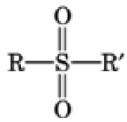
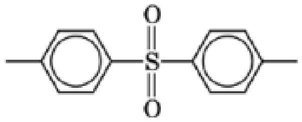
*Kirk-Othmer Encyclopedia of Chemical Technology.*

# POLYMERS CONTAINING SULFUR, POLYSULFONES

A polysulfone is characterized by the presence of the sulfone group as part of its repeating unit. Polysulfones may be aliphatic or aromatic. Aliphatic polysulfones (R and R′ are alkyl groups) were synthesized by radical-induced copolymerization of olefins and sulfur dioxide and characterized many years ago. However, they never demonstrated significant practical utility due to their relatively unattractive physical properties, not withstanding the low cost of their raw materials (1, 2). The polysulfones discussed in this article are those based on an aromatic backbone structure. The term polysulfones is used almost exclusively to denote aromatic polysulfones.



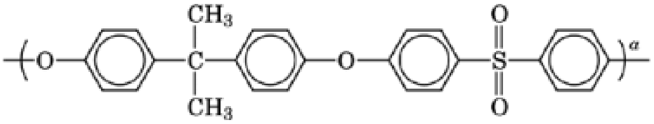
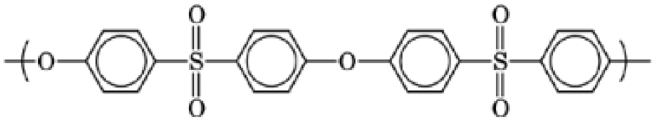
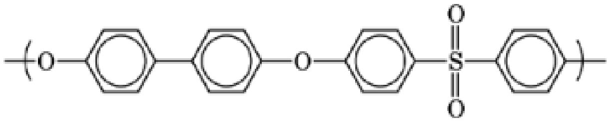
$$R-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-R'$$



Polysulfones are a class of amorphous thermoplastic polymers characterized by high glass-transition temperatures, good mechanical strength and stiffness, and outstanding thermal and oxidative resistance. These polymers are characterized by the presence of the para-linked diphenylsulfone group **(2)** as part of their backbone repeat units. By virtue of their mechanical, thermal, and other desirable characteristics, these polymers enjoy an increasingly wide and diversified range of commercial applications. The basic repeat unit of any polysulfone always contains sulfone, aryl, and ether units as part of the main backbone structure and are thus often referred to in the polymer literature as poly(arylethersulfone)s. Other names include polysulfones, polyethersulfones, and polyarylsulfones and the lack of standardization in nomenclature has often resulted in confusion as to the meaning of a designation. The different designations are somewhat arbitrary and all refer to the same class of polymers.

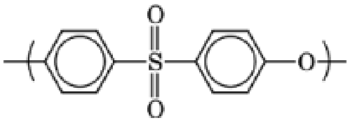
In addition to sulfone, phenyl units, and ether moieties, the main backbone of polysulfones can contain a number of other connecting units. The most notable such connecting group is the isopropylidene linkage which is part of the repeat unit of the well-known bisphenol A-based polysulfone. It is difficult to clearly describe the chemical makeup of polysulfones without reference to the chemistry used to synthesize them. There are several routes for the synthesis of polysulfones, but the one which has proved to be most practical and versatile over the years is by aromatic nucleophilic substitution. This polycondensation route is based on reaction of essentially equimolar quantities of 4,4′-dihalodiphenylsulfone (usually dichlorodiphenylsulfone (DCDPS)) with a bisphenol in the presence of base thereby forming the aromatic ether bonds and eliminating an alkali salt as

**Table 1. Chemical Structures and Glass-Transition Temperatures, $T_g$, of PSF, PES, and PPSF[a]**

| Polymer | Repeat unit structure | $T_g$, °C |
|---|---|---|
| polysulfone |  | 185 |
| polyethersulfone[b,c] |  | 220 |
| polyphenylsulfone[d] |  | 220 |

[a] Bisphenol A polysulfone [25135-51-7].

[b] PES repeat unit structure can alternatively be drawn as



[c] Victrex polyethersulfone [25667-42-9].

[d] RADEL R polyphenylsulfone [25608-64-4].

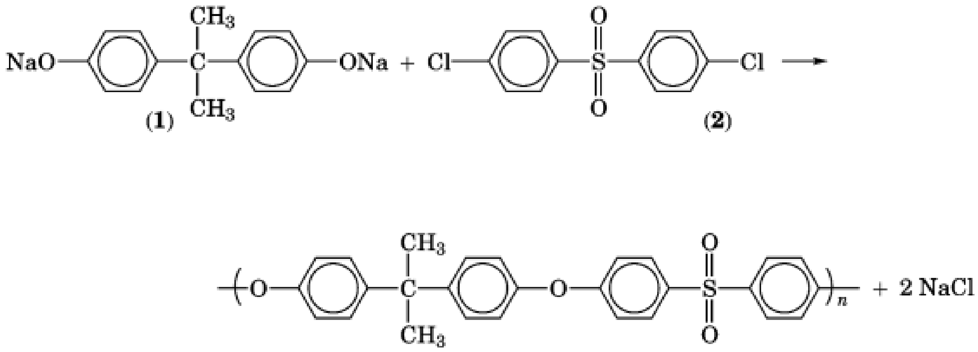
a by-product. This route is employed almost exclusively for the manufacture of polysulfones on a commercial scale.

The diphenylsulfone group is supplied to the repeat unit of all polysulfones by DCDPS; the differentiating species between various polysulfones comes from the choice of bisphenol. There are three commercially important polysulfones referred to generically by the common names polysulfone (PSF), polyethersulfone (PES), and polyphenylsulfone (PPSF). The repeat units of these polymers are shown in Table 1.

## 1. Polymerization

### 1.1. Nucleophilic Substitution Route

Commercial synthesis of poly(arylethersulfone)s is accomplished almost exclusively via the nucleophilic substitution polycondensation route. This synthesis route, discovered at Union Carbide in the early 1960s (3, 4), involves reaction of the bisphenol of choice with 4,4′-dichlorodiphenylsulfone in a dipolar aprotic solvent in the presence of an alkali base. Examples of dipolar aprotic solvents include *N*-methyl-2-pyrrolidinone (NMP), dimethyl acetamide (DMAc), sulfolane, and dimethyl sulfoxide (DMSO). Examples of suitable bases are sodium hydroxide, potassium hydroxide, and potassium carbonate. In the case of polysulfone (PSF) synthesis, the reaction is a two-step process in which the dialkali metal salt of bisphenol A **(1)** is first formed *in situ* from bisphenol A [80-05-7] by reaction with the base (eg, two molar equivalents of NaOH), followed by the nucleophilic substitution reaction of **(1)** with 4,4′-dichlorodiphenylsulfone [80-07-9] **(2)**. Polysulfone is typically prepared as described in Reference 5 according to equation **1** where *n=40*–60. The minimum degree of polymerization is dictated by the minimum molecular weight required to achieve useful mechanical properties from the polymer. For polysulfone, this corresponds to a reduced viscosity of about 0.35 dL/g (in chloroform at 25°C and 0.2 g/dL concentration).



