvements in barrier properties and chemical and UV resistance, but thermal stability deteriorates (11). The glass-transition temperature (T_g) of SAN varies nonlinearly with acrylonitrile content, showing a maximum at 50 mol % AN. The alternating SAN copolymer has the highest T_g (12,13). The fatigue resistance of SAN increases with AN content to a maximum at 30 wt %, then decreases with higher AN levels (14). The effect of acrylonitrile incorporation on SAN resin properties is shown in Table 2.

3. SAN Chemical Properties and Analytical Methods

SAN resins show considerable resistance to solvents and are insoluble in carbon tetrachloride, ethyl alcohol, gasoline, and hydrocarbon solvents. They are swelled by solvents such as benzene, ether, and toluene. Polar solvents such as acetone, chloroform, dioxane, methyl ethyl ketone, and pyridine will dissolve SAN (16). The interactions of various solvents and SAN copolymers containing up to 52% acrylonitrile have been studied along with their thermodynamic parameters, ie, the second virial coefficient, free-energy parameter, expansion factor, and intrinsic viscosity (17).

The properties of SAN are significantly altered by water absorption (18). The equilibrium water content increases with temperature while the time required decreases. A large decrease in T_g can result. Strong aqueous bases can degrade SAN by hydrolysis of the nitrile groups (19).

The molecular weight of SAN can be easily determined by either intrinsic viscosity or size-exclusion chromatography (SEC). Relationships for both multipoint and single point viscosity methods are available (20,21). The intrinsic viscosity and molecular weight relationships for azeotropic copolymers have been given (22,23):

$$[\eta] = 3.6 \times 10^{-4}\, M_w^{0.62} \text{ dL/g in MEK at } 30^\circ\text{C}$$

$$[\eta] = 2.15 \times 10^{-4}\, M_w^{0.68} \text{ dL/g in THF at } 25^\circ\text{C}$$

$$[\eta] = \frac{\eta_{sp}/c}{1 + k_\eta \eta_{sp}}$$

where k_η=0.21 for MEK at 30°C and 0.25 for THF at 25°C.

Chromatographic techniques are readily applied to SAN for molecular weight determination. Size-exclusion chromatography or gel permeation chromatography (GPC) (24) columns and conditions have been described for SAN (25). Chromatographic detector differences have been shown to be of the order of only 2–3% (26). High-pressure precipitation chromatography can achieve similar molecular weight separation (27). Liquid chromatography (LC) can be used with secfractioned samples to determine copolymer composition (28). Thin-layer chromatography will also separate SAN by compositional (monomer) variations (27).

Residual monomers in SAN have been a growing environmental concern and can be determined by a variety of methods. Monomer analysis can be achieved by polymer solution or directly from SAN emulsions (29) followed by "head space" gas chromatography (GC) (28,29). Liquid chromatography (LC) is also effective (32).

4. SAN Manufacture

The reactivities of acrylonitrile and styrene radicals toward their monomers are quite different, resulting in SAN copolymer compositions that vary from their monomer compositions (33). Further complicating the reaction is the fact that acrylonitrile is soluble in water (see ACRYLONITRILE) and slightly different behavior is observed between water-based emulsion and suspension systems and bulk or mass polymerizations (34). SAN copolymer compositions can be calculated from copolymerization equations (35) and published reactivity ratios (36). The difference in radical reactivity causes the copolymer composition to drift as polymerization proceeds, except at the azeotrope composition where copolymer composition matches monomer composition. Figure 1 shows these compositional variations (37). When SAN copolymer compositions vary significantly, incompatibility results, causing loss of optical clarity, mechanical strength, and moldability, as well as heat, solvent, and chemical resistance (38). The termination step has been found to be controlled by diffusion even at low conversions, and the termination rate constant varies with acrylonitrile content. The average half-life of the radicals increases with styrene concentration from 0.3 s at 20 mol % to 6.31 s with pure styrene (39). Further complicating SAN manufacture is the fact that both the heat (40,41) and rate (42) of copolymerization vary with monomer composition.

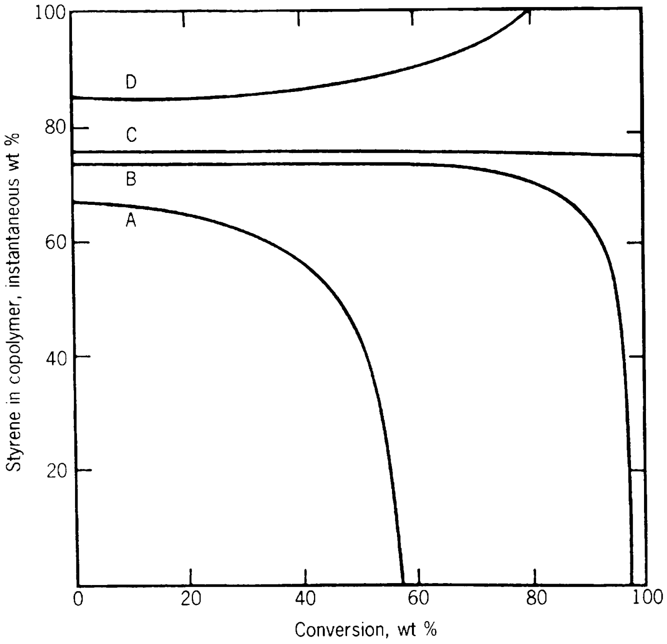


Fig. 1. Approximate compositions of styrene–acrylonitrile copolymers formed at different conversions starting with various monomer mixtures (35): S/AN = A, 65/36; B, 70/30; C, 76/24; D, 90/10.

