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Theoretical Study on Structure of Polymeric Sulfur

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The average molecular weight of insoluble sulfur was determined by iodometric titration. The insoluble sulfur structural unit was built by Anorphous cell and optimized based on density functional theory in materials studio software. Moreover, the density of insoluble sulfur structural unit was simulated using molecular dynamics method and the density of insoluble sulfur prepared by melting method was measured by pycnometer method. The density and XRD pattern of simulation value and experimental value was compared. The results showed that the average molecular weight of insoluble sulfur was about 2900, which meant that the number of sulfur atoms in polymeric chain was about 90. The simulation density (2.178 g/cm^3) agreed well with experimental density (2.165 g/cm^3) and relative error was 0.6 %. Moreover, the XRD pattern of simulation and experiment were similar in some degree, which validated the reliability of molecular structure built and optimized.

Keywords: Insoluble sulfur, Molecular weight, Molecular dynamics, Materials studio.

INTRODUCTION

Insoluble sulfur (IS), by definition, polymeric sulfur which is insoluble in carbon disulfide. Insoluble sulfur prepared by quenching sulfur liquid, polymeric sulfur allotrope is used as non-blooming vulcanizing agent in the rubber-making industry. Due to the high dispersion and good stability, insoluble sulfur can meet the requirements of sulfur ejection on the rubber surface and occupy the market of rubber vulcanizing agent.

Nowadays, to develop the new extractant of insoluble sulfur that aims to replace the carbon disulfide is a research focus. There are less research on molecular structure and molecular weight of insoluble sulfur. Cataldo[1] on the basis of previous work[2,3], put forward the helical structure of insoluble sulfur based on the study by X-ray diffraction of powders. Pinkus and Piette[4] envisioned another structure of insoluble sulfur-annular superposition structure. Kozhevnikov *et al.*[5] confirmed that polymeric sulfur is a solution of long chain molecules in monomeric solvent. Ezzine *et al.*[6] used extend Hückel theory to determine the lowest energy conformation for all 1D, 2D and real 3D structure of polymeric sulfur based on the previous work[7,8]. Olkhov and Jurkowski[9] made, from spectrometry experiments, a thermo mechanical analysis of different kind sulfurs. However, for reasons that insoluble sulfur in superstructure is insoluble in common solvents, the traditional molecular structure determination method cannot be used to characterize insoluble sulfur, therefore, the real molecular structure and molecular weight distribution are still unknown.

Recently, with the advancement of computer technology, the molecular dynamics method (MD) simulation has already been applied in the study of material in a certain scale. The molecular dynamics method simulation becomes an important method to predict mechanical properties of polymeric materials[10-14]. However, at present, there is still no definite and direct report about the molecular simulation of insoluble sulfur. In this work, we use molecular simulation method to research the average molecular weight and structure of insoluble sulfur.

EXPERIMENTAL

In the experiment, pure sulfur (99.99 %, Puguang Co., China) were melt at 115 °C for 2 days. The long times required for complete melting were typical for polymers and then a small amount of stabilizer-I_2 was added to prevent polymeric sulfur which was not stable at room temperature reverting to cycloocta sulfur.

Average molecular weight measurement: The molecular weight of insoluble sulfur was determined by iodometric titration. According to the reaction mechanism, it is assumed that: (1) the single structure of polymeric sulfur is linear long chain; (2) there is an iodine atom at each polymeric sulfur long chain terminal.

Based on these assumptions, we have calculated the molecular weight of insoluble sulfur through mass of insoluble sulfur, the whole amount of substance of I_2 and the amount of substance of I_2 in the soluble sulfur. The molecular weight of insoluble sulfur can be calculated as follows.

$$M = \frac{m}{n}$$

$$n = n_0 - n_1$$

where M is the average molecular weight of insoluble sulfur, m is the mass of insoluble sulfur, n is the amount of substance of insoluble sulfur, n_0 is the whole amount of substance of I_2 added in the reaction, n_1 is the amount of substance of I_2 in the soluble sulfur, so the residual I_2 react with $\cdot S_{8n}\cdot$. In this experiment, n_1 is calculated through spectrophotometry.

Insoluble sulfur density measurement: Pycnometer method is a kind of accurate density determination method. Ren *et al.*[13] used this method to determine the density of heavy oil fractions.