(1)

**Table 2. Glass-Transition Temperatures of Polysulfones Produced from the Polycondensation of Dichlorodiphenylsulfone with Various Bisphenols**$^a$

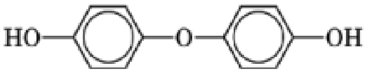
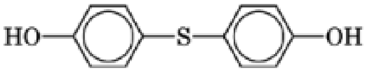
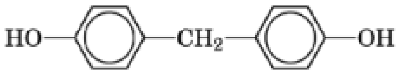
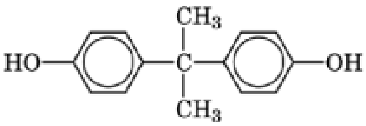
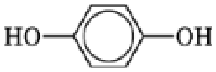
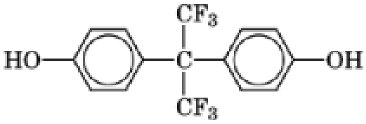
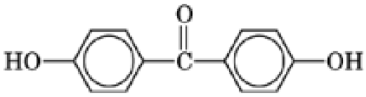
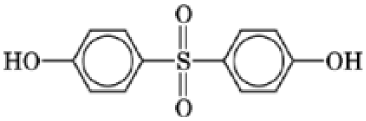
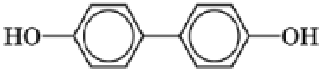
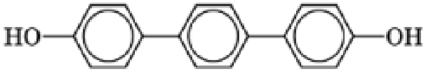
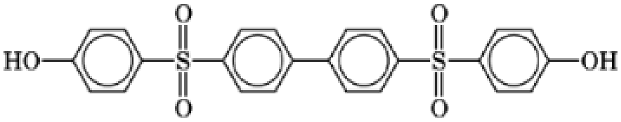
| Bisphenol | Structure | $T_g$,$^b$ °C |
|---|---|---|
| 4,4′-dihydroxydiphenyl oxide |  | 170 |
| 4,4′-dihydroxydiphenyl sulfide |  | 175 |
| 4,4′-dihydroxydiphenyl methane |  | 180 |
| 2,2-bis(4-hydroxyphenyl)propane |  | 185 |

**Table 2.** ***Continued***

| Bisphenol | Structure | $T_g$,[b] °C |
|---|---|---|
| hydroquinone |  | 200 |
| 2,2-bis(4-hydroxyphenyl)-perfluoropropane |  | 205 |
| 4,4′-dihydroxybenzo-phenone |  | 205 |
| 4,4′-dihydroxydiphenyl sulfone |  | 220 |
| 4,4′-dihydroxydiphenyl |  | 220 |
| 1,4-bis(4-hydroxyphenyl)-benzene |  | 250 |
| 4,4′-bis(4″-hydroxyben-zenesulfonyl)diphenyl |  | 265 |

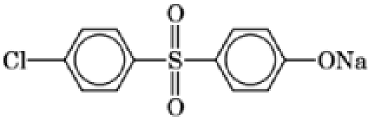
[a] Ref. 17.

[b] Glass-transition values reported rounded to nearest 5°C.

The rate of polymerization in this type of reaction depends on both the basicity of the bisphenol salt and the electron-withdrawing capacity of the activating group (in this case sulfone) in the dihalide monomer. The difluoride-based sulfone monomer is more reactive than the dichloride and thus gives higher polymerization rates, but the latter is by far the more economical raw material. Another important consideration in reactivity and the attainment of high molecular weight is the purity of the 4,4′-isomer in the dichlorodiphenyl sulfone monomer. Chlorines in the meta position on the phenyl ring are not activated and do not undergo nucleophilic displacement. Hence, a significant presence of the 3,4′-isomer of the sulfone monomer can act as a monofunctional terminating species for the polycondensation and prevent the attainment of target molecular weights. Factors governing rates of reaction have been discussed (6).

DMSO is an effective solvent for the polymerization as it affords good solubility for both the polymer and disodium bisphenol A [2444-90-8]. Typical polymerization temperatures for polysulfone are in the range 130–160°C. At temperatures below 130°C, the polymerization slows down considerably due to poor solubility of the disodium bisphenol A salt.

The reaction of NaOH with bisphenol A generates water. This water must be thoroughly removed from the system to allow the reaction to be driven to completion, and more importantly, to preclude any residual water in the system from hydrolyzing part of the DCDPS monomer **(2)**. Before the introduction of DCDPS for the polymerization step, all but traces of water must be removed. Failure to do so results in regeneration of NaOH, which rapidly reacts with DCDPS to form the monosodium salt of 4-chloro-4′-hydroxydiphenylsulfone [18995-09-0] **(3)** (6).



**(3)**

With as little as 0.5% hydrolysis of the sulfone monomer, the polymerization stoichiometric balance is sufficiently upset to prevent high molecular weight polymer from being achieved. The dependence of maximum attainable PSF molecular weight on water content during polymerization can be inferred from Figure 1.

Molecular weight control for nucleophilic condensation polymerizations of this type is achieved by one of several methods: (*1*) the addition of a monohalogen compound such as chloromethane once target molecular weight is achieved; ie, such compounds terminate chain growth by reacting with available sodium phenate end groups forming nonreactive methoxyl end groups on the chains; (*2*) excess DCDPS monomer can be used to limit the maximum attainable molecular weight via stoichiometric imbalance; (*3*) monohydric phenols or monohalo-activated aromatic compounds can also be used as chain terminators. Generally, the first or the second method (or a combination of them) is used. In the case of termination methods (*2*) or (*3*), the terminator is typically added at the beginning of the reaction with the monomer charge. The actual effect of any such terminator depends on its relative reactivity as well as the amount added. The terminator unbalances the stoichiometry of the two monomers thereby placing a ceiling on the maximum theoretically attainable molecular degree of polymerization according to Carothers' principle of functionality. A mole ratio of unity for the two parent monomers results in the highest attainable molecular weight as illustrated in Figure 2. The most favorable reaction rates are also achieved by maintaining the monomer ratio at or very near unity.

The polymerizations of polyethersulfone (PES) and polyphenylsulfone (PPSF) are analogous to that of PSF, except that in the case of these two polymers, solvents which are higher boiling than DMSO are needed due to the higher reaction temperatures required. Diphenyl sulfone, sulfolane, and NMP are examples of suitable solvents for PES and PPSF polymerizations. Chlorobenzene or toluene are used as cosolvents at low concentrations. These cosolvents form an azeotrope with water as they distill out of the reaction mixture, thereby keeping the polymerization medium dehydrated. Potassium carbonate is a suitable choice for base. The synthesis of PES and PPSF differ from the PSF case in that the reaction is carried out in a single-step

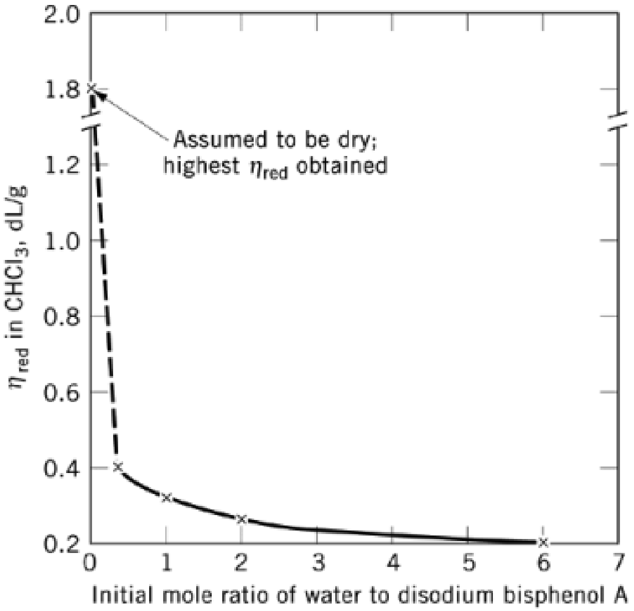
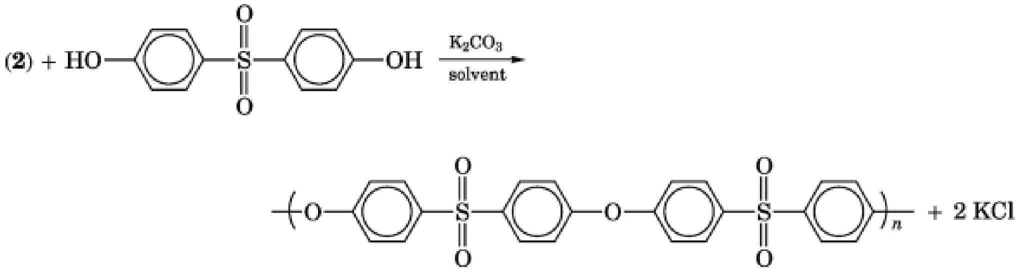
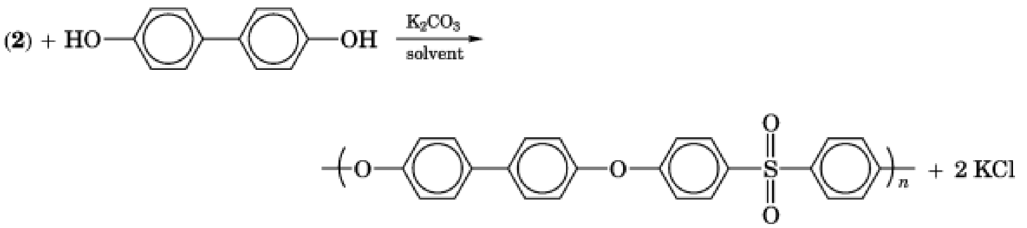


**Fig. 1.** Effect of water presence in polysulfone polymerization on maximum attainable polymer reduced ($\eta_{red}$) viscosity.

process. In other words, the formation of the dipotassium salt of the bisphenol is not completed in a separate first step. Equations 2 and 3 represent polymerizations based on the dipotassium salts of bisphenol S and biphenol to make PES and PPSF, respectively.