The early kinetic models for copolymerization, Mayo's terminal mechanism (43) and Alfrey's penultimate model (44), did not adequately predict the behavior of SAN systems. Copolymerizations in DMF and toluene indicated that both penultimate and antepenultimate effects had to be considered (45, 46). The resulting reactivity model is somewhat complicated, since there are eight reactivity ratios to consider.

The first quantitative model, which appeared in 1971, also accounted for possible charge-transfer complex formation (47). Deviation from the terminal model for bulk polymerization was shown to be due to antepenultimate effects (48). The work with numerical computation and ^{13}C-nmr spectroscopy data on SAN sequence distributions indicates that the penultimate model is the most appropriate for bulk SAN copolymerization (49, 50). A kinetic model for azeotropic SAN copolymerization in toluene has been developed that successfully predicts conversion, rate, and average molecular weight for conversions up to 50% (51).

An emulsion model that assumes the locus of reaction to be inside the particles and considers the partition of AN between the aqueous and oil phases has been developed (52). The model predicts copolymerization results very well when bulk reactivity ratios of 0.32 and 0.12 for styrene and acrylonitrile, respectively, are used.

Commercially, SAN is manufactured by three processes: emulsion, suspension, and continuous mass (or bulk).

4.1. Emulsion Process. The emulsion polymerization process utilizes water as a continuous phase with the reactants suspended as microscopic particles. This low-viscosity system allows facile mixing and heat transfer for control purposes. An emulsifier is generally employed to stabilize the water-insoluble monomers and other reactants, and to prevent reactor fouling. With SAN the system is composed of water, monomers, chain-transfer agents for molecular weight control, emulsifiers, and initiators. Both batch and semibatch processes are employed. Copolymerization is normally carried out at 60 to 100°C to conversions of ~97%. Lower-temperature polymerization can be achieved with redox-initiator systems (53).

Figure 2 shows a typical batch or semibatch emulsion process (54). A typical semibatch emulsion recipe is shown in Table 3 (55).

The initial charge is placed in the reactor, purged with an inert gas such as N_2, and brought to 80°C. The initiator is added, followed by addition of the remaining charge over 100 min. The reaction is completed by maintaining agitation at 80°C for 1 h after monomer addition is complete. The product is a free-flowing white latex with a total solids content of 35.6%.

Compositional control for other than azeotropic compositions can be achieved with both batch and semibatch emulsion processes. Continuous addition of the faster reacting monomer, styrene, can be practiced for batch systems, with the feed rate adjusted by computer through gas chromatographic monitoring during the course of the reaction (56). A calorimetric method to control the monomer feed rate has also been described (10). For semibatch processes, adding the monomers at a rate that is slower than copolymerization can achieve

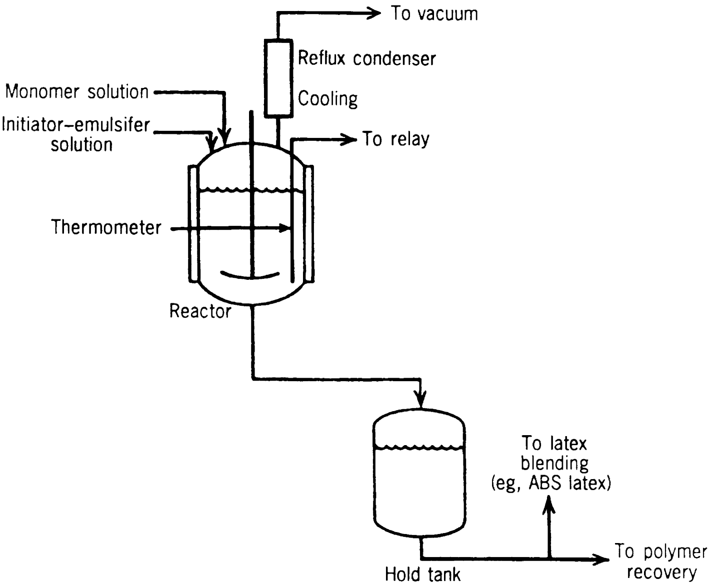


Fig. 2. Styrene–acrylonitrile batch emulsion process (54).

Table 3. **Semibatch Mode Emulsion Recipe for SAN Copolymers**

Ingredient	Parts
Initial reactor charge	
acrylonitrile	90
styrene	111
Na alkanesulfonate (emulsifier)	63
$K_2S_2O_8$ (initiator)	0.44
4-(benzyloxymethylene)cyclohexene (mol wt modifier)	1
water	1400
Addition charge	
acrylonitrile	350
styrene	1000
Na alkanesulfonate (emulsifier)	15
$K_2S_2O_8$ (initiator)	4
4-(benzyloxymethylene)cyclohexene (mol wt modifier)	10
water	1600

equilibrium. It has been found that constant composition in the emulsion can be achieved after ca 20% of the monomers have been charged (57).

