Plastic Sulfur

If molten liquid sulfur is quenched from 350 °C rapidly to 20 °C by spraying into cold water, the resulting solid sulfur is known as "plastic sulfur". Fibers obtained this way have helical $S_\infty$ chains with ten sulfur atoms for every helix repeat length. In addition, this type of sulfur is a composite material, having cyclic $S_8$ molecules packed into cavities between the fibers.

When liquid sulfur is discharged into cold seawater in an undersea volcanic eruption, probably the form of sulfur generated is plastic sulfur.

Sulfur Rings

Most of the allotropes of sulfur consist of molecular rings, $S_n$, where $n = 6$-20. The most stable of these rings is $S_8$, a molecule having S–S interatomic distances of 2.05 Å and belonging to the $D_{4d}$ point group. Commercially available sulfur consists mostly of $S_8$ molecules, but it typically has a bright yellow color (characteristic of elemental sulfur) that comes from a small amount of $S_7$ impurity. Pure $S_8$ is pale yellow-green.

Another impurity that may be present in volcanic sulfur is $S_7$Se, where one of the sulfur atoms in the eight-membered ring is replaced with selenium.

Hexasulfur

Molecular hexasulfur has been synthesized in various ways. One way is via the thermal decomposition of $S_2I_2$, itself being generated by reaction of 2 KI with $S_2Cl_2$, analogous to the organic Finkelstein reaction. Using this method, it is possible to obtain $S_6$ in ca. 36% yield after separation from other $S_{2n}$ molecules by fractional precipitation.

Of course, it would be desirable to have a reaction for selective generation of $S_6$, and the organometallic reagent known as titanocene pentasulfide has been developed for this purpose. It has the formula $\text{Cp}_2\text{TiS}_5$, and a molecular structure featuring a six-membered TiS$_5$ ring that effectively acts as a source of $S_2^{2-}$ because of the polarity (sulfur negative, titanium positive) of the Ti–S bonds. Accordingly, $S_6$ has been synthesized in 87% yield by the reaction of $\text{Cp}_2\text{TiS}_5$ with $\text{SCl}_2$, giving titanocene dichloride ($\text{Cp}_2\text{TiC}_2$) as the organometallic co-product of the reaction. Additionally generated in the reaction are small amounts of $S_{12}$. The sulfur dichloride reagent, $\text{SCl}_2$, does not have a long shelf life; it must be generated, distilled, and used while still fresh.

Heptasulfur, Nonasulfur, and Decasulfur

The seven-membered ring compound $S_7$ can also be generated in a selective reaction employing titanocene dichloride together with $S_2Cl_2$. Pure $S_7$ is not thermally stable and must be stored below −50 °C.

The molecular $S_9$ ring has been prepared similarly, by reaction of $\text{Cp}_2\text{TiS}_5$ with $S_4\text{Cl}_2$.

In the case of $S_{10}$, the synthesis method is different. Here $\text{SO}_2\text{Cl}_2$ is employed effectively as a source of chlorine and $\text{SO}_2$ gas as a leaving group. The balanced reaction uses $2 \text{Cp}_2\text{TiS}_5 + 2 \text{SO}_2\text{Cl}_2$ to provide $S_{10}$, $2 \text{SO}_2 \uparrow$, and 2 equiv of titanocene dichloride.
Sulfur as a Crystalline Mixture of Rings

When equal amounts of $S_6$ and $S_{10}$ are recrystallized together from CS$_2$, the crystals so obtained consist of equal amounts of $S_6$ and $S_{10}$ molecules. These crystals have a melting point of 92 °C. It has been said that this is the only solid allotrope of an element containing molecules of different sizes, but this use of the term “allotrope” is probably not appropriate here given our accepted definition.

Twelve- and Twenty-Membered Rings

The $S_{12}$ molecule provides a nice example of $D_{3d}$ symmetry, while $S_{20}$ molecules take on a $D_4$ structure.

Vulcanization

An important application of elemental sulfur is its combination with natural and synthetic rubber in the process known as vulcanization. The most important synthetic polymer processed this way is polystyrene/polybutadiene, which when vulcanized is used to make automobile tires and other products. The vulcanization process installs –SS$_n$S– cross-links between the polymer chains, making the rubber hard and not sticky.

The $S_2$ Molecule

Just like when comparing nitrogen and phosphorus, in the case of oxygen and sulfur the light element is a gas while the heavier element adopts a variety of solid allotropes. What are the properties of $S_2$? One way this has been approached is by the synthesis of a bicyclic disulfide molecule, C$_5$H$_6$S$_2$, that could release $S_2$ in a thermal retro Diels-Alder reaction. The $S_2$ so-generated in the presence of 2,3-dimethylbutadiene led to detectable formation of a new cyclic disulfide product, interpreted as evidence for the intermediacy of $S_2$ as a reactive transient.

Where is $S_2$ found in nature? The very close approach to earth of comet IRAS-Araki-Alcock 1983 VII led to the observation of UV emission spectra showing the presence of $S_2$ close to the cometary nucleus!