(2)



(3)

An alternative synthesis route for PES involves the partial hydrolysis of dichlorodiphenyl sulfone **(2)** with base to produce 4-chloro-4′-hydroxydiphenylsulfone [7402-67-7] **(3)** followed by the polycondensation of this difunctional monomer in the presence of potassium hydroxide or potassium carbonate (7).

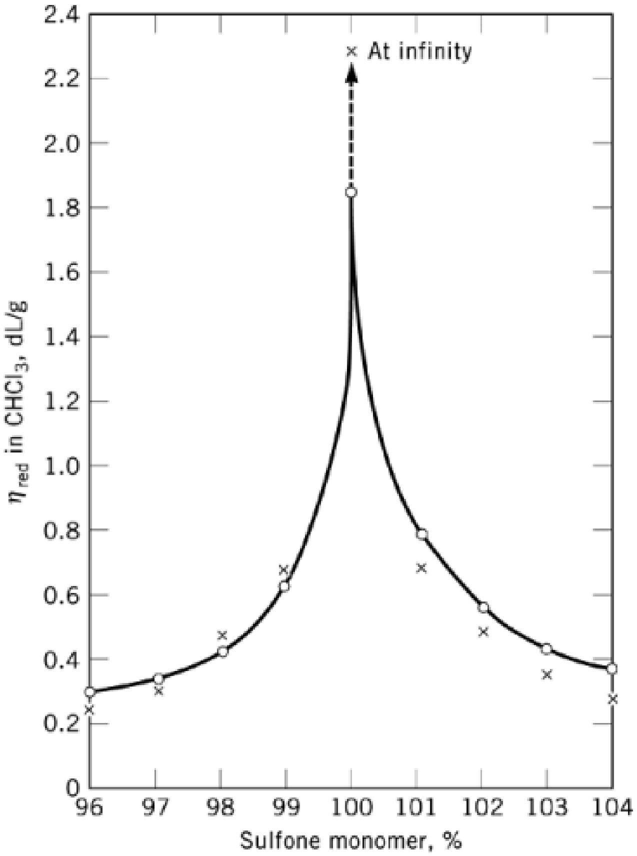


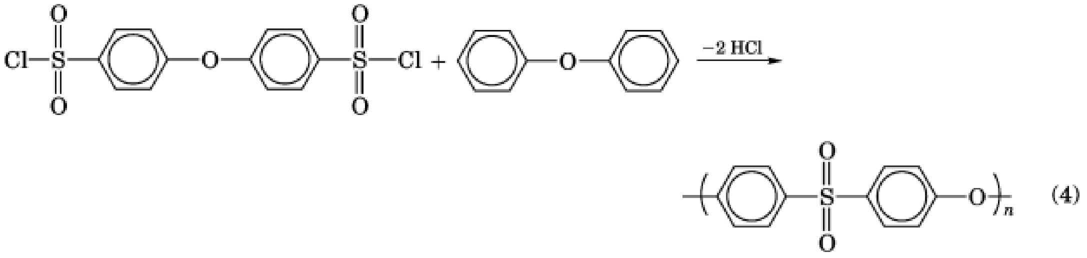
**Fig. 2.** Effect of stoichiometric imbalance in polysulfone polymerization on maximum attainable polymer reduced ($\eta_{red}$) viscosity where (×) is theoretical, and (○), experimental.

As a variation on the base-catalyzed nucleophilic displacement chemistry described, polysulfones and other polyarylethers have been prepared by cuprous chloride-catalyzed polycondensation of aromatic dihydroxy compounds with aromatic dibromo compounds. The advantage of this route is that it does not require that the aromatic dibromo compound be activated by an electron-withdrawing group such as the sulfone group. Details of this polymerization method, known as the Ullmann synthesis, have been described (8).

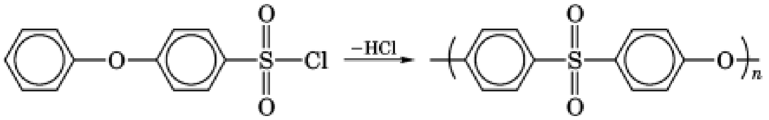
A method for the polymerization of polysulfones in nondipolar aprotic solvents has been developed and reported (9, 10). The method relies on phase-transfer catalysis. Polysulfone is made in chlorobenzene as solvent with (2.2.2)cryptand as catalyst (9). Less reactive crown ethers require dichlorobenzene as solvent (10). High molecular weight polyphenylsulfone can also be made by this route in dichlorobenzene; however, only low molecular weight PES is achievable by this method. Cross-linked polystyrene-bound (2.2.2)cryptand is found to be effective in these polymerizations which allow simple recovery and reuse of the catalyst.

### 1.2. Other Synthesis Routes

Several alternative routes to the nucleophilic substitution synthesis of polysulfones are possible. Polyethersulfone can be synthesized by the electrophilic Friedel-Crafts reaction of bis(4-chlorosulfonylphenyl)ether [121-63-1] with diphenyl ether [101-84-8] (11–13).

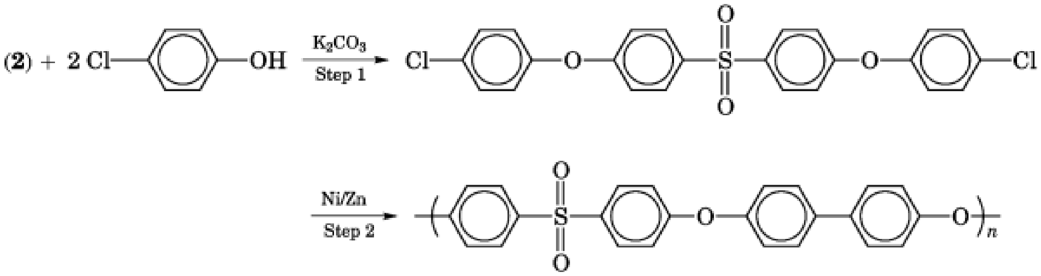

(4)

The same reaction can be carried out using 4-chlorosulfonyldiphenyl ether [1623-92-3] as a single monomer:


(5)

The single-monomer route (eq. **5**) is preferred as it proves to give more linear and para-linked repeat unit structures than the two-monomer route. Other sulfone-based polymers can be similarly produced from sulfonyl halides with aromatic hydrocarbons. The key step in these polymerizations is the formation of the carbon–sulfur bond. High polymers are achievable via this synthesis route although the resulting polymers are not always completely linear.

An elegant synthesis method which is specific to sulfone polymers containing phenyl–phenyl linkages (such as PPSF) is the nickel-catalyzed coupling of aryl dihalides. The scheme for this synthesis involves a two-step process. First, an aromatic dihalide intermediate is formed which carries the backbone features of the desired polymer. This aromatic dihalide intermediate is then self-coupled in the presence of zero-valent nickel, triphenylphosphine, and excess zinc to form the biphenyl- or terphenyl-containing polymer. Application of this two-step scheme to PPSF can be depicted as follows:



The first step in this scheme is a classical aromatic nucleophilic substitution. Details of the method have been expounded (14–17). References 14 and 15 are concerned with the synthesis of the diaryl halide intermediate whereas References 16 and 17 discuss the synthesis of the polymers, with emphasis on the polymerization of PPSF by this route.

Oxidative coupling of aromatic compounds via the Scholl reaction has been applied successfully to synthesize a polyarylethersulfone (18). High molecular weight polymer was obtained upon treating 4,4′-di(1-naphthoxy)diphenylsulfone and 4,4′-di(1-naphthoxy)benzophenone with ferric chloride. Equimolar amounts of the Lewis acid are required and the method is limited to naphthoxy-based monomers and other systems that can undergo the Scholl reaction.

