

Polymerization of commercial Mexican sulfur

R.W. Gómez, J.L. Pérez M., V. Marquina, R. Ridaura, and M.L. Marquina
*Facultad de Ciencias, Universidad Nacional Autónoma de México,
 Mexico City, 04510, Mexico.*

Recibido el 9 de junio de 2006; aceptado el 6 de noviembre de 2006

As it is well known, the physical characteristics of sulfur exhibit a wide range of interesting phenomena around 160°C [1]: a) A shear viscosity change of four orders of magnitude over a 25°C interval [2]. b) Changes in density and in sound velocity. c) Its color becomes darker and its refractive index and dielectric permittivity reach a minimum. d) Of special interest, because of its possible industrial applications, is the polymerization process that occurs at around 160°C. Studies made in ultra pure sulfur (99.999%) have shed some light on this phenomenon, but a coherent picture is still missing. The properties of sulfur are strongly affected by impurities and dissolved gases, so that a great deal of care is necessary when performing these experiments. If the purpose is to take advantages of these properties for industrial applications, one must rule out the use of ultra-pure sulfur and think in terms of a simple process with a commercial substance. In this work we shall report some infrared spectroscopy, Raman spectroscopy and X-ray diffraction results obtained in our attempts at the polymerization of commercial Mexican sulfur.

Keywords: Raman and infrared spectroscopy; diffraction.

Las características físicas del azufre cambian en forma notable cuando su temperatura es de alrededor de 160°C: a) Un cambio de cuatro órdenes de magnitud en la viscosidad laminar, en un intervalo de 25°C. b) Cambios en su densidad y en la velocidad del sonido. c) Su color se hace más oscuro y su índice de refracción y permitividad eléctrica, muestran un mínimo. d) Además existe un interés especial en el proceso de polimerización que ocurre en torno a esa temperatura, debido a que el azufre polimerizado puede tener aplicaciones industriales. Estudios realizados en azufre extra puro (99.999 %) han permitido avanzar en el entendimiento de estos fenómenos, pero aún no se tiene una explicación completa de ellos. Las propiedades del azufre cambian mucho por la presencia de impurezas y gases disueltos en él, por lo que, si se quieren utilizar sus características para uso industrial, hay que proceder con azufre comercial y no de gran pureza. En este trabajo se reportan algunos resultados de espectroscopia infrarroja, espectroscopia Raman y difracción de rayos-X obtenidos en experimentos diseñados para obtener la polimerización de azufre mexicano comercial.

Descriptores: Espectroscopias Raman e infrarroja; difracción de rayos X; polimerización.

PACS: 78.30.-j; 78.30.Jw

1. Introduction

Sulfur occurs in a large number of allotropic forms in the solid state, of which we shall mention only a few. A complete list of ambient and high pressure allotropes can be found in Ref. 3:

- a) Rhombic sulfur, octahedral sulfur (S_8 rings), or alpha-sulfur is a yellow crystalline solid that crystallizes from a solution in carbon disulphide. It consists of eight sulfur atoms in the molecule in a ring structure.
- b) Monoclinic sulfur, prismatic sulfur, or beta-sulfur is a yellow crystalline solid that is obtained during the solidification of molten sulfur, when long prismatic needles form on the walls of the container and can be separated from the still molten liquid by pouring off the latter. It also consists of eight sulfur atoms in the molecule in a ring structure, but arranged within the crystal in a different manner from that in rhombic sulfur.
- c) Plastic or gamma-sulfur, is a tough elastic substance that is formed when molten sulfur is poured into cold water.

d) Amorphous sulfur S_μ is the insoluble white amorphous solid that remains when flowers of sulfur are extracted with carbon disulphide.

e) Colloidal sulfur, which is also known as delta-sulfur, is a yellow crystalline solid.

The changes observed around $T_c = 159^\circ\text{C}$ in several of the sulfur properties can be explained by a λ -type (or second-order) transition [4, 5] in which the specific heat has an abrupt rise near T_c and then decreases less rapidly when $T > T_c$. Above T_c , the S_8 rings polymerize to form long entangled chains. As a result, the liquid sulfur changes color and becomes extremely viscous.