To determine the density of insoluble sulfur by pycnometer, firstly, the mass of insoluble sulfur and the pycnometer which was full of water are both determined. Then the insoluble sulfur was put into the pycnometer, which led to amount of water spilled from the pycometer. Obviously, the volume of insoluble sulfur put into pycbometer was the same as the spilled water.

$$V = \frac{m_{\text{spilled water}}}{\rho_{\text{spilled water}}} = \frac{m_{IS}}{\rho_{IS}}$$

$$\rho_{IS} = \frac{m_{IS}}{m_{\text{spilled water}}}\rho_{\text{spilled water}}$$

where m_{IS} is the mass of insoluble sulfur put into the pynometer, $m_{\text{spilled water}}$ is the mass of water spilled from the pynometer.

Characterization of insoluble sulfur: X-ray powder patterns (XRD, Rigaku, D/MAX 2550 VB/PC) was used to verify the reliability of molecular structure built and optimized. The diffractometer was equipped with copper source radiation source (λ = 1.542 Å), operating at 40 kV and 100 mA and the scanning rate was 8° (2θ) per minute. The scan range was from 10° to 80°.

Molecular unit structure build and optimization: Amorphous cell module in materials studio software is used to built the periodic structure and discover module is employed to calculate molecular mechanics and molecular dynamic. Moreover, the main simulation parameters are as follows: COMPASS force field, the first *ab initio* force field[15]; summation method of electrostatic and van der Walls is respectively atom based and group based; temperature control by Andersen method; pressure control by Berendsen method; integral step of molecular kinetics of 1 fs.

The steps of model construction and calculation process are as follows:

Building of a model of S_8: Soluble sulfur (S_8) is the raw material of insoluble sulfur, thus, the S_8 chain was built by Amorphous Module and its structure was optimized by Dmol^3 module.

Building of the polymer chain of I-S_{8n}-I: To the S_8 chain structure built and optimized, we set Head Atom and Tail Atom from the menu bar as Build | Build Polymers | Repeat Unit to get the repeated unit, then set the chain length and the tactility, obtain the model of the polymer chain and add two iodine atoms at the polymeric sulfur long chain terminal.

Geometry optimization: To avoid erroneous results in the subsequent simulation in molecular dynamics simulation, the polymeric sulfur long chain structure should be optimized based on density functional theory (DFT).

Building the insoluble sulfur unit cell model: We used the amorphous cell module to construct the periodic structure model of complex amorphous materials. Select Build | Build Crystal to open the build crystal dialog, set the size to get a periodic empty cell model, then copy and paste the particle cell model to this empty cell.

Density simulation of insoluble sulfur unit structure: To obtain the true density of material, the molecular dynamics simulation is calculated. The cell density gradually increases under external pressure and the system can be further compressed by the increasing pressure *via* NPT simulation. Then we use Forcite module to analysis module to open the Dynamics dialog. The true density of this unit cell model can be obtained from the calculation result.

XRD simulation of insoluble sulfur unit structure: Reflex module of Materials Studio was used to calculate the powder diffraction of the insoluble sulfur unit structure cell. The calculation parameters were the same to experimental parameters.

RESULTS AND DISCUSSION

Average molecular weight determination: Firstly, we draw standard working curve between substance concentration of I_2 and absorbance of solution. The standard working curve is shown in Fig. 1.

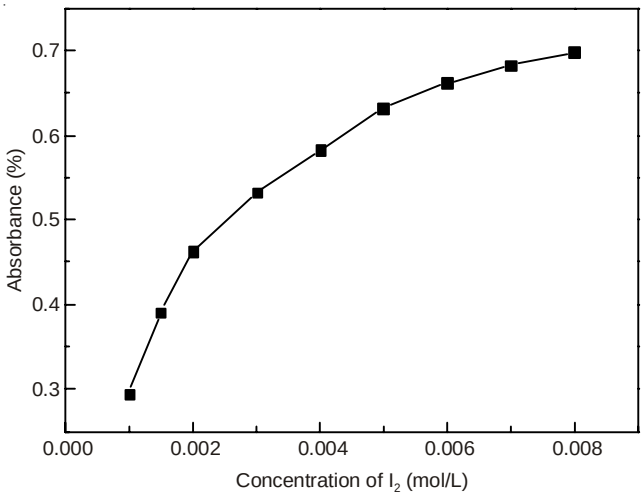

Fig. 1. Standard working curve between absorbance and concentration of I_2

The curve obtained can be approximately written as:

$$y = 0.1652 \ln(c) + 1.5134$$

where y is the absorbance of I_2, c is the concentration of I_2 in solution.