## 2. Properties

### 2.1. Structure–Property Relationships

The characteristic feature of each of the polymers in Table 1 is the highly resonant diaryl sulfone grouping. As a consequence of the sulfur atom being in its highest state of oxidation and the enhanced resonance of the sulfone group being in the para position, these resins offer outstanding thermal stability and resistance to thermal oxidation. The thermal stability is further augmented by the high bond dissociation energies inherent in the aromatic backbone structure. As a result, these polymers can be melt fabricated at temperatures of up to 400°C with no adverse consequences. The high degree of oxidative stability also allows for prolonged or continuous exposure to temperatures of anywhere between 150–190°C, depending on polymer, formulation, and use conditions. The ether linkages in these polymers contribute to chain flexibility leading to mechanical toughness and favorable melt rheological properties. The relatively inert ether and sulfone backbone functionalities contribute to resistance against hydrolysis and chemical attack by acids and bases. Medical and food contact applications for polysulfones are possible in part because of this characteristic.

The high glass-transition temperature, $T_g$, of polysulfones is attributed to the rigid phenyl rings in the backbone and also the sulfone group which increases $T_g$ by providing strong dipole interactions and restricting rotation of the aromatic units relative to other connecting groups. The ether groups in these polymers are the main flexibilizing units and the $T_g$ of polysulfones is inversely to the ether content in the backbone on a repeat unit weight basis. Other connecting groups can contribute either an increase or decrease in chain rigidity and $T_g$ depending on the conformational freedom and polarity of those units. The most convenient way to tailor properties of a polysulfone to specific needs is through the selection of the bisphenol. The $T_g$s of polysulfones based on the polycondensation of DCDPS with different bisphenols are listed in Table 2.

The three polysulfones in Table 1 exhibit several important common attributes, but there are distinguishing features for each member of this group. Examination of the repeat unit formulas shows that a primary distinguishing feature of PES is that it contains almost double the sulfone group content on a weight basis compared to PSF. Another differentiation is that the flexibilizing isopropylidene unit is absent in PES. As a consequence of these structural changes, the $T_g$ of PES is 35°C higher than that of PSF. On the other hand, because the sulfone group is the most hygroscopic moiety in the backbone of these polymers and the isopropylidene is hydrophobic, the moisture uptake at equilibrium is significantly lower for PSF than it is for PES (Table 3). The ability to maintain water absorption of a plastic at a minimum is desirable for most engineering applications. Thus backbone structure of a polysulfone is tied to physical properties and ultimately to performance in various applications.

Mechanical properties of aromatic polysulfones are intimately tied to backbone structure. For the achievement of good strength and toughness together with favorable melt processing characteristics the first and foremost requirement is a linear (unbranched) and para-linked structure for the aryl groups in the backbone. The nature of the permanent deformation mechanism is not the same in all polysulfones. Rather, it is dependent on subtle backbone structural features, the best illustration of which is the step improvement in impact and toughness properties of PPSF over those of PES and PSF. The dependence of polysulfone mechanical toughness on backbone structural features has been discussed in detail (19).

### 2.2. Physical, Chemical, and Optical Properties

Aromatic polysulfones possess several common key attributes including high glass-transition temperatures (generally $> 170°C$) and a high degree of thermal oxidative stability (Table 3). Thermal oxidative stability of PSF, PES, and PPSF can be inferred from the thermogravimetric data shown in Figure 3. Because of their fully amorphous nature, these resins exhibit optical transparency. The glass-transition temperature of polysulfones produced via nucleophilic polycondensation can be tailored by the choice of the bisphenol as illustrated in Table

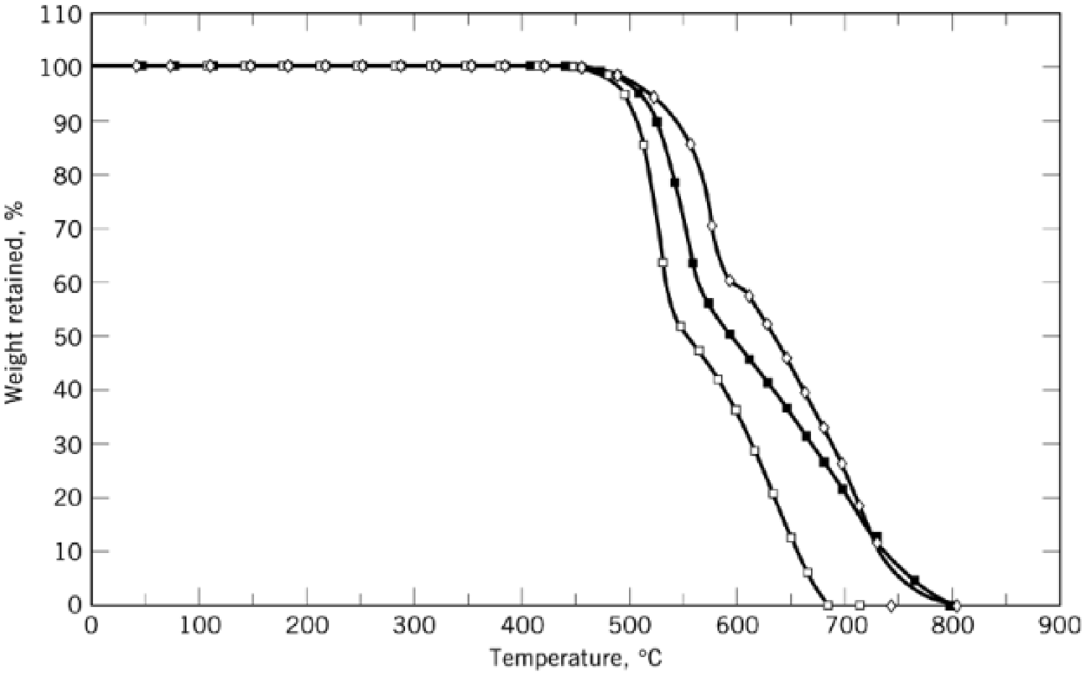


**Fig. 3.** Thermogravimetric analysis (tga) curves in air for (□) PSF, (■) PES, and (◇) PPSF. Tga in nitrogen at a heating rate of 10°C/min (17).

2. By virtue of the chemically nonlabile aromatic ether backbone, these polymers exhibit superb resistance to hydrolysis in hot water and steam environments. Furthermore, they can withstand acidic and alkali media over a wide range of concentrations and temperatures.

In addition to conferring transparency on these polymers, the amorphous noncrystallizable nature of polysulfones assures minimal shrinkage during fabrication of the resins into finished parts. The absence of crystallinity also assures dimensional stability during the service life of the parts where high use temperatures are encountered. Good dimensional stability is important to many structural and engineering applications.

Although commercially available polysulfones are transparent in their natural form, they show a slight yellow–amber tinge. This color is related to the high melt processing temperatures required during resin manufacture and finishing steps. Great progress has been made over the years in controlling and minimizing color (yellowness) in polysulfones. Among the three commercially available polysulfones, the bisphenol A-based polymer (PSF) exhibits the lowest color and highest transmittance of visible light. The light transmittance value ranges given in Table 3 are based on the color ranges that are typical for commercially available grades.

Because of the presence of the sulfone moiety, polysulfones are slightly hygroscopic. Absorbed water expands linear dimensions of a polysulfone of the order of 0.010–0.012% for every 0.1 wt % of moisture absorbed. This dimensional change is relatively small, but it can be important in applications where very close dimensional tolerances are a requirement. In addition to effecting small dimensional changes, absorbed moisture causes a slight plasticization of the plastic, contributing to some lowering of stiffness and strength in hot, wet environments. This effect is again small and can be easily compensated for by judicious part design and engineering.

