


Article

Chemical Oxidative Polymerization of Methylene Blue: Reaction Mechanism and Aspects of Chain Structure

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Abstract: The kinetic regularities of the initial stage of chemical oxidative polymerization of methylene blue under the action of ammonium peroxodisulfate in an aqueous medium have been established by the method of potentiometry. It was shown that the methylene blue polymerization mechanism includes the stages of chain initiation and growth. It was found that the rate of the initial stage of the reaction obeys the kinetic equation of the first order with the activation energy $49 \text{ kJ} \cdot \text{mol}^{-1}$. Based on the proposed mechanism of oxidative polymerization of methylene blue and the data of MALDI, EPR, and IR spectroscopy methods, the structure of the polymethylene blue chain is proposed. It has been shown that polymethylene blue has a metallic luster, and its electrical conductivity is probably the result of conjugation over extended chain sections and the formation of charge transfer complexes. It was found that polymethylene blue is resistant to heating up to a temperature of 440 K and then enters into exothermic transformations without significant weight loss. When the temperature rises above 480 K, polymethylene blue is subject to endothermic degradation and retains 75% of its mass up to 1000 K.

Keywords: oxidative polymerization; methylene blue; polymethylene blue; electrical conductivity of polymers; paramagnetic polymers

1. Introduction

The ability to control the properties and morphology of thin films of electroactive polymethylene blue [1] during the electrochemical polymerization of methylene blue [2] opens up prospects for the use of this polymer. Although research aimed at establishing the laws of synthesis and properties of polymethylene blue is still not enough, it has already found application for the manufacture of electrochemical sensors. For example, using polymethylene blue, it has been shown that it is possible to determine the nitrite ion [3], 4-nitrophenol [4], acrylamide [5], and thiols and amino acid derivatives [6]. The successful use of polymethylene blue for the detection of natural substances, such as catechins in green tea [7], pyridoxine [8], DNA [9], hemoglobin [10], and xanthan and

uric acid [11], give hope for the creation of new analyzers for medical and biological purposes. The methylene blue polymer can act as a trap for hydroxyl radicals [12], is an effective adsorbent [13], and is promising for creating supercapacitors [14]. Films based on polymethylene blue have a high conductivity of about $103 \text{ S} \cdot \text{cm}^{-1}$, which is of interest for the creation of conducting glasses [15]. Polymethylene blue can also be synthesized by chemical oxidation of methylene blue by the action of ammonium peroxodisulfate [9].

Although the area of possible application of polymethylene blue is rapidly expanding, the chain structure of this polymer remains a matter of debate [5,7,15–17]. The mechanism of photopolymerization of unsaturated compounds in the presence of methylene blue and reducing agents was described earlier [18,19], but the details of the mechanism of chemical oxidative polymerization of the methylene blue dye itself have not been established [17]. Therefore, this article aims to establish the kinetics and mechanism of chemical oxidative polymerization of methylene blue, as well as to consider the chain structure, thermal stability, and the nature of paramagnetism of polymethylene blue. In this work, based on the analysis of the results of MALDI, EPR, IR spectroscopy, and kinetic data, it is proposed that the mechanism of oxidative polymerization includes the stage of conversion of molecular dimers of methylene blue (stabilized by charge transfer) into radical cations of covalent dimers of methylene blue, which initiate the subsequent addition of the monomer.