Based on the absorbance of each sample, we calculated the concentration of I_2 in the soluble sulfur, then the amount of substance of I_2 react with $\cdot S_{8n}\cdot$ can be determined. The calculation results are shown in Table-1.

TABLE-1
CALCULATION RESULTS OF AMOUNT OF SUBSTANCE OF I_2 REACT WITH $\cdot S_{8n}\cdot$

Total I_2 (mol)	Absorbance	I_2 in soluble sulfur (mol)	I_2 reacted with $\cdot S_{8n}\cdot$ (mol)
0.1	0.989	0.042	0.058
0.1	0.977	0.039	0.061
0.1	0.977	0.039	0.061
0.1	0.964	0.036	0.064
0.1	0.985	0.041	0.059

As the structure of insoluble sulfur assumed, the amount of substance of I_2 reacts with $\cdot S_{8n}\cdot$ and insoluble sulfur is the same. Thus, the average molecular weight of insoluble sulfur can be calculated and the results are shown in Table-2.

TABLE-2
AVERAGE MOLECULAR WEIGHT OF INSOLUBLE SULFUR BY IODOMETRIC TITRATION

Insoluble sulfur (mol)	Mass of insoluble sulfur (g)	Molecular weight
0.058	142.2	2945
0.061	151.4	2987
0.061	146.3	2865
0.064	154.8	2877
0.059	143.4	2913

As shown in Table-2, the average molecular weight of insoluble sulfur is about 2900, which means that the number of sulfur atoms in each polymeric chain is about 90.

Molecular model of insoluble sulfur simple-chain: Soluble sulfur (S_8), as the raw material of insoluble sulfur, its structure optimized is shown in Fig. 2. Based on the calculation results of average molecular weight of insoluble sulfur, the geometry optimization model which includes 90 sulfur atoms and 2 iodine atoms built by Materials Studio is shown in Fig. 3.

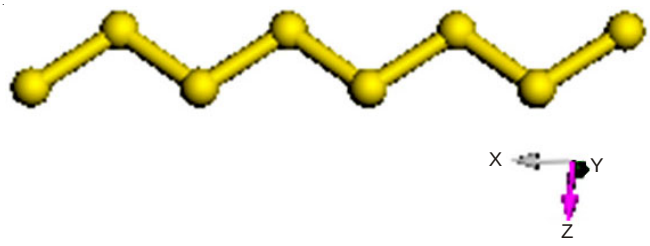

Fig. 2. Molecular structure of S_8 single-chain after geometry optimization

As can be seen in Fig. 3, after optimization, the insoluble sulfur single-chain is a kind of helix structure, which is in accordance with the assumption of Tuinstra[16]. Obviously, the insoluble sulfur single chain is composed of three repeated unit which contains 30 sulfur atoms.

Density of simulation and experiment: The true density simulation can be calculated *via* Forcite module of materials studio. Firstly, the structure of insoluble sulfur unit cell model after optimization by molecular dynamics are shown in Fig. 4.

To validate the reliability of density simulation parameters, we calculated the density of water molecular, ethanol molecular and soluble sulfur (S_8). The comparison of simulation data and experimental data is shown in Table-3.

Fig. 3. Molecular model of insoluble sulfur single-chain after geometry optimization