Residual monomers in the latex are avoided either by effectively reacting the monomers to polymer or by physical or chemical removal. The use of *tert*-butyl peroxypivalate as a second initiator toward the end of the polymerization or the use of mixed initiator systems of $K_2S_2O_8$ and *tert*-butyl peroxybenzoate (58) effectively increases final conversion and decreases residual monomer levels. Spray devolatilization of hot latex under reduced pressure has been claimed to be effective (58). Residual acrylonitrile also can be reduced by postreaction with a number of agents such as monoamines (59) and dialkylamines (60), ammonium–alkali metal sulfites (61), unsaturated fatty acids or their glycerides (62, 63), their aldehydes, esters of olefinic alcohols, cyanuric acid (64,65), and myrcene (66).

The copolymer latex can be used “as is” for blending with other latexes, such as in the preparation of ABS, or the copolymer can be recovered by coagulation. The addition of electrolyte or freezing will break the latex and allow the polymer to be recovered, washed, and dried. Process refinements have been made to avoid the difficulties of fine particles during recovery (67,68).

The emulsion process can be modified for the continuous production of latex. One such process (70) uses two stirred-tank reactors in series, followed by insulated hold tanks. During continuous operation, 60% of the monomers are continuously charged to the first reactor with the remainder going into the second reactor. Surfactant is added only to the first reactor. The residence time is 2.5 h for the first reactor where the temperature is maintained at 65°C for 92% conversion. The second reactor is held at 68°C for a residence time of 2 h and conversion of 95%.

4.2. Suspension Process.

Like the emulsion process, water is the continuous phase for suspension polymerization, but the resultant particle size is larger, well above the microscopic range. The suspension medium contains water, monomers, molecular weight control agents, initiators, and suspending

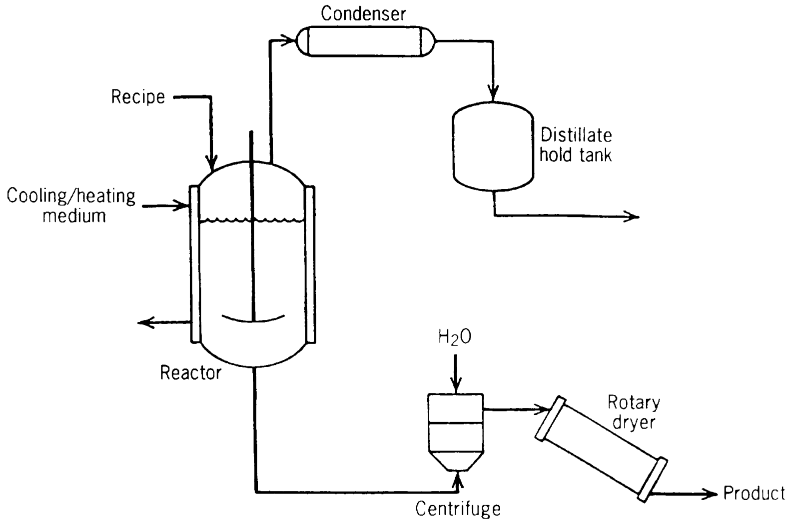


Fig. 3. Styrene–acrylonitrile suspension process (71).

aids. Stirred reactors are used in either batch or semibatch mode. Figure 3 illustrates a typical suspension manufacturing process while a typical batch recipe is shown in Table 4 (71). The components are charged into a pressure vessel and purged with nitrogen. Copolymerization is carried out at 128°C for 3 h and then at 150°C for 2 h. Steam stripping removes residual monomers (72), and the polymer beads are separated by centrifugation for washing and final dewatering.

Compositional control in suspension systems can be achieved with a corrected batch process. A suspension process has been described where styrene monomer is continuously added until 75–85% conversion, and then the excess acrylonitrile monomer is removed by stripping with an inert gas (73,74).

Elimination of unreacted monomers can be accomplished by two methods: dual initiators to enhance conversion of monomers to product (75–77) and steam stripping (72,78). Several process improvements have been claimed for dewatering beads (79), to reduce haze (80–83), improve color (84–88), remove monomer (89,90), and maintain homogeneous copolymer compositions (73,74,91).

Table 4. **Batch-Mode Recipe for SAN Copolymers**[a]

Ingredient	Parts
acrylonitrile	30
styrene	70
dipentene (4-isopropenyl-1-methylcyclohexene)	1.2
di-*tert*-butyl peroxide	0.03
acrylic acid–2-ethylhexyl acrylate (90:10) copolymer	0.03
water	100

[a] Ref. 71.

4.3. Continuous Mass Process. The continuous mass process has several advantages, including high space–time yield and good-quality products uncontaminated with residual ingredients such as emulsifiers or suspending agents. SAN manufactured by this method generally has superior color and transparency and is preferred for applications requiring good optical properties. It is a self-contained operation without waste treatment or environmental problems since the products are either polymer or recycled back to the process.

In practice, the continuous mass polymerization is rather complicated. Because of the high viscosity of the copolymerizing mixture, complex machinery is required to handle mixing, heat transfer, melt transport, and devolatilization. In addition, considerable time is required to establish steady-state conditions in both a stirred tank reactor and a linear flow reactor. Thus system start-up and product grade changes produce some off-grade or intermediate-grade products. Copolymerization is normally carried out between 100 and 200°C. Solvents are used to reduce viscosity or the conversion is kept to 40–70%, followed by devolatilization to remove solvents and monomers. Devolatilization is carried out from 120 to 260°C under vacuum at less than 20 kPa (2.9 psi). The devolatilized melt is then fed through a strand die, cooled, and pelletized.