2. Experimental

2.1. Materials and Methods

Methylene blue and ammonium peroxodisulfate were purchased from Sigma–Aldrich. Double-distilled water was used as a reaction medium. Vibrational spectra of the samples were recorded in potassium bromide pellets using a Nicolet 380 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). MALDI spectra were recorded on an Ultraflex II mass spectrometer (Bruker, Karlsruhe, Germany) with an accelerating voltage of 25 kV with Nd: YAG laser (355 nm) desorption from a DHB matrix. EPR spectra of solid samples of methylene blue and polymethylene blue were recorded on a commercial spectrometer Bruker EMX (Bruker, Karlsruhe, Germany) (For EPR measurements, we used the devices of the Core Facility of the Emanuel Institute of Biochemical Physics, Russian Academy of Sciences “New Materials and Technologies”). Photographs of methylene blue samples and the product of its oxidative polymerization were obtained using a stereoscopic microscope Lomo MSP-2-2SD equipped with an MC-5 electronic camera (Lomo Microsystems, St. Petersburg, Russia); images were processed using the MCview (Lomo Microsystems, St. Petersburg, Russia) software package. TGA and DSC were recorded at a heating rate of $10 \text{ degrees} \cdot \text{min}^{-1}$ in a nitrogen flow ($70 \text{ mL} \cdot \text{min}^{-1}$) on an STA 449 F3 Jupiter instrument (NETZSCH, Weyhe-Dreye, Germany). XRD was recorded using a Malvern Panalytical Aeris XRD benchtop X-ray diffractometer (Malvern, Worcestershire, UK).

2.2. Synthesis of Polymethylene Blue

An amount of 0.320 g of methylene blue was dissolved in 50 mL of bidistillate (a CODYSON CDS-300 17269 ultrasonic bath (Codyson, Moscow, Russia) was used to accelerate the dissolution). A solution of 0.912 g of ammonium peroxodisulfate in 50 mL of bidistillate was also prepared. The solutions were mixed, and the reaction was carried out at a temperature of 298 K for 18 h. The resulting precipitate was filtered off, washed on a filter with 25 portions of water, 100 mL each, and then dried at a temperature of 323 K.

2.3. Kinetics of Polymerization of Methylene Blue

An amount of 0.160 g of methylene blue was dissolved in 50 mL of bidistillate. A solution of 0.456 g of ammonium peroxodisulfate was also prepared and dissolved in 50 mL of bidistillate. The electrode of an F20-Standard pH meter manufactured by Mettler Toledo was placed in an aqueous solution of a monomer, and a solution of an oxidizing agent was quickly added, recording the pH values at specified time intervals. Kinetic studies were carried out under thermostating conditions at temperatures of 298 K, 308 K, and 318 K.

3. Results and Discussion

The time dependences of proton concentrations obtained under the conditions of oxidative polymerization of methylene blue at different temperatures are shown in Figure 1.

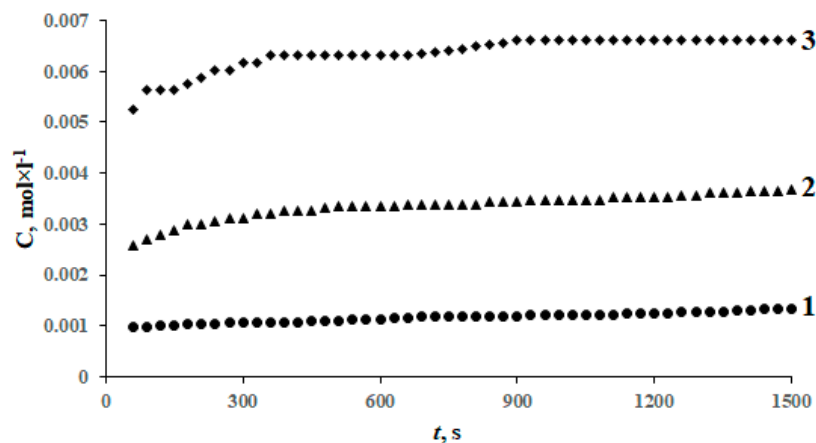


Figure 1. Kinetic curves of methylene blue polymerization at the following temperatures: 1–298 K; 2–308 K; 3–318 K (methylene blue concentration $5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; concentration of ammonium peroxodisulfate $0.02 \text{ mol} \cdot \text{L}^{-1}$).

After a short period of rapid increase in the concentration of protons, the rate of their release decreases significantly (Figure 1). In this case, it takes at least several hours to complete the reaction with the formation of an insoluble polymer. Thus, a significant part of methylene blue is rapidly oxidized, followed by a slower stage associated with the formation of a water-insoluble polymer. The time boundaries of the stage of rapid oxidation of the monomer, presumably with the formation of a dimer, are clearly traced (Figure 1) and are about 750, 510, and 360 min at temperatures of 298 K, 308 K, and 318 K, respectively. By the indicated times, the concentration of protons in the system is $1.19 \cdot 10^{-3}$, $3.52 \cdot 10^{-3}$, and $6.31 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ at temperatures of 298 K, 308 K, and 318 K, respectively.