Based on chemical equilibrium, Tobolsky and Eisenberg [6] developed a theory to describe the polymerization transition in liquid sulfur in terms of an equilibrium constant, $K_1 = \exp\{(T\Delta S_1 - \Delta H_1)/RT\}$, that describes the initiation of polymerization through the opening of the S_8 rings and another one, $K_P = \exp\{(T\Delta S_P - \Delta H_P)/RT\}$, that describes the propagation of the reaction; in these expressions, T, S, H and R stand for the absolute temperature, entropy, enthalpy and universal gas constant, respectively. In this theory, the concentration c_p of polymers and the concentration c_m of

monomers incorporated in the polymers are given by

$$c_p = \frac{K_1 c_0}{1 - K_p c_0} \quad c_m = \frac{K_1 c_0}{(1 - K_p c_0)^2} \quad (1)$$

where c_0 is the concentration of S_8 rings at equilibrium and satisfies the following “equation of state”:

$$c_0 + c_m = c_0 + \frac{K_1 c_0}{(1 - K_p c_0)^2} = c_\infty, \quad (2)$$

where c_∞ stands for initial concentration of S_8 rings. At low temperatures, c_p and c_m are very small and $c_0 \approx c_\infty$. However, when $K_p(T) \approx 1/c_0$, both c_p and c_m change rapidly and the system polymerizes.

More recently, Wheeler, Kennedy and Pfeuty [7] put forward a model in which an analogy between the theory of phase transitions [8] and critical phenomena is applied to the polymerization equilibrium problem. This model describes quite well the measured weight fraction of polymeric sulfur made by Koh and Klement [9] and reasonably well the heat capacity per mol measurements made by West [10]. Notwithstanding these and other theoretical works, the structural changes around T_c are not yet fully understood.

One of the many applications of sulfur in industry is its use in the production of radial tires, because the adhesion of the rubber compound to the steel-cord requires high levels of insoluble (polymeric) sulfur. With normal sulfur, this high level would lead to blooming during storage in the unvulcanized state. This bloom destroys the desired tackiness of the compound.

The usual way to obtain insoluble sulfur is not an efficient one, and the main purpose of this work is to begin an investigation to find a simple and advantageous process that can be used in the preparation of huge quantities of polymeric sulfur.

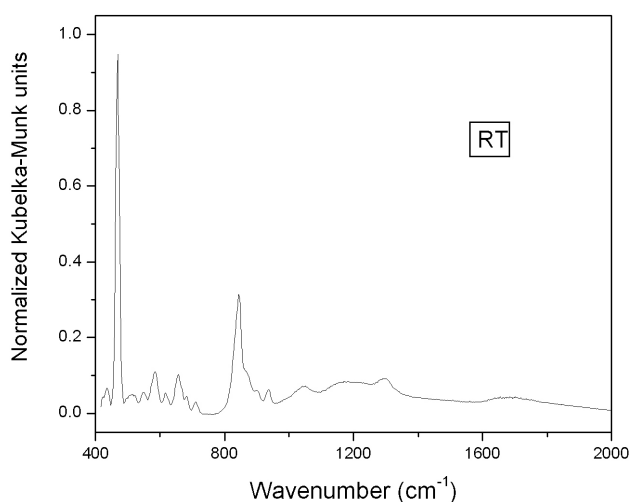


FIGURE 1. Room temperature infrared diffuse reflectance spectrum of commercial sulfur.

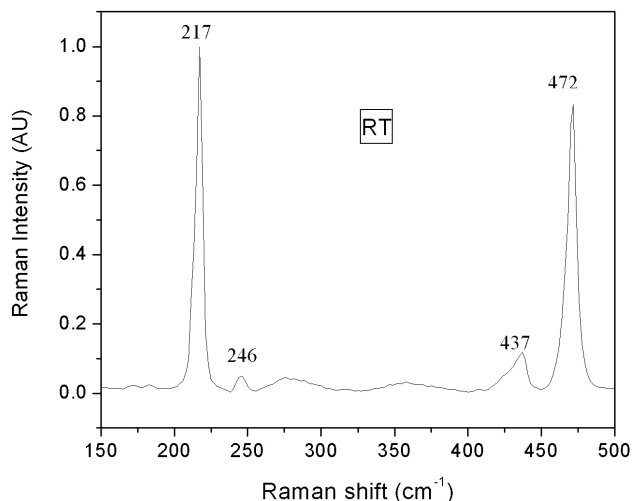


FIGURE 2. Room temperature Raman spectrum of commercial sulfur.