A schematic of a continuous bulk SAN polymerization process is shown in Figure 4 (92). The monomers are continuously fed into a screw reactor, where copolymerization is carried out at 150°C to 73% conversion in 55 min. Heat of polymerization is removed through cooling of both the screw and the barrel walls. The polymeric melt is removed and fed to the devolatilizer to remove unreacted monomers under reduced pressure (4 kPa or 30 mm Hg) and high temperature (220°C). The final product is claimed to contain less than 0.7% volatiles. Two devolatilizers in series are found to yield a better quality product as well as better operational control (93,94).

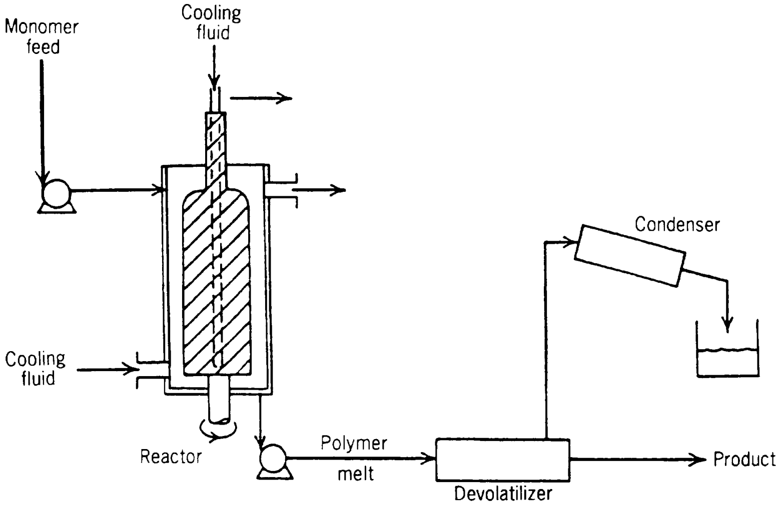


Fig. 4. Styrene–acrylonitrile continuous mass process (92).

Two basic reactor types are used in the continuous mass process, the stirred tank reactor (95) and the linear flow reactor. The stirred tank reactor consists of a horizontal cylinder chamber equipped with various agitators (96, 97) for mixing the viscous melt and an external cooling jacket for heat removal. With adequate mixing, the composition of the melt inside the reactor is homogeneous. Operation at a fixed conversion, with monomer make-up added at an amount and ratio equal to the amount and composition of copolymer withdrawn, produces a fixed composition copolymer. The two types of linear flow reactors employed are the screw reactor (92) and the tower reactor (97). A screw reactor is composed of two concentric cylinders. The reaction mixture is conveyed toward the outlet by rotating the inner screw, which has helical threads, while heat is removed from both cylinders. A tower reactor with separate heating zones has a scraper agitator in the upper zone, while the lower portion generates plug flow. In the linear flow reactors the conversion varies along the axial direction as does the copolymer composition, except where operating at the azeotrope composition. A stream of monomer must be added along the reactor to maintain SAN compositional homogeneity at high conversions. A combined stirred tank followed by a linear flow reactor process has been disclosed (97). Through continuous recycle copolymerization, a copolymer of identical composition to monomer feed can be achieved, regardless of the reactivity ratios of the monomers involved (98).

The devolatilization process has been developed in many configurations. Basically, the polymer melt is subjected to high temperatures and low pressures to remove unreacted monomer and solvent. A two-stage process using a tube and shell heat exchanger with enlarged bottom receiver to vaporize monomers has been described (94). A copolymer solution at 40–70% conversion is fed into the first-stage exchanger and heated to 120–190°C at a pressure of 20–133 kPa and then discharged into the enlarged bottom section to remove at least half of the unreacted acrylonitrile. The product from this section is then charged to a second stage and heated to 210–260°C at <20 kPa. The devolatilized product contains ~1% volatiles. Preheating the polymer solution and then flashing it into a multipassage heating zone at lower pressure than the preheater produces essentially volatile-free product (93, 99). SAN can be steam stripped to quite low monomer levels in a vented extruder that has water injected at a pressure greater than the vapor pressure of water at that temperature (100).

A twin-screw extruder is used to reduce residual monomers from ca 50 to 0.6%, at 170°C and 3 kPa with a residence time of 2 min (96). In another design, a heated casing encloses the vented devolatilization chamber, which encloses a rotating shaft with specially designed blades (101, 102). These continuously regenerate a large surface area to facilitate the efficient vaporization of monomers. The devolatilization equipment used for the production of polystyrene and ABS is generally suitable for SAN production.

4.4. Processing. SAN copolymers may be processed using the conventional fabrication methods of extrusion, blow molding, injection molding, thermoforming, and casting. Small amounts of additives, such as antioxidants, lubricants, and colorants, may also be used. Typical temperature profiles for injection molding and extrusion of predried SAN resins are as follows (103).