It is noteworthy that the kinetic data for the initial stage of the oxidative polymerization of methylene blue are in satisfactory agreement with the first-order equation of the reaction rate (1).

$$-\frac{dC_M}{dt} = kC_M \quad (1)$$

where: C_M —monomer concentration; t —time; k —reaction rate constant.

The concentration of the monomer reacted during the initial stage should be proportional to the change in the concentration of protons; therefore, the fulfillment of Equation (2) should be expected.

$$C_M = X(C_{\max} - C) \quad (2)$$

where: C —current proton concentration; C_{\max} —maximum concentration of protons attained at the initial stage of the reaction; X —proportionality ratio.

After substitution of (2) into (1), separation of variables and subsequent integration from C_0 to C and from 0 to t leads to Equation (3).

$$\ln(C_{\max} - C) = -kt + \ln(C_{\max} - C_0) \quad (3)$$

where: C_0 —initial concentration of protons.

Kinetic Equation (3) satisfactorily agrees with the experimental data for the initial stage of methylene blue polymerization (Figure 2).

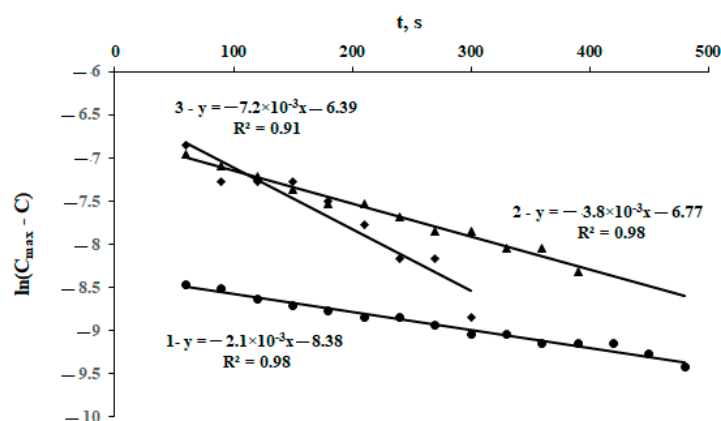


Figure 2. Linear anamorphoses of kinetic curves in coordinates “ $\ln(C_{\max} - C)$ vs. t ”, obtained for the polymerization of methylene blue (0.005 M) at the following temperatures: 1–298 K; 2–308 K; 3–318 K.

The values of the rate constants determined from the tangents of the slope of straight lines in the coordinates “ $\ln(C_{\max} - C)$ vs. t ” are $2.1 \cdot 10^{-3}$, $3.8 \cdot 10^{-3}$, and $7.2 \cdot 10^{-3} \text{ s}^{-1}$ at temperatures of 298, 308, and 318 K, respectively. The temperature dependence of the rate constant of the oxidative polymerization of methylene blue is linear in the coordinates “ $\ln k$ vs. T^{-1} ” (Figure 3). The activation energy for polymerization of methylene blue is $49 \text{ kJ} \cdot \text{mol}^{-1}$, and the preexponential factor is $7.9 \cdot 10^5 \text{ s}^{-1}$.