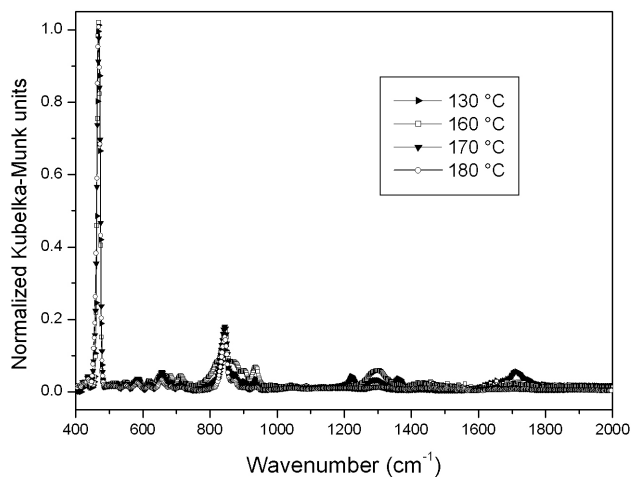


FIGURE 3. Infrared diffuse reflectance spectra of sulfur after heat treatment.

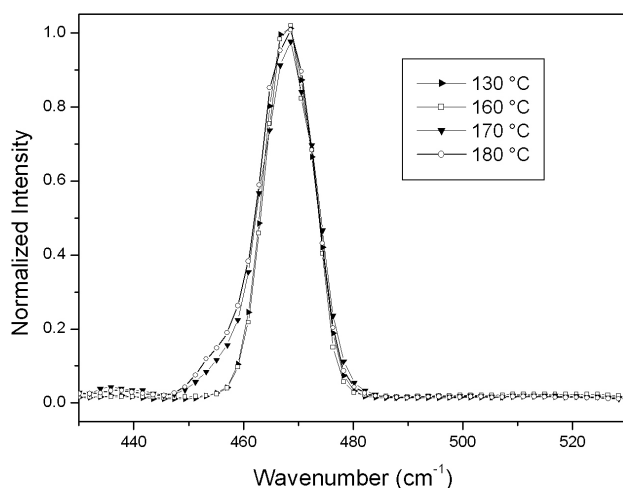


FIGURE 4. The region around the 470 cm^{-1} band of the Infrared diffuse reflectance spectra of sulfur after heat treatment.

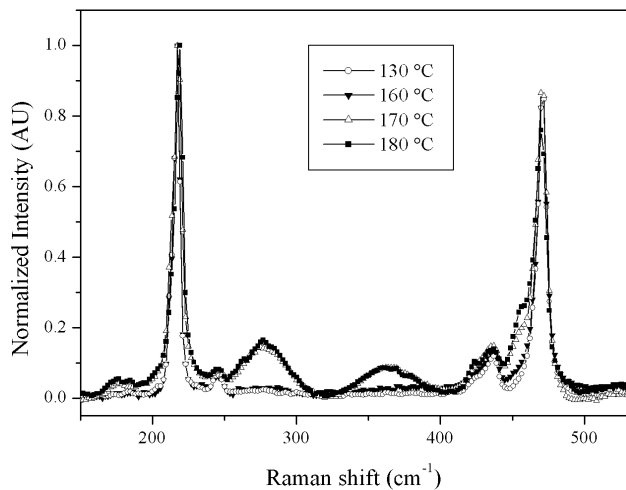
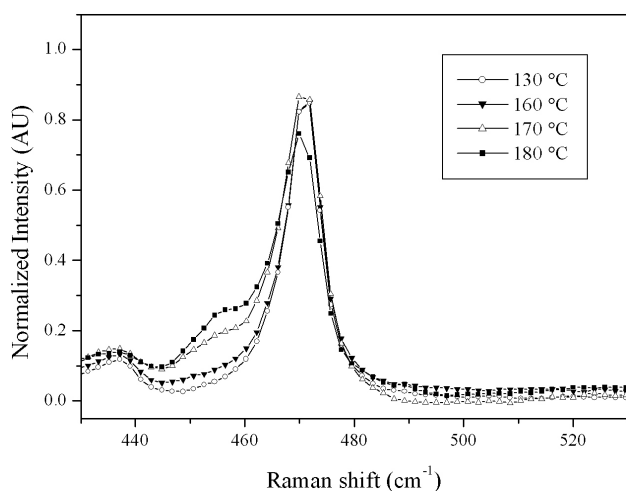


FIGURE 5. Raman spectra of sulfur after heat treatment.