**Table 3. Physical and Thermal Properties of PSF, PES, and PPSF**

| Property | ASTM test method | PSF | PES | PPSF |
|---|---|---|---|---|
| color | | light yellow | light amber | light amber |
| haze[a], % | D1004 | <7 | <7 | <7 |
| light transmittance[b], % | | 80 | 70 | 70 |
| refractive index | D1505 | 1.63 | 1.65 | 1.67 |
| density, g/cm$^3$ | D1505 | 1.24 | 1.37 | 1.29 |
| glass-transition tempera-ture[c], °C | | 185 | 220 | 220 |
| heat deflection tempera-ture[d], °C | D648 | 174 | 204 | 207 |
| continuous service tempera-ture[e], °C | | 160 | 180 | 180 |
| coefficient of linear thermal expansion | D696 | $5.1 \times 10^{-5}$ | $5.5 \times 10^{-5}$ | $5.5 \times 10^{-5}$ |
| specific heat at 23°C, J/(g·K)[f] | | 1.00 | 1.12 | 1.17 |
| thermal conductivity, W/(m·K)[g] | C177 | 0.26 | 0.18 | 0.35 |
| water absorption, % | | | | |
| in 24 h | D570 | 0.22 | 0.61 | 0.37 |
| at equilibrium | D570 | 0.62 | 2.1 | 1.1 |
| mold shrinkage, cm/cm | D955 | 0.005 | 0.006 | 0.006 |
| temperature at 10% weight loss (tga)[h] | | | | |
| in nitrogen | | 512 | 547 | 550 |
| in air | | 507 | 515 | 541 |

[a] As measured on 3.1-mm thick specimens.

[b] Typical values; varies with color. All three resins are transparent.

[c] Onset value as measured by differential scanning calorimetry.

[d] As measured on 3.1-mm thick ASTM specimens under a load of 1.82 MPa (264 psi).

[e] Practical maximum long-term use temperatures for PSF and PES based on UL 746 thermal rating data; value for PPSF is estimated.

[f] To convert J/(g·K) to Btu/(lb·°F), divide by 4.184.

[g] To convert W/(m·K) to Btu/(h·ft·°F), multiply by 1.874.

[h] Thermogravimetric analysis (tga) run at heating rate of 10°C/min and 20 mL/min gas (nitrogen or air) flow rate.

### 2.3. Mechanical Properties

Polysulfones are rigid and tough with practical engineering strength and stiffness properties even without reinforcement. Their strength and stiffness at room temperature are high compared to traditional aliphatic backbone amorphous plastics. The polymers exhibit ductile yielding over a wide range of temperatures and deformation rates. High unnotched impact resistance has been tied to a second-order ($\beta$) transition which is observed in these polymers under dynamic mechanical thermal analysis. The $\beta$-transition occurs at around $-100°\mathrm{C}$ and is believed to be due to two mechanisms. The first involves 180 degree flips of aromatic units about the ether bond (20). The second has been proposed to be a concerted motion of the sulfone group with complexed absorbed water (21). The presence of moisture increases the magnitude of the $\beta$-transition peak although it is not necessary for its existence. The effect of polysulfone backbone structure on the sub-$T_g$ relaxations has been the subject of detailed study (22).

The room temperature mechanical properties of bisphenol A, bisphenol S, and biphenol-based polysulfones are given in Table 4. The elastic limit (yield) elongation among these polymers is highest for PPSF; PES offers slightly higher tensile strength than the other two polymers. Otherwise the tensile and flexural properties for these three polymers are quite comparable. The main distinguishing feature in PPSF mechanical properties is its very high notched impact strength and the ability of the resin to retain a high degree of ductility after prolonged heat exposure. The data in Table 4 represent short-term mechanical properties under simple loading conditions. These values should only be regarded as typical values for generic polysulfone, polyethersulfone, and polyphenylsulfone of practical molecular weights. Mechanical performance assessment of an engineering polymer for consideration in a specific end use should include long-term aspects such as creep and fatigue

**Table 4. Room Temperature Mechanical Properties of PSF, PES, and PPSF**

| Property | ASTM test method | PSF | PES | PPSF |
|---|---|---|---|---|
| tensile[a] (yield) strength, MPa[b] | D638 | 70.3 | 83.0 | 70.0 |
| tensile modulus, GPa[c] | D638 | 2.48 | 2.60 | 2.30 |
| elongation at yield, % | D638 | 5.7 | 6.5 | 7.2 |
| elongation at break, % | D638 | 75 | 40 | 90 |
| flexural strength, MPa[b] | D790 | 106 | 111 | 91 |
| flexural modulus, GPa[c] | D790 | 2.69 | 2.90 | 2.40 |
| compressive strength, MPa[b] | D695 | 96 | 100 | 99 |
| compressive modulus, GPa[c] | D695 | 2.58 | 2.68 | 1.73 |
| shear (yield) strength, MPa[b] | D732 | 41.4 | 50 | 62 |
| notched Izod impact, J/m[d,e] | D256 | 69 | 85 | 694 |
| tensile impact, kJ/m$^2$ [f] | D1822 | 420 | 340 | 400 |
| Poisson ratio, at 0.5% strain | | 0.37 | 0.39 | 0.42 |
| Rockwell hardness | D785 | M69 | M88 | M86 |
| abrasion resistance,[g] mg/1000 cycles | D1044 | 20 | 19 | 20 |

[a] Tensile, flexural, and impact properties based on 3.1-mm thick ASTM specimens.
[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·lbf/in., divide by 53.38.
[e] No break for unnotched samples.
[f] To convert kJ/m$^2$ to ft·lbf/in.$^2$, divide by 2.10.
[g] Taber abrasion test using CS-17 wheel and 1000-g load for 1000 cycles.

properties where applicable. Temperature and environmental factors should also be taken into consideration.

The effect of temperature on PSF tensile stress–strain behavior is depicted in Figure 4. The resin continues to exhibit useful mechanical properties at temperatures up to 160°C under prolonged or repeated thermal exposure. PES and PPSF extend this temperature limit to about 180°C. The dependence of flexural moduli on temperature for polysulfones is shown in Figure 5 with comparison to other engineering thermoplastics.

The tensile and flexural properties as well as resistance to cracking in chemical environments can be substantially enhanced by the addition of fibrous reinforcements such as chopped glass fiber. Mechanical properties at room temperature for glass fiber-reinforced polysulfone and polyethersulfone are shown in Table 5.

### 2.4. Flammability

An important consideration in the selection of thermoplastic resins involves the need for good flame retardancy characteristics (see Flame retardants). Polysulfones exhibit excellent inherent burning resistance characteristics compared to many engineering thermoplastics. The wholly aromatic polysulfones such as PES and PPSF possess particularly outstanding flame retardancy and very low smoke release characteristics. The flammability of PSF is also good but can be enhanced further by the addition of a small proportion of a nonhalogen-based flame retardant. This forms the basis of the UDEL P-1720 commercial polysulfone grade from Amoco Corporation. Flammability properties of various polysulfones are given in Table 6.

### 2.5. Electrical Properties

Polysulfones offer excellent electrical insulative capabilities and other electrical properties as can be seen from the data in Table 7. The resins exhibit low dielectric constants and dissipation factors even in the GHz (microwave) frequency range. This performance is retained over a wide temperature range and has permitted

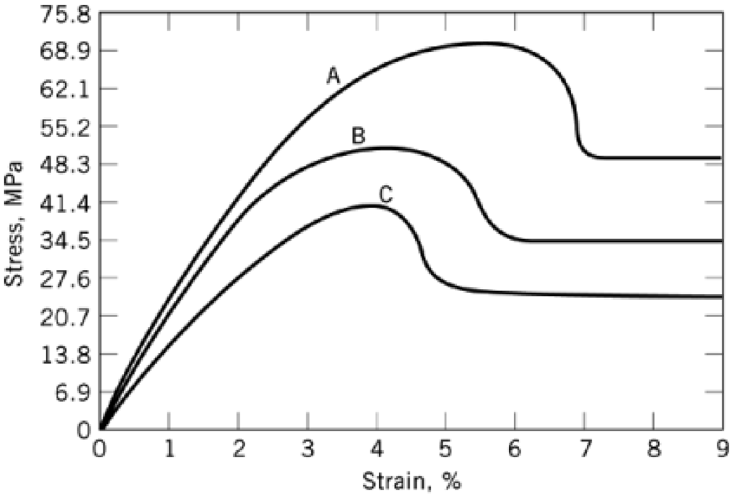


**Fig. 4.** Tensile stress–strain curves for polysulfone showing yield behavior at A, 20°C; B, 99°C; and C, 149°C. To convert MPa to psi, multiply by 145.

