Sulfur-containing emulsions under alternative non-thermal initiation: a way to increase the energy efficiency of chemical processes

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Abstract. Currently, there is a tendency to develop chemical and chemical-technological processes that consume as little energy as possible. Recently, ionizing and microwave radiation began to be used for these purposes in the chemical industry, since conventional heating can be slow and inefficient, which increases energy consumption. Polymer sulfur, which is one of the modifications of elemental sulfur, has a number of valuable properties, however, the existing methods for its synthesis are characterized by high energy consumption and therefore are disadvantageous. In order to develop a more efficient method for the synthesis of polymer sulfur, the processes that occur in sulfur-containing emulsions under the influence of ionizing and microwave radiation, and the products formed in these processes are investigated.

1. Introduction

Sulfur-containing polymers are widely known for many years [1]. Polymer sulfur has high impact strength, high resistance to aggressive media, lack of thermal shrinkage in composites, insolubility in rubber, etc., so it can be used in industry for the vulcanization of rubber and as a plasticizer in concrete or ceramics. But high energy consumption of polymer sulfur synthesis processes limits its application.

Less energy intensive is the radiation initiation of chemical processes. Radiolysis and subsequent chemical transformations have been studied very well [2]. In the case of radiation initiation, in principle, an increase in the temperature of the process is not required, while it is possible to carry out the process at high speeds at low temperatures, and the likelihood of side processes is reduced. The speed of the process does not change over time, and the reaction can be completely stopped by removing the reaction system from the irradiation zone or removing the source. This makes it possible to relatively quickly and easily control the initiation rate and properties of the resulting polymers [3-8].

Polymerization processes under the influence of microwave radiation were considered in common earlier [9]. Microwave initiation is widely used in polymer synthesis [10–14], it is applicable for liquid, solid, and paste media. Microwave heating is fast and efficient. The use of microwave energy
instead of traditional methods can significantly simplify the technological scheme, eliminating all processes and devices associated with the preparation of the coolant, as well as significantly reduce the amount of harmful wastes [14].

2. Materials and methods

In the studies elemental sulfur $S_8$, benzene $C_6H_6$, toluene $C_6H_5CH_3$, and a number of the emulsifiers were used. Benzene and toluene was chosen as the reaction media for carrying out the processes, since their high radiation resistance and high dissolving ability related to elemental sulfur. As components of complex reaction systems anionic and nonionic emulsifiers were used, which physicochemical properties are given in table 1.

Table 1. Physicochemical properties of emulsifiers.

| №  | Name of the emulsifier       | $M$, g/mol   | $\rho$, g/cm$^3$ | $T_{melt}$, K |
|----|-----------------------------|--------------|------------------|--------------|
| 1  | Sodium carboxymethyl cellulose SCMC | $25-30 \cdot 10^3$ | 1.59             | –            |
| 2  | Sodium dodecyl sulfate SDS   | 288.38       | 1.01             | 478          |
| 3  | Sodium dioctyl sulfosuccinate SDSS | 444.55       | –                | 428          |
| 4  | Triton X-100                | 625          | 1.07             | 279          |
| 5  | Triton X-305                | 1526         | 1.09             | –            |

Purification of sulfur was carried out by recrystallization by a standard method. The emulsion preparation procedure was as follows: 200 ml of benzene and a weighed portion of purified sulfur were placed in a 500 ml round bottom flask; the flask was heated for 1 h under reflux; the resulting solution was cooled, filtered and placed in a dark place before use.

We studied emulsions of sulfur in benzene with various emulsifiers under different conditions (table 2). When choosing an emulsifier for emulsions and subsequent polymerization under the action of high-energy radiation, into account must be taken long-term aggregative stability (in the field of radiation) and the possibility to extract the resulting product from the emulsion.

Table 2. Characteristics of studied emulsions.

| №  | Emulsifier | Ionizing radiation | Microwave radiation |
|----|------------|--------------------|---------------------|
| 1  | SCMC       | +                  | –                   |
| 2  | SDS        | +                  | +                   |
| 3  | SDSS       | +                  | +                   |
| 4  | Triton X-100 | –                  | +                   |
| 5  | Triton X-305 | –                 | +                   |

To prepare emulsions, the water solutions of emulsifiers were prepared. Then, 10 ml of sulfur solution in benzene was added in a beaker with 90 ml of water solution of emulsifier, and subjected to ultrasonic treatment (UZDN-1) for 15 min. Several preliminary experiments have shown that such a time is sufficient for complete dispersion.

The emulsions were placed in test tubes and closed with lids. They were irradiated by ionizing radiation ($P = 0.108$ Gy/s, $^{60}$Co) or by microwave radiation (2.45 GHz, Biotage Initiator$^+$).