Molding Temperatures	
Cylinder	193–288°C
Mold	49–88°C
Melt	218–260°C
Extrusion Temperatures	
Hopper zone	water-cooled
Rear zone	177–204°C
Middle zone	210–232°C
Torpedo zone and die	204–227°C

5. Other Copolymers

Acrylonitrile copolymerizes readily with many electron-donor monomers other than styrene and more than eight hundreds of acrylonitrile copolymers have been registered with *Chemical Abstracts* and a comprehensive listing of reactivity ratios for acrylonitrile copolymerizations is readily available (36, 104). Copolymerization mitigates the undesirable properties of acrylonitrile homopolymer, such as poor thermal stability and poor processability. At the same time, desirable attributes such as rigidity, chemical resistance, and excellent barrier properties are incorporated into melt-processable resins.

Barex (trademark of BP AMOCO Chemicals) resins, commercial high barrier resin produced by BP Amoco Chemicals, are copolymer of acrylonitrile and methyl acrylate [96-33-3]. This resin are excellent example of the use of acrylonitrile to provide gas and aroma/flavor barrier, chemical resistance, high tensile strength, and stiffness, and utilization of a comonomer to provide thermal stability and processability. In addition, modification with an elastomer provides toughness and impact strength. This material has a unique combination of useful packaging qualities, including transparency, and are excellent barriers to permeation by gases, organic solvents, and most essential oils. Barex resins also prevent the migration and scalping of volatile flavors and odors from packaged foods and fruit juice products (105,112). They also provide protection from atmospheric oxygen. Barex resins meet FDA compliance for direct food contact applications.

Barex resin extruded sheet and/or calendered sheet (112) can be easily thermoformed into lightweight, rigid containers (105,106). Packages can be printed, laminated, or metallized. Recent developments in extrusion and injection blow molding (105,107), laminated film structures (105,108), and coextrusion (105, 109) have led to packaging uses for a variety of products. Barex resins are especially well suited for bottle production. This acrylonitrile copolymer also provides a good example of the dependence of properties on the degree and temperature of orientation (110,111). Figure 5 illustrates the improvement in tensile strength, elongation, and the ability to absorb impact energy due to orientation (111) by Barex resins (for example, Barex 210). Tensile strength and impact strength increase with the extent of stretching, and decrease with the orientation temperature, and oxygen permeability decreases with orientation. These

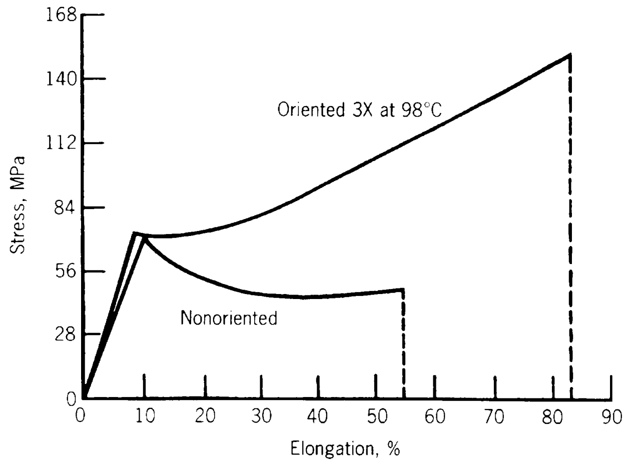


Fig. 5. Stress elongation of Barex 210 sheet (111). To convert MPa to psi, multiply by 145.

orientation properties have led to the commercialization Barex resins to fruit juice containers in France (112). Some typical physical properties of Barex resins are shown in Table 5.

Acrylonitrile–methyl acrylate–indene terpolymers, by themselves, or in blends with acrylonitrile–methyl acrylate copolymers, exhibit even lower oxygen and water permeation rates than the indene-free copolymers (113,114). Terpolymers of acrylonitrile with indene and isobutylene also exhibit excellent barrier

Table 5. **Physicial/Mechanical Properties of Commercial Barex Resins**[a]

	Barex 210[b]	Barex 218[b]	ASTM Method
specific gravity (23°C) (g/cm^3)	1.15	1.11	D 792
tensile strength, yield (MPa[c])	65.5	51.7	D 638
flexual modulus (GPa[d])	3.38	2.69	D 790
melt index (200c, 27.5 lbs)	3	3	D 1238
notched Izod impact (J/m[e])	267	481	D 790
heat deflection temperature (°C[f])	77	71	D 648
Gas permeability			
oxygen (23°C, 100% RH) $\frac{\text{nmol}}{\text{m·s·GPa}}$[f]	1.54	3.09	D 3985
carbon dioxide (23°C, 100% RH) $\frac{\text{nmol}}{\text{m·s·GPa}}$	2.32	3.09	D 3985
water vapor (38°C, 90% RH) $\frac{\text{nmol}}{\text{m·s·MPa}}$[g]	12.7	19.1	F 1249-90

Barex is a registered trademark of BP Amoco.

[a] Product literature.

[b] Extrusion grade.

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

[d] To convert GPa to psi, multiply by 145,000.

[e] To convert J/m to ft lb/in., divide by 53.39.

[f] To convert from $\frac{\text{nmol}}{\text{m·s·GPa}}$ to $\frac{\text{cc−mm}}{\text{m}^2\text{·24h·bar}}$, divide by 5.145.