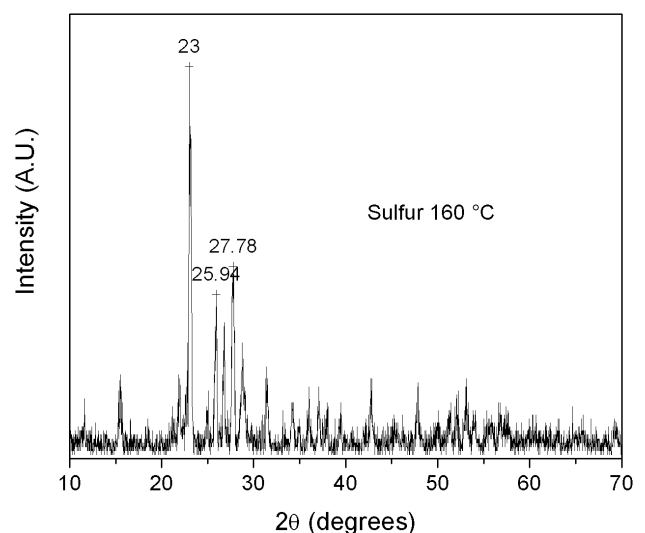
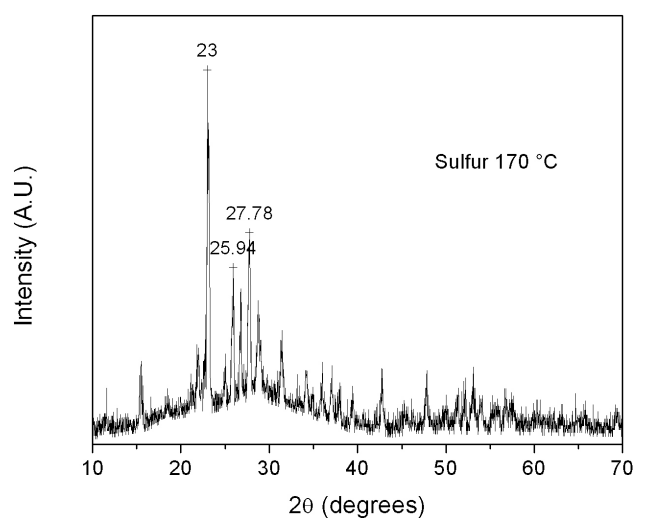
FIGURE 6. The region around the 470 cm^{-1} band of the Raman spectra of sulfur after heat treatment.

2. Experimental results

Different heat treatments were given to commercial sulfur in order to determine if the original material had changed from one allotropic form to another. Our first step in finding an indication that such changes had taken place was to obtain room temperature Raman spectra and infrared diffuse reflectance spectra of our treated samples. The infrared spectra were recorded by a 4 cm^{-1} resolution FT spectrometer (Nicolet system 800). The Raman spectra were recorded by the same FT spectrometer with a Raman accessory that works in back scattering geometry, at an excitation line of 1064 nm (Nd:YAG laser), with a filter that allows recording spectra from 200 cm^{-1} up and a Ge detector cooled with liquid nitrogen. In Fig. 1 we show the room temperature infrared spectrum, from 400 cm^{-1} to 2000 cm^{-1} , of the commercial sulfur used in this work and in Fig. 2 the corresponding Raman spectrum from 150 cm^{-1} to 550 cm^{-1} . This last figure shows the two main Raman bands, associated with

S-S stretching vibration at $\sim 472 \text{ cm}^{-1}$ and the S-S-S bending vibration at $\sim 217 \text{ cm}^{-1}$. Other less intense modes are also shown at 437 cm^{-1} and 246 cm^{-1} . In Fig. 3 we show the room temperature infrared spectra of sulfur heat treated at different temperatures, where noticeable changes with respect to the spectrum of sulfur without heat treatment can be observed. For reasons that will be clear in the following paragraph, we show in Fig. 4 the region around the 472 cm^{-1} band. Figs. 5 and 6 show the corresponding Raman spectra.

Besides the 275 cm^{-1} and 375 cm^{-1} bands, associated with the development of S_7 and S_6 species [11], the important region to be worried about is that near 472 cm^{-1} , because the increasing band around $450\text{--}460 \text{ cm}^{-1}$ in the Raman spectra is associated with the escalation of polymerization [12]. Actually, the degree of polymerization can be obtained through the relative intensity between these two bands, obtained by fitting them with Lorentzian profiles [13]. To our knowledge,

FIGURE 7. X-ray diffraction pattern of the sample heat treated at 160°C .FIGURE 8. X-ray diffraction pattern of the sample heat treated at 160°C .