**Table 5. Properties of Glass Fiber-Reinforced (GR) Polysulfone and Polyethersulfone**

| | | Polysulfone, % GR | | | Polyethersulfone, % GR | | |
|---|---|---|---|---|---|---|---|
| Property | ASTM test method | 10 | 20 | 30 | 10 | 20 | 30 |
| tensile strength, MPa[a] | D638 | 77.9 | 96.5 | 108 | 86 | 105 | 126 |
| tensile modulus, GPa[b] | D638 | 3.65 | 5.17 | 7.38 | 3.8 | 5.7 | 8.6 |
| tensile elongation, % | D638 | 4.1 | 3.2 | 2.0 | 5.8 | 3.2 | 1.9 |
| flexural strength, MPa[a] | D790 | 128 | 148 | 154 | 145 | 162 | 179 |
| flexural modulus, GPa[b] | D790 | 3.79 | 5.52 | 7.58 | 4.1 | 5.2 | 8.1 |
| Izod impact, J/m[c] | D256 | 64 | 69 | 74 | 48 | 59 | 75 |
| tensile impact, kJ/$m^2$[d] | D1822 | 101 | 114 | 109 | 59 | 65 | 71 |
| heat deflection temperature, °C | D648 | 179 | 180 | 181 | 211 | 214 | 216 |
| CLTE[e], mm/mm·°C | D696 | 3.6 | 2.5 | 2.0 | 3.6 | 3.1 | 3.1 |
| specific gravity | D1505 | 1.33 | 1.40 | 1.49 | 1.43 | 1.51 | 1.58 |
| mold shrinkage, mm/mm | D955 | 0.004 | 0.003 | 0.002 | 0.005 | 0.004 | 0.003 |

[a] To convert MPa to psi, multiply by 145.
[b] To convert GPa to psi, multiply by 145,000.
[c] To convert J/m to ft·lbf/in., divide by 53.38.
[d] To convert kJ/$m^2$ to ft·lbf/$in.^2$, divide by 2.10.
[e] Coefficient of linear thermal expansion.

applications such as printed wiring board substrates, electronic connectors, lighting sockets, business machine components, and automotive fuse housings, to name a few. The desirable electrical properties along with the inherent flame retardancy of polysulfones make these polymers prime candidates in many high temperature electrical and electronic applications.

### 2.6. Resistance to Chemical Environments and Solubility

As a rule, amorphous plastics are susceptible, to various degrees, to cracking by certain chemical environments when the plastic material is placed under stress. The phenomenon is referred to as environmental stress cracking (ESC) and the resistance of the polymer to failure by this mode is known as environmental stress cracking

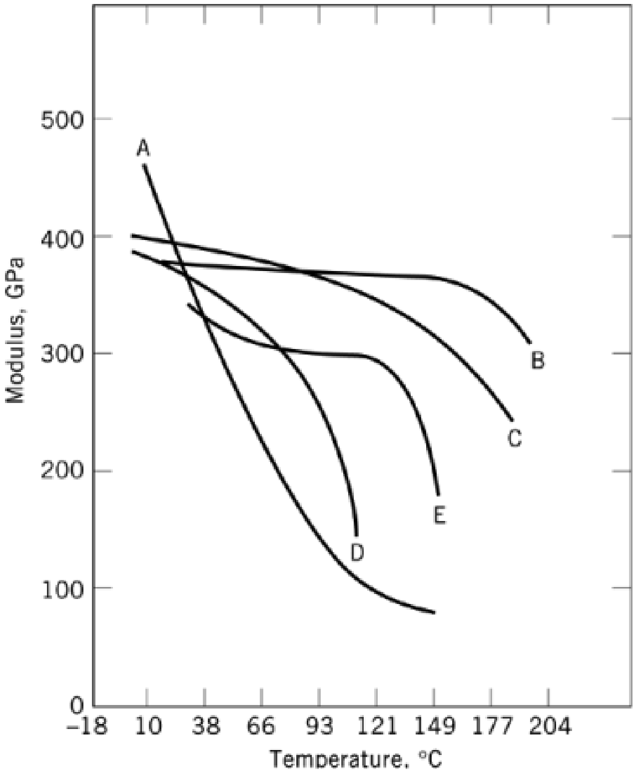


**Fig. 5.** Flexural modulus–temperature curves of C, polysulfone and B, polyethersulfone compared to the moduli curves of A, polyacetal; D, heat-resistant ABS; and E, polycarbonate. To convert GPa to psi, multiply by 145,000.

**Table 6. Flammability and Burning Behavior of PSF, PES, and PPSF**

| Property | Test method | PSF | PES | PPSF |
|---|---|---|---|---|
| flammability rating | UL 94 | V0 at 6.1 mm | V0 at 0.8 mm | V0 at 0.8 mm |
| limiting oxygen index | ASTM D286 | 30.0 | 38.0 | 38.0 |
| smoke density[a] | ASTM E662 | 90 at 1.5 mm | 35 at 6.2 mm | 30 at 6.2 mm |
| self-ignition temperature, °C | ASTM D 1929 | 621[b] | 502[b] | |

[a] Specific optical density, $D_m$, flaming condition.
[b] Thickness.

resistance (ESCR). The tendency of a polymer to undergo ESC depends on several factors, the most important of which are applied stress, temperature, and the concentration of the aggressive species. Polysulfones, being completely amorphous, exhibit susceptibility to stress cracking by some organic environments. The potency of the stress cracking agent is generally related to the match between the solubility parameter of the solvent with that of the polymer. For example, PSF, which has solubility parameter $\delta = 21.8$ $(J/cm^3)^{1/2}$, resists aliphatic hydrocarbons (lower $\delta$) and most alcohols (higher $\delta$), but readily undergoes stress cracking by ketones which have $\delta$-values sufficiently close to that of the polymer.

The exact mechanism of environmental stress cracking of a polymer is still not completely understood, but in essence it involves a weakening of the secondary intermolecular forces between polymeric segments due to the solubility of the chemical in the polymer. A number of crazes are generated at stressed polymer surfaces

**Table 7. Electrical Properties of PSF, PES, and PPSF**

| Property | ASTM test method | PSF | PES | PPSF |
|---|---|---|---|---|
| dielectric strength[a], kV/mm | D149 | 16.6 | 15.5 | 14.6 |
| volume resistivity, $\Omega\cdot$cm | D257 | $7 \times 10^{16}$ | $9 \times 10^{16}$ | $9 \times 10^{15}$ |
| dielectric constant, Hz | D150 | | | |
| at 60 | | 3.18 | 3.65 | 3.44 |
| $10^3$ | | 3.17 | 3.65 | 3.45 |
| $10^6$ | | 3.19 | 3.52 | 3.45 |
| dissipation factor, Hz | D150 | | | |
| at 60 | | 0.0008 | 0.0019 | 0.0006 |
| $10^3$ | | 0.0008 | 0.0023 | |
| $10^6$ | | 0.0051 | 0.0048 | 0.0076 |

[a] Thickness $= 3.2$ mm.

as a result, and if the number of crazes is large the stress level is moderated and cracking is prevented, or at least delayed. If only a few crazes form, on the other hand, they tend to grow readily and propagate as cracks resulting in rupture.

The ESCR performance of PSF, PES, and PPSF is summarized in Table 8. These polymers are highly resistant to hydrolysis by hot aqueous media, including boiling water, high pressure steam, mineral acids and alkalies, and salt solutions. This resistance is usually a key reason behind the selection of polysulfones over the other engineering plastics like polycarbonates, polyesters, polyamides, and polyetherimides (23). The resistance to stress cracking by organic solvents varies according to the one-dimensional solubility parameter concept described. The most problematic chemical families are aromatics, chlorinated hydrocarbons, ketones, and esters. The resistance of the three polysulfones to these and other environments in general follows the ascending order $\mathrm{PSF} < \mathrm{PES} < \mathrm{PPSF}$ as illustrated in Table 8. When the aggressive environment does not actually dissolve or swell the polymer, the ESCR problem can usually be overcome by the use of a glass fiber-reinforced grade of the polysulfone resin of interest. Glass fiber or any other effective reinforcing agent usually provides enough added load-bearing capability to compensate for the ESCR deficiency of the polymer.