[g] To convert from $\frac{\text{nmol}}{\text{m·s·MPa}}$ to $\frac{\text{g−mm}}{\text{m}^2\text{·24h·atm}}$, divide by 6.35.

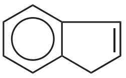
properties (115), and permeation of gas and water vapor through acrylonitrile–styrene–isobutylene terpolymers is also low (116,117).

Copolymers of acrylonitrile and methyl methacrylate (118) and terpolymers of acrylonitrile, styrene, and methyl methacrylate (119,120) are used as barrier polymers. Acrylonitrile copolymers and multipolymers containing butyl acrylate (121–124), ethyl acrylate (125), 2-ethylhexyl acrylate (121,124,126,127), hydroxyethyl acrylate (123), vinyl acetate (122,128), vinyl ethers (128,129), and vinylidene chloride (124,125,130–132) are also used in barrier films, laminates, and coatings. Environmentally degradable polymers useful in packaging are prepared from polymerization of acrylonitrile with styrene and methyl vinyl ketone (133).

Acrylonitrile multipolymers containing methyl methacrylate, α-methyl styrene, and indene are used as PVC modifiers to melt blend with PVC. These PVC modifiers not only enhance the heat distortion temperature but also improve the processability of the PVC compounds (134–138). The acrylonitrile multipolymers grafted on the elastomer phase provide the toughness and impact strength of the PVC compounds with high heat distortion temperature and good processability (139,140). Table 6 gives the structures, formulas, and CAS Registry Numbers for several comonomers of acrylonitrile.

Although the arrangement of monomer units in acrylonitrile copolymers is usually random, alternating or block copolymers may be prepared by using special techniques. For example, the copolymerization of acrylonitrile, like that of other vinyl monomers containing conjugated carbonyl or cyano groups, is changed in the presence of certain Lewis acids. Effective Lewis acids are metal compounds with nontransition metals as central atoms, including alkylaluminum halides, zinc halides, and triethylaluminum. The presence of the Lewis acid increases the tendency of acrylonitrile to alternate with electron-donor

Table 6. **Monomers Commonly Copolymerized with Acrylonitrile**

Monomer	Molecular formula	Structural formula	CAS Registry Number
methyl methacrylate	$C_5H_8O_2$	$CH_2{=}C(CH_3)COOCH_3$	[80-62-6]
methyl acrylate	$C_4H_6O_2$	$CH_2{=}CHCOOCH_3$	[96-33-3]
indene	C_9H_8		[95-13-6]
isobutylene	C_4H_8	$CH_2{=}C(CH_3)_2$	[115-11-7]
butyl acrylate	$C_7H_{12}O_2$	$CH_2{=}CHCOOC_4H_9$	[141-32-2]
ethyl acrylate	$C_5H_8O_2$	$CH_2{=}CHCOOC_2H_5$	[140-88-5]
2-ethylhexyl acrylate	$C_{11}H_{20}O_2$	$CH_2{=}CHCOOC_8H_{17}$	[103-11-7]
hydroxyethyl acrylate	$C_5H_8O_3$	$CH_2{=}CHCOOC_2H_4OH$	[818-61-1]
vinyl acetate	$C_4H_6O_2$	$CH_2{=}CHOOCCH_3$	[108-05-4]
vinylidene chloride	$C_2H_2Cl_2$	$CH_2{=}C(Cl)_2$	[75-35-4]
methyl vinyl ketone	C_4H_6O	$CH_2{=}CHCOCH_3$	[78-94-4]
α-methylstyrene	C_9H_{10}	$CH_2{=}C(CH_3)C_6H_5$	[98-83-9]
vinyl chloride	C_2H_3Cl	$CH_2{=}CHCl$	[75-01-4]
4-vinylpyridine	C_7H_7N	$CH_2{=}CHC_5H_4N$	[100-43-6]
acrylic acid	$C_3H_4O_2$	$CH_2{=}CHCOOH$	[79-10-7]

molecules, such as styrene, α-methylstyrene, and olefins (141–145). This alternation is often attributed to a ternary molecular complex or charge-transfer mechanism, where complex formation with the Lewis acid increases the electron-accepting ability of acrylonitrile, which results in the formation of a molecular complex between the acrylonitrile–Lewis acid complex and the donor molecule. This ternary molecular complex polymerizes as a unit to yield an alternating polymer. Cross-propagation and complex radical mechanisms have also been proposed (146).

A number of methods such as ultrasonics (147), radiation (148), and chemical techniques (149–151), including the use of polymer radicals, polymer ions, and organometallic initiators, have been used to prepare acrylonitrile block copolymers (152). Block comonomers include styrene, methyl acrylate, methyl methacrylate, vinyl chloride, vinyl acetate, 4-vinylpyridine, acrylic acid, and *n*-butyl isocyanate.

The living radical polymerization system (atom transfer radical polymerization, ATRP has been developed recently which allows for the controlled polymerization of acrylonitrile and comonomers and to produce the well-defined linear homopolymer, statistical copolymers, block copolymers, and gradient copolymers (153–156). The well-defined diblock copolymers comprising a polystyrene and an acrylonitrile–styrene (or isoprene) copolymer sequence are prepared by living radical polymerization system (157,158). The stereospecific acrylonitrile polymers are made by solid-state urea clathrate polymerization (159) and organometallic compounds of alkali and alkaline earth metals initiated polymerization (160).