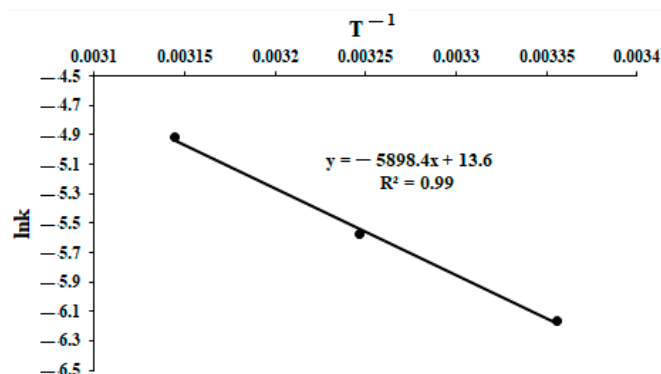
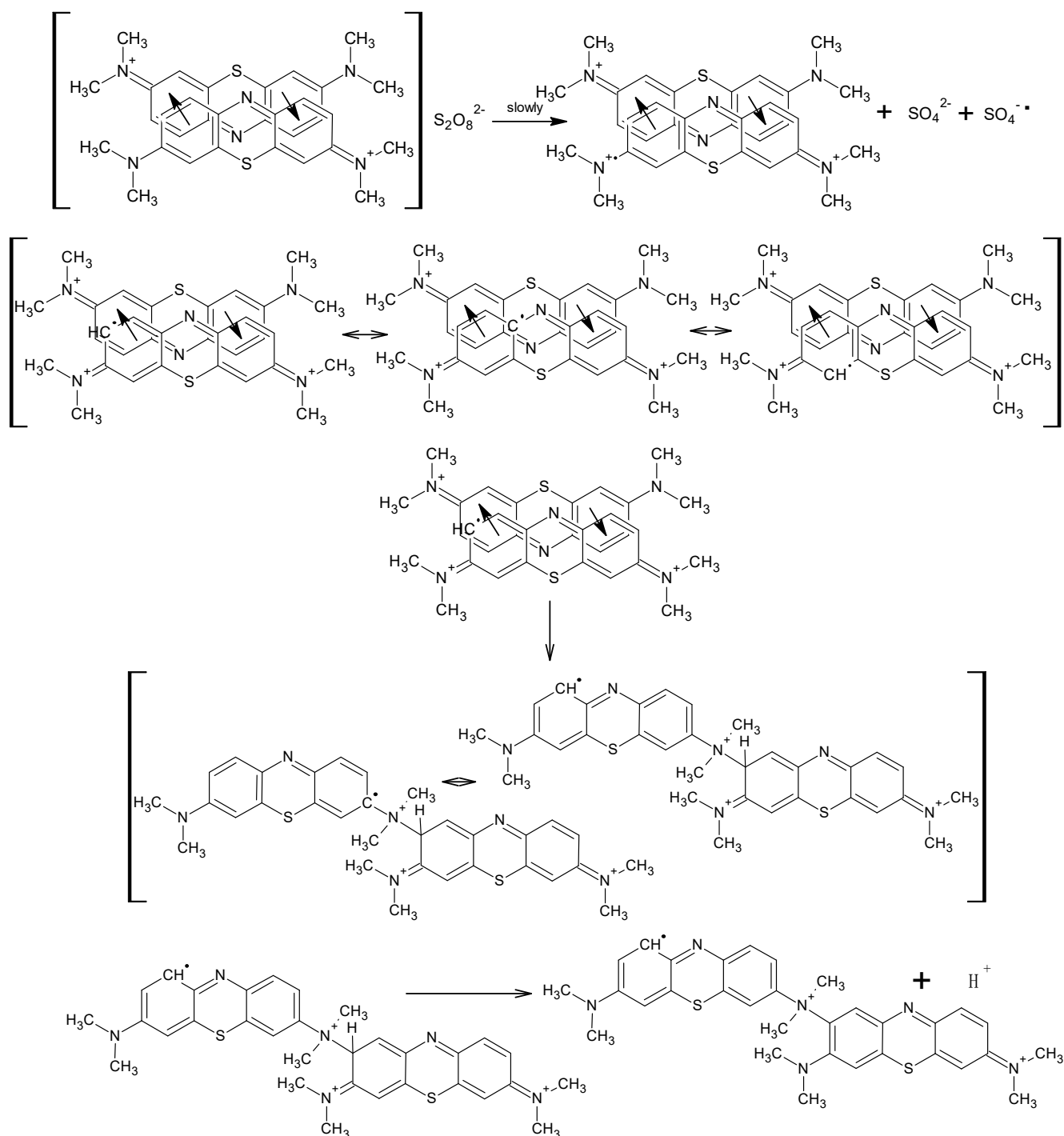