Solubility of the three commercial polysulfones follows the order $\mathrm{PSF} > \mathrm{PES} > \mathrm{PPSF}$. At room temperature, all three of these polysulfones as well as the vast majority of other aromatic sulfone-based polymers can be readily dissolved in a few highly polar solvents to form stable solutions. These solvents include NMP, DMAc, pyridine, and aniline. 1,1,2-Trichloroethane and 1,1,2,2-tetrachloroethane are also suitable solvents but are less desirable because of their potentially harmful health effects. PSF is also readily soluble in a host of less polar solvents by virtue of its lower solubility parameter. These solvents include tetrahydrofuran (THF), 1,4-dioxane, chloroform, dichloromethane, and chlorobenzene. The relatively broad solubility characteristics of PSF have been key in the development of solution-based hollow-fiber spinning processes in the manufacture of polysulfone asymmetric membranes (see Hollow-fiber membranes). The solvent list for PES and PPSF is short because of the propensity of these polymers to undergo solvent-induced crystallization in many solvents. When the PES structure contains a small proportion of a second bisphenol comonomer, as in the case of RADEL A (Amoco Corp.) polyethersulfone, solution stability is much improved over that of PES homopolymer.

### 2.7. Radiation Resistance

Polysulfones exhibit resistance to many electromagnetic frequencies of practical significance, including microwave, visible, and infrared. Especially notable is the excellent resistance to microwave radiation, which has contributed to the excellent fit of polysulfones in cookware applications. Polysulfone also shows good resistance to x-rays, electron beam (24), and gamma (25, 26) radiation under many practical application conditions.

**Table 8. Resistance[a, b] of Natural (Unreinforced) PSF, PES, and PPSF Resins to Various Chemical Environments[c]**

| Environment | Ranking | | |
|---|---|---|---|
| | PSF | PES | PPSF |
| hydrocarbons | | | |
| aliphatic | 1 | 1 | 1 |
| aromatic | 10 | 9 | 7 |
| chlorinated | 10 | 8 | 8 |
| alcohols/glycols | 2 | 2 | 2 |
| esters | 9 | 8 | 6 |
| ketones | 10 | 8 | 7 |
| amines | | | |
| aliphatic | 2 | 1 | 1 |
| aromatic | 8 | 7 | 6 |
| electrolyte solutions | 1 | 1 | 1 |
| acids[d] | 3 | 2 | 1 |
| bases | 3 | 2 | 1 |
| surfactants | | | |
| ionic | 1 | 1 | 1 |
| nonionic | 5 | 4 | 3 |

[a] Ranking codes: 1 = excellent; 5 = good; 10 = very poor.
[b] Data are for comparative purposes only; actual resistance depends on many factors including stress, temperature, concentration, and exposure duration.
[c] Stress cracking resistance is substantially enhanced in the presence of reinforcement such as glass fibers.
[d] Nonoxidizing.

Like the majority of aromatic polymers, polysulfones exhibit poor resistance to ultraviolet light. Polysulfones absorb in the uv region, with attendant discoloration and losses in mechanical properties due to polymer degradation at and directly beneath the exposed surface. Prolonged exposure to sunlight is therefore not recommended for these polymers in neat form. Retention of mechanical integrity is improved with pigmentation and/or reinforcement of the resin, and full resistance to uv is achieved when the resins are pigmented with carbon black. Painting is another option that can be used to avoid the effects of uv light. The retention of mechanical integrity of PPSF upon exposure to uv light is somewhat better than it is for either PSF or PES, especially when the resin is in an opaque form. This is a consequence of the more ductile nature of PPSF compared to both PSF and PES.

## 3. Fabrication

As with most linear amorphous polymers, polysulfones are fully thermoplastic materials and readily flow at temperatures $\geq 150^{\circ}\mathrm{C}$ above their respective glass-transition temperatures. The backbone structure is extremely thermally stable during melt processing, remaining unchanged even when subjected to several melt fabrication cycles. Polysulfones can be melt-processed on conventional equipment used for thermoplastics fabrication. Typical melt viscosity behavior as a function of shear rate is shown in Figure 6 for polysulfones and some other polymers. As illustrated from these plots, the shear thinning characteristics of polysulfones are much more muted than they are for aliphatic backbone polymers such as polyethylene and polystyrene. The rheological behavior of polysulfones is fundamentally more similar to that of bisphenol A polycarbonate.

Injection molding is the most common fabrication technique. Melt temperatures for PSF injection molding can be in the range 325–400°C depending on part thickness, length, and complexity. PES and PPSF are generally molded using temperatures in the range 360–400°C. Mold temperatures suitable for PSF injection

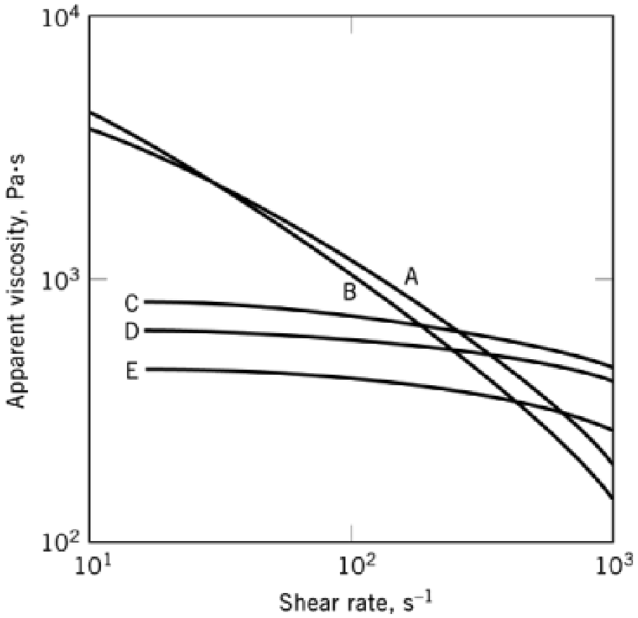


**Fig. 6.** Melt viscosity dependence on shear rate for various polymers: A, low density polyethylene at 210°C; B, polystyrene at 200°C; C, UDEL P-1700 polysulfone at 360°C; D, LEXAN 104 polycarbonate at 315°C; and E, RADEL A-300 polyethersulfone at 380°C.

molding are in the range 100–170°C; for PES and PPSF this range is 120–190°C. Lower mold temperatures can be used but are not recommended as they can result in unacceptably high levels of molded-in residual stresses in the parts. Because of the relatively high viscosities of polysulfones and the limited shear-thinning they exhibit over practical shear rate ranges, the generous sizing of runners and gates in mold design is recommended. The insensitivity to shear has the beneficial effect of yielding parts that are low in molecular orientation and hence much more nearly isotropic than those molded from many other thermoplastics.

Polysulfones are easily processible by other thermoplastic fabrication techniques, including extrusion, thermoforming, and blow molding. Extrusion into film, sheet, tubing, or profile can be accomplished on conventional extrusion equipment with a metering screw of moderate depth having a 2.5:1 compression ratio. Stock temperatures during extrusion of PSF, PES, and PPSF are in the range 315–375°C depending on resin viscosity grade and type of product being produced. A common fabrication technique is sheet extrusion followed by thermoforming. Prior to thermoforming, the sheet must be dry to prevent foaming. The surface temperatures required to produce sag are in the range 230–260°C for PSF and 275–305°C for PES and PPSF. Blow molding is possible on most commercial blow molding equipment provided that equipment is capable of maintaining melt temperatures in the 300–360°C range.

Once formed, parts made of polysulfones (particularly those produced by injection molding) can be annealed to reduce molded-in stress. Increased part stiffness, dimensional stability, and resistance to creep during service life are generally enhanced by reducing molded-in stresses. More importantly, the resistance of the part to environmental stress cracking or crazing is usually improved if molded-in stresses are minimized. Annealing can be easily accomplished either in an air oven or a glycerol bath. Typical time–temperature conditions for properly annealing polysulfones in an air oven are 1 h/170°C for PSF and 1 h/200°C for PES and PPSF. Annealing at similar temperatures by immersion in hot glycerol can be accomplished in 1–5 min. Because over-annealing may result in a reduction of impact toughness the use of conservative molding practices, most notably a hot mold, to produce low stress parts is preferred whenever contact with aggressive chemical environments is anticipated during the service life of the component.

Prior to melt processing, the resin must be dried to reduce the level of absorbed atmospheric moisture, which can be as high as 0.8 wt %, to below 0.05 wt %. The presence of significant amounts of moisture during melt processing causes structural and appearance defects in the fabricated parts due to bubbling and foaming of the trapped moisture. Drying to the target 0.05 wt % moisture can be easily achieved in a circulating hot air oven or a dehumidifying hopper dryer in 3–4 h at 135–165°C. Drying temperatures can be increased up to 180°C for PES and PPSF, if needed to cut down on drying time.