Acrylonitrile has been grafted onto many polymeric systems. In particular, acrylonitrile grafting has been used to impart hydrophilic behavior to starch (161–163) and polymer fibers (164). Exceptional water absorption capability results from the grafting of acrylonitrile to starch, and the use of 2-acrylamido-2-methylpropanesulfonic acid [15214-89-8] along with acrylonitrile for grafting results in copolymers that can absorb over 5000 times their weight of deionized water (165). For example, one commercial product made by General Mills, Inc., Super Slurper, is a modified starch suitable for disposable diapers, surgical pads and paper towels applications. Acrylonitrile polymers also provide some unique applications. Hollow fibers of acrylonitrile polymers as ultrafiltration membrane materials are used in the pharmaceutical and bioprocessing industries (166). Polyacrylonitrile-based electrolyte with $Li/LiMn_2O_4$ salts is used for solid-state batteries (167). Polyacrylonitrile is also used as a binding matrix for composite inorganic ion exchanger (168).

6. Economic Aspects

SAN has shown steady growth since its introduction in the 1950s. The combined properties of SAN copolymers such as optical clarity, rigidity, chemical and heat resistance, high tensile strength, and flexible molding characteristics, along with reasonable price have secured their market position. Among the plastics with which SAN competes are acrylics, general-purpose polystyrene, and polycarbonate. SAN supply and demand are difficult to track because more than 75% of the resins produced are believed to be used captively for ABS compounding and in the production of acrylonitrile–styrene–acrylate (ASA) and acrylonitrile–EPDM–styrene (AES) weatherable copolymer (169). SAN is considered to be only an intermediate product and not a separate polymer in the production processes for these materials.

There are two major producers of SAN for the merchant market in the United States, Bayer Corporation and the Dow Chemical Company, which market these materials under the names of Lustran and Tyril, respectively. Bayer became a U.S. producer when it purchsed Monsanto's styrenics business in December 1995 (170). Some typical physical properties of these have been shown in Table 1. These two companies also captively consume the SAN for the production of ABS as well as SAN-containing weatherable polymers. The other two U.S. SAN producers either mainly consume the resin captively for ABS and ASA polymers (GE Plastics) or tool produce for a single client (Zeon Chemicals). BASF is expected to become a more aggressive SAN supplier in the United States when its Altamira, Mexico, stryenics plant comes on in early 1999. Overall, U.S. SAN consumption has been relatively stable for the last few years, ranging from $(43–44.5)\times10^3$ metric tons (95–98 million pounds) between 1994 and 1996. Most markets for SAN are growing at only GDP rates. Consumption growth for SAN in 1996–2001 is expected to continue at an average annual rate approximation that of GDP growth at 2%. Use for packaging will be flat and the automotive application may disappear altogether; other markets, however, are expected to increase at annual rates between 2.3% and 5.9%. Production and consumption figures for SAN resin in recent years are shown in Table 7 (170).

Table 7. **U.S. Production/Consumption of SAN (10^3 metric tons, dry-weight basis)**

	Production	Consumption[a]
1985	39.5	34.1
1986	41.8	35.9
1987	57.3	38.6[b]
1988	67.3	41.4
1989	51.4	34.1
1990	61.4	37.3
1991	49.5	37.7
1992	51.4	38.2
1993	47.7	40
1994	62.7	44.5[c]
1995	59.1	43.6[c]
1996	55.5	43.6[c]
1997	43.6	—[c]

[a] Includes captive consumption for uses other than ABS compounding and ASA/AES polymers production.

[b] According to the SPI, 45 metric tons of SAN resin were consumed domestically in 1987. Industry believes this figure to be incorrect. An estimate of 38.6 metric tons is believed to be more accurate.

[c] Reported SPI data for 1996–1997 includes both U.S. and Canadian information and, therefore, are not included in this table. The stated CEH statistics represent consumption only.

7. Health and Safety Factors

SAN resins themselves appear to pose few health problems in that SAN resins are allowed by FDA to be used by the food and medical for certain applications under prescribed conditions (171). The main concern over SAN resin use is that of toxic residuals, eg, acrylonitrile, styrene, or other polymerization components such as emulsifiers, stabilizers, or solvents. Each component must be treated individually for toxic effects and safe exposure level.

Acrylonitrile is believed to behave as an enzyme inhibitor of cellular metabolism (172), and it is classified as a probable human carcinogen of medium carcinogenic hazard (173) and can affect the cardiovascular system and kidney and liver functions (172). Direct potential consumer exposure to acrylonitrile through consumer product usage is low because of little migration of the monomer from such products; the concentrations of acrylonitrile in consumer products are estimated to be less than 15 ppm in SAN resins. OSHA's permissible exposure limit for acrylontrile is 2 ppm as an 8-h time-weighted average with no eye or skin contact; the acceptable ceiling limit is 10 ppm; and the action level, the concentration level that triggers the standard for monitoring, etc, is 1 ppm. Further information on the toxicology and human exposure to acrylonitrile is available (174–176) (see ACRYLONITRILE).