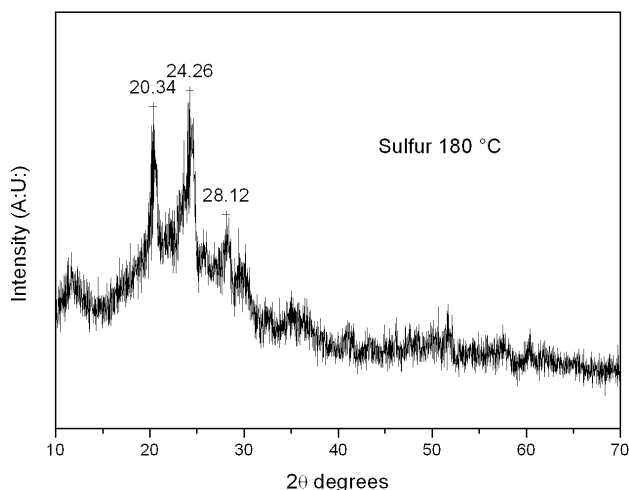


FIGURE 9. X-ray diffraction pattern of the sample heat treated at 160°C.

the similar behavior that we find in this region in the IR spectra of our samples has not been reported, but our results suggest that the same type of analysis could also be made. However, that is not the purpose of this work and it will be left for a future careful analysis of the complete IR and Raman spectra.

Once we had a quick and reliable way to find out if the material had suffered some changes, we proceeded to find out what type of changes had taken place, so we obtained X-ray diffraction patterns of the 160, 170 and 180°C samples, which are shown in Figs. 7, 8 and 9, respectively.

As can be seen in the figures, in going from 160 to 180°C the X-ray spectrum changes due to an amorphization process, in accordance with the Raman results. Moreover, the emergence of new peaks (or at least their relative growth) is to be associated with S_6 and S_7 formation as a result of the heat treatment. That is, the spectra in Figs. 8 and 9 correspond to an admixture of S_6 , S_7 and S_8 rings and a fraction of polymeric S_μ . A cross-check of the degree of polymerization could be done by a crystallinity analysis of these spectra.

3. Conclusions

The two main purposes of this work have been achieved:

- we have developed a reliable process by which we are able to polymerize sulfur;
- we have shown that *ex situ* Raman spectroscopy, and to a lesser extent infrared spectroscopy, are ready ways to find out if, after a heat treatment, crystalline sulfur has been transformed to an admixture of crystalline and polymeric sulfur; and
- as a side achievement, the possibility of quantification of the polymeric fraction through the IR spectra has been devised, even though more work is necessary to firmly establish it.

Acknowledgements

This work was partially supported by DGAPA, UNAM, project IN110005

- R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.* **65**, (1943) 639.
- V.F. Kozhevnikov, W.B. Payne, J.K. Olson, C.L. McDonald, and C.E. Inglefield *J. Chem. Phys.* **121** (15) (2004) 7379.
- M.W. Wong, Y. Steudel, and R. Steudel *J. Chem. Phys.* **121** (12) (2004) 5899.
- J. Ruiz-García, E. M. Anderson, and S. C. Creer, *J. Phys. Chem.* **93** (1989) 6980.
- H. Terasaki, T. Kato, K. Funakoshi, A. Suzuki, and S. J. Urakawa *J. Phys.: Condens. Matter* **16** (2004) 1707.
- A.V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.* **81** (1959) 780.
- J.C. Wheeler, S.J. Kennedy, and P. Pfeuty. *Phy. Rev. Lett.* **65** (1980) 1748.
- H.E. Stanley, *Phase transitions and critical phenomena* (Clarendon Press, Oxford, 1971).
- J.C. Koh and W. Klemet, *J. Chem. Phys.* **74** (1970) 4280.
- E.D. West, *J. Am. Chem. Soc.* **81** (1959) 29.
- R. Steudel and B. Eckert, *J. Phys. Chem.* **121** (2004) 6573.
- A.G. Kalamounias, D.Th. Kastrissios, and S.N. Yannopoulos, *J. non-Cryst. Solids* **326** and **327** (2003) 115.
- A.G. Kalamounias, K.S. Andikopoulos, and S.N. Yannopoulos, *J. Chem. Phys.* **118** (2003) 8460.