After irradiation, the tubes were opened, the solution was filtered, the precipitate was washed with distilled water and dried at room temperature. The synthesized products were investigated by photon correlation spectroscopy (Photocor Compact-Z spectrometer), scanning electron microscopy with elemental analysis (JSM 6510 LV SSD X-MAX), and X-ray diffractometry (Dron 3M diffractometer) on the basis of the Center for Collective Use of the Dmitry Mendeleev University of Chemical Technology of Russia.
3. Results
After the effect of the ionizing radiation on the emulsions as the products were obtained the sulfur-containing precipitates of light yellow color. After filtering the irradiated emulsions the samples of precipitates were analyzed to determine the average particle size and particle structure of precipitates. On the microphotographs (figures 1, 2) one can see that two fractions prevail in the systems. Larger particles are agglomerates, their shape is close to rhombic and monoclinic, their size varies in the range 110–170 μm. The particle size of the fine fraction is 10–50 μm. The sample from system 2 with SDS also contains particles of an amorphous-fibrous structure, which may be a sign of an oligomeric or polymeric structure. It should be noted that the particles in sample 3 with SDSS also have a shape close to rhombic and monoclinic, but, unlike the particles in sample 2, they are 10 times smaller and close to nanoscale particle, and also in sample 3 particles of an amorphous-fibrous structure are absent.

![Figure 1. SEM micrograph of sulfur-containing precipitate from sample 2. [SDS] = 1% wt., D = 2.33 kGy.](image1)

![Figure 2. SEM micrograph of sulfur-containing precipitate from sample 2 (points of composition determination are indicated). [SDSS] = 1% wt., D = 2.33 kGy.](image2)

Micrographs of particles of sulfur-containing samples confirm the theoretical idea that the polymerization proceeds in a narrow zone inside a polymer-monomer particle located on the interface, and, in accordance with this, is determined by the particle surface area, concentration and nature of the emulsifier. The depth of the reaction zone depends on the diffusion properties of macromolecules, radicals, and other components of the reaction. It is important to consider the ratio of the diffusion rates of these particles to the chain growth rates. The radicals initiating the reaction form either in the surface zone or enter the reaction zone from the aqueous phase.

Elemental analysis of the surface (table 3) showed an increased carbon content in the surface layer (34-65% wt.), as well as the presence of sodium (1% wt.). The presence of carbon in the sulfur-containing samples indicates the possibility that an organic emulsifier is involved in the formation of initiating particles.

4. Discussion
To determine the structure of sulfur-containing precipitates, X-ray diffraction was used, the results are presented in figures 3, 4. The presence of distinct peaks in the X-ray diffraction patterns of the samples indicates the crystal structure of sulfur-containing samples. However, in the regions of 60–70° there are no distinct peaks, which may indicate an amorphous structure. The observed X-ray amorphous halo is a sign of the polymer structure of the product.
Table 3. Elemental analysis of the surface of sulfur-containing samples.

| Sample | Element, % wt. |   |   |
|-------|----------------|---|---|
|       | C  | S  | Na |
| 1     | 65 | 34 | 1  |
| 2     | 34 | 66 | 0  |
| 3     | 0  | 100| 0  |

Figure 3. XRD of sulfur-containing precipitate from sample 2. [SDS] = 1% wt., D = 2.33 kGy.

Figure 4. XRD of sulfur-containing precipitate from sample 3. [SDS] = 1% wt., D = 2.33 kGy.

The systems 2–5 were also treated by microwave radiation with the frequency 5.45 GHz. The parameters of the processes of microwave heating of the systems with ionic (SDS, system 2) and non-ionic (Triton X-100, system 4) emulsifiers are presented on the figures 5, 6, respectively.
It can be noted that the power consumption for carrying out the process with nonionic emulsifiers is about 180–200 W, while for ionic emulsifiers this value is about 50 W. This can be explained by the fact that ionic conductivity increases the efficiency of microwave heating, and lower power consumption is required to maintain the required temperature.

It is also worth noting that in the case of an ionic emulsifier, heating occurs more sharply, while the heating curve with a nonionic emulsifier is smoother. This can also be explained by the ionic conductivity factor. In systems 2-5 the precipitates of sulfur-containing granules were obtained, which shape is close to spherical.

5. Conclusion

By SEM and XRD, the structure of sulfur-containing precipitates obtained under radiation irradiation was determined. Two fractions of particles of both crystalline and amorphous structures were observed. The presence of an amorphous structure suggests that polymer (oligomer) was formed. The
XRF analysis indicates a high proportion of sulfur (66–100% wt.) and carbon (34–65% wt.) in the precipitates. The presence of carbon indicates the possibility of the participation of an organic emulsifier in the formation of initiating particles.

Using microwave radiation it was found that due to the low thermal conductivity of benzene, which is part of the emulsion, local overheating of the mixture occurs. In this regard, it was concluded that it is necessary to increase the pressure during the reaction. When carrying out the reaction at a temperature of 433.15 K and a pressure of 0.8 MPa, it was found that maintaining the temperature during the process requires less power consumption for ionogenic surfactants than for nonionic ones. This factor may be due to the fact that ionic conductivity increases the efficiency of microwave heating. This is also evidenced by a sharper heating of the emulsion based on ionic surfactant compared to nonionic. During the reaction, a sulfur-containing precipitate is formed as granules with the spherical and close to spherical shapes.

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