## 4. Blends and Alloys

The blending of two or more polymers to achieve unique property combinations of the parent polymers continues to be an attractive way to tailor existing commercial polymers to specific end use requirements. The blending of polysulfones with other polymers presents opportunities, but at the same time poses some significant technical challenges. Miscibility of PSF or PES with any nonsulfone-based polymer is extremely rare. Some examples of limited miscibility have been discussed (27–31). Only one of these cases involves stable one-phase behavior in the melt state (31). The inert nature of the phenyl, sulfone, and ether moieties precludes interchain reactions, such as ester–ester interchange, which can facilitate the achievement of miscibility in otherwise immiscible systems. As a result, blends of PSF or PES with other nonsulfone-based polymers generally rely on interfacial adhesion and good shear mixing during compounding to produce an intimately mixed blend with good mechanical compatibility. None of the binary blends comprising PSF, PES, and PPSF are miscible, although their blends form mechanically compatible mixtures with relatively stable phase morphologies. Properties of these blends are available (32–34). Blends comprising two or more polysulfones can provide a convenient way to achieve specific properties or simply to reduce cost.

One of the factors precluding blending of polysulfones and commodity polymers such as styrenics and polyolefins is the fact that these polymers do not possess the requisite thermal stability to endure melt processing in the temperature range that is required for polysulfones. As a result, there are few commercially available polymer classes that make good candidates for blending with polysulfones. These are, in general, other engineering thermoplastics such as polycarbonates, some polyester, polyimides (qv), polyaryletherketones, and poly(phenylene sulfide) (PPS). Polymer blends involving polysulfones are discussed in numerous patents and journal articles, eg, a study (35) dealing with the interaction energies of polysulfones with several polymers as they relate to miscibility. Properties of PSF–PPS blends are well documented (36, 37). Another study (38) describes the mechanical and rheological properties of PSF when blended with a thermotropic liquid crystalline polyester.

For reasons that are not fully understood, PPSF exhibits generally improved compatibility characteristics over either PSF or PES in a number of systems. An example of this is blends of PPSF with polyaryletherketones (39, 40). These blends form extremely finely dispersed systems with synergistic strength, impact, and environmental stress cracking resistance properties. Blends of PPSF with either PSF or PES are synergistic in the sense that they exhibit the super-toughness characteristic of PPSF at PSF or PES contents of up to 35 wt % (33, 34). The miscibility of PPSF with a special class of polyimides has been discovered and documented (41). The miscibility profile of PPSF with high temperature ($T_g > 230^\circ\mathrm{C}$) polysulfones has been reported (42).

Proprietary blend formulations based on polysulfone, polyethersulfone, and polyphenylsulfone are sold commercially by Amoco Corporation to meet various end use requirements. The blends based on polysulfone are sold under the MINDEL trademark. A glass fiber-reinforced blend based on PES is offered under the trade name RADEL AG-360. This offers most of the performance characteristics of 30% glass fiber-reinforced polyethersulfone but at a lower cost. Two blend product lines are offered based on PPSF. These are designated as the RADEL R-4000 and R-7000 series of products. The former is a lower cost alternative to RADEL R PPSF homopolymer offering most of the performance attributes unique to PPSF. The R-7000 series of resins have been formulated for use in aircraft interiors for civil air transport. They exhibit a very high degree of resistance to flammability and smoke release.

## 5. Health and Safety

Polysulfones are chemically inert polymers for the most part and to date (ca 1996) have no known negative health effects. These polymers have been used for many years in applications where safety is of the utmost importance. Numerous grades comply with U.S. and international governmental regulations for direct food contact. UDEL (Amoco Corp.) polysulfone has been in use for food processing (qv), plumbing, and medical and prosthetic device applications since the 1960s. Various grades of UDEL polysulfone and RADEL A polyethersulfone meet U.S. Food and Drug Administration (FDA) requirements for direct food contact. Similar approvals are given by the U.S. National Sanitation Foundation under Standard 51 permitting use of certain polysulfone and polyethersulfone resins in food processing equipment. RADEL R polyphenylsulfone complies with *U.S. Pharmacopeia* Class VI requirements for use in medical device components.

The thermally and oxidatively stable backbones of polysulfones preclude development of any significant amount of toxic volatile degradation by-products when the resins are heated during melt processing. The polymers remain essentially odorless when injection-molded at stock temperatures of up to 380°C. At temperatures above 380°C, trace amounts of sulfur dioxide, methane, and other organic compounds and residual solvents begin to be evolved. As with other plastic materials, adequate ventilation of the molding area is recommended when injection-molding polysulfones.

## 6. Uses

Polysulfones are used in a wide variety of applications that take advantage of hydrolytic and acid/caustic stability, clarity, and high heat deflection temperatures. These application areas include consumer items (ie, cookware and appliances), electrical and electronic packaging and substrates, automotive, aerospace, and a host of industrial and plumbing uses. The resistance of polysulfones to chemical attack has resulted in their use in chemical processing equipment. Examples of components in this area are corrosion-resistant pipe, pumps, filter modules, support plates, and tower packing. Glass-reinforced grades can be used in very severe chemical environments for enhanced resistance and long service life.

Polysulfones also offer desirable properties for cookware applications, eg, microwave transparency and environmental resistance to most common detergents. Resistance to various sterilizing media (eg, steam, disinfectants, and gamma radiation) makes polysulfones the resin family of choice for many medical devices. Uses in the electrical and electronic industry include printed circuit boards, circuit breaker components, connectors, sockets, and business machine parts, to mention a few. The good clarity of PSF makes it attractive for food service and food processing uses. Examples of applications in this area include coffee decanters and automated dairy processing components.

One unique application area for PSF is in membrane separation uses. Asymmetric PSF membranes are used in ultrafiltration, reverse osmosis, and ambulatory hemodialysis (artificial kidney) units. Gas-separation membrane technology was developed in the 1970s based on a polysulfone coating applied to a hollow-fiber support. The PRISM (Monsanto) gas-separation system based on this concept has been a significant breakthrough in gas-separation technology (see Membrane technology). Additional details are available on the use of polysulfone in membrane separations (43), as well as gas transport properties of polysulfone and polyethersulfone (44–48).

**Table 9. Manufacturers and Trade Names of Commercially Available Polysulfones**[a]

| Supplier | Polysulfone types offered | Trade name |
|---|---|---|
| Amoco Corp. | PSF | UDEL |
| | PES | RADEL A |
| | PPSF | RADEL R |
| BASF Corp. | PSF | ULTRASON S |
| | PES | ULTRASON E |
| Sumitomo Chemical Co. | PES | SUMIKAEXCEL |

[a] As of November 1, 1995.

Polysulfone, polyethersulfone, and polyphenylsulfone may be used interchangeably in many applications. In general, polysulfone is selected because of its lower cost. PES is selected over PSF in applications demanding higher temperatures and/or additional environmental resistance. PPSF represents a step improvement over PES in hydrolytic stability, impact, and chemical resistance with similar temperature capabilities to those of PES. It is selected only when both PSF and PES fail to meet engineering performance requirements. Examples of PPSF uses include steam-autoclaveable surgical sterilization trays, transformer magnet wire coatings, and aircraft interior parts.

## 7. Economic Aspects

There are three commercial suppliers that manufacture polysulfones: Amoco Corporation in the United States, BASF Corporation in Germany, and Sumitomo Chemical Company in Japan. A listing of the resins supplied by each of these companies along with the trade names particular to each of these suppliers is shown in Table 9. All three companies supply a polyethersulfone-type product. Polysulfone, on the other hand, is supplied by Amoco and BASF, and Amoco is the sole supplier of polyphenylsulfone.

As of November 1, 1995, the price range of UDEL polysulfone resins in large quantities was $9.10–$12.03/kg depending on grade and color. RADEL A polyethersulfone grades sold for $10.46–$13.26/kg and the prices of RADEL R polyphenylsulfone resins were in the range $15.75–$25.95/kg. MINDEL resins based on polysulfone had list prices between $6.72–$7.42/kg.

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