Styrene, a main ingredient of SAN resins, is a possible human carcinogen (IARC Group 2B/EPA-ORD Group C). It is an irritant to the eyes and respiratory tract, and while prolonged exposure to the skin may cause irritation and central nervous system effects such as headache, weakness, and depression, harmful amounts are not likely to absorbed through the skin. OSHA has set permissible exposure limits for styrene in an 8-h time-weighted average at 100 ppm; the acceptable ceiling limit (short-term, 15 min, exposure limit at 200 ppm) (177); and the acceptable maximum peak at 600 ppm (5-min max. peak in any 3 h). For more information on styrene environmental issues, see the CEH Styrene marketing research report (178,179).

In September 1996, the EPA issued a final rule requiring producers of certain thermoplastics to reduce emissions of hazardous air pollutants from their facilities. The final rule seeks to control air toxins released during the manufacture of seven types of polymers and resins, including SAN.

8. Uses

Acrylonitrile copolymers offer useful properties, such as rigidity, gas barrier, chemical and solvent resistance, and toughness. These properties are dependent upon the acrylonitrile content in the copolymers. SAN copolymers offer low cost, rigidity, processability, chemical and solvent resistance, transparency, and heat resistance in which the properties provide the advantages over other competing transparent/clear resins, such as: polymethyl methacrylate, polystyrene, polycarbonate, and styrene–butadiene copolymers. SAN copolymers are widely used in goods such as housewares, packaging, appliances, interior automotive lenses, industrial battery cases, and medical parts. U.S. consumption of SAN resins in major industrial markets are shown in Table 8.

Table 8. **SAN Copolymer Uses**[a]

Application	Articles
appliances	air conditioner parts, decorated escutcheons, washer and dryer instrument panels, washing machine filter bowls, refrigerator shelves, meat and vegetable drawers and covers, blender bowls, mixers, lenses, knobs, vacuum cleaner parts, humidifiers, and detergent dispensers
automotive	batteries, bezels, instrument lenses, signals, glass-filled dashboard components, and interior trim
construction	safety glazing, water filter housings, and water faucet knobs
electronic	battery cases, instrument lenses, cassette parts, computer reels, and phonograph covers
furniture	chair backs and shells, drawer pulls, and caster rollers
housewares	brush blocks and handles, broom and brush bristles, cocktail glasses, disposable dining utensils, dishwasher-safe tumblers, mugs, salad bowls, carafes, serving trays, and assorted drinkware, hangers, ice buckets, jars, and soap containers
industrial	batteries, business machines, transmitter caps, instrument covers, and tape and data reels
medical	syringes, blood aspirators, intravenous connectors and valves, petri dishes, and artificial kidney devices
packaging	bottles, bottle overcaps, closures, containers, display boxes, films, jars, sprayers, cosmetics packaging, liners, and vials
custom molding	aerosol nozzles, camera parts, dentures, disposable lighter housings, fishing lures, pen and pencil barrels, sporting goods, toys, telephone parts, filter bowls, tape dispensers, terminal boxes, toothbrush handles, and typewriter keys

[a] Refs. 9 and 103.

Acrylonitrile copolymers have been widely used in films and laminates for packaging (180–184) due to their excellent barrier properties. In addition to laminates (185–189), SAN copolymers are used in membranes (190–193), controlled-release formulations (194,195), polymeric foams (196,197), fire-resistant compositions (198,199), ion-exchange resins (200), reinforced paper (201), concrete and mortar compositions (202,203), safety glasses (204), solid ionic conductors (205), negative resist materials (206), electrophotographic toners (207), and optical recording as well (208). SAN copolymers are also used as coatings (209), dispersing agents for colorants (210), carbon-fiber coatings for improved adhesion (211), and synthetic wood pulp (212). SAN copolymers have been blended with aromatic polyesters to improve hydrolytic stability (213), with methyl methacrylate polymers to form highly transparent resins (214), and with polycarbonate to form toughened compositions with good impact strength (215–218). Table 8 lists the most common uses of SAN copolymers in major industrial markets (9,101). Some important modifications of SAN copolymers are listed in Table 9.

Acrylonitrile has contributed the desirable properties of rigidity, high-temperature resistance, clarity, solvent resistance, and gas impermeability to many polymeric systems. Its availability, reactivity, and low cost ensure a continuing market presence and provide potential for many new applications.

Table 9. **Modified SAN Copolymers**

Modifier	Remarks	Reference
polybutadiene	ABS, impact resistant	[a]
EPDM rubber[b]	impact and weather resistant	218, 219
polyacrylate	impact and weather resistant	220, 221
poly(ethylene–*co*-vinyl acetate) (EVA)	impact and weather resistant	222
EPDM + EVA	impact and weather resistant	223
silicones	impact and weather resistant	224
chlorinated polyethylene	impact and weather resistant and flame retardant	225
polyester, cross-linked	impact resistant	226
poly(α-methylstyrene)	heat resistant	227
poly(butylene terephthalate)	wear and abrasion resistant	228
ethylene oxide–propylene oxide copolymers	used as lubricants to improve processibility	229
sulfonation	hydrogels of high water absorption	230
glass fibers	high tensile strength and hardness	231

[a] See ACRYLONITRILE POLYMERS, ABS RESINS.

[b] Ethylene–propylene–diene monomer rubber.

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