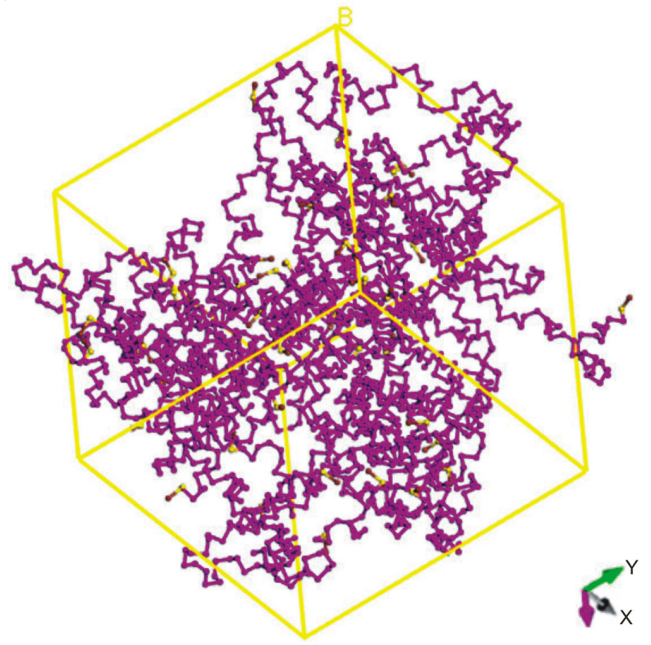

Fig. 4. Insoluble sulfur unit cell model after calculation

TABLE-3
SIMULATION DATA, EXPERIMENTAL DATA AND RELATIVE ERROR OF THREE KIND OF MOLECULE

Molecule	Simulation data (g/cm^3)	Experiment data (g/cm^3)	Relative error (%)
Water	1.017	1.002	1.47
Ethanol	0.781	0.773	1.02
S_8	1.944	1.955	0.51

As Table-3 displays, the relative error between simulation data and experimental data is very small, which means that the density simulation parameters and calculation flow designed are applicable. Then we simulated the density of insoluble sulfur ith the same parameters. Through calculation, the temperature fluctuate around 298K in a small scale which indicates that the system dynamics simulation have reached equilibrium. Finally, the unit cell is about 5 nm and the density is about 2.178 g/cm^3.

The density of insoluble sulfur measured by pycnometer method is 2.165 g/cm^3. It is clear that the simulation data is close to the experimental data and the relative error is ± 0.6 %. The result means that the insoluble sulfur structure built by Materials Studio is reasonable.

XRD results of simulation and experiment: The XRD patterns of simulation and experiment are shown in Fig. 5. Through observation, it is clear that insoluble sulfur is a kind of amorphous polymer. By comparing the simulation and experimental data, obviously, the insoluble sulfur unit structure built and optimized is similar to the real insoluble sulfur structure in some degree, which also means that the insoluble sulfur unit structure built and optimized is reasonable.

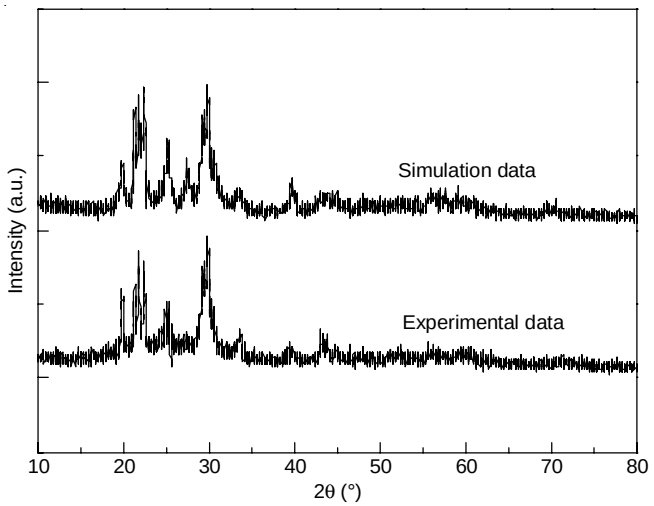

Fig. 5. XRD patterns of simulation and experiment

Conclusions

Based on the average molecular weight measurement of insoluble sulfur, density simulation and measurement of insoluble sulfur, including some hypothesis, we inferenced the average molecular weight and structural unit of insoluble sulfur.

• Through the method of iodometric titration and some hypothesis, the average molecular weight of insoluble sulfur was about 2900, which meant that the number of sulfur atoms in each polymeric chain was about 90. The model of insoluble sulfur unit structure was built and optimized and the result showed that insoluble sulfur single-chain is a kind of helix structure.

• To taste the reliability of molecular structure, the density of simulation data and experimental data were compared and then the XRD patterns of simulation and experiment were also compared. Finally, the average density of insoluble sulfur was about 2.178 g/cm^3. The density of insoluble sulfur prepared by melting method measured by pycnometer method was about 2.165 g/cm^3. The XRD patterns of simulation and experiment were similar in some degree.

• The result that simulation data agreed well with experiment data showed that the molecular structure was reliable in some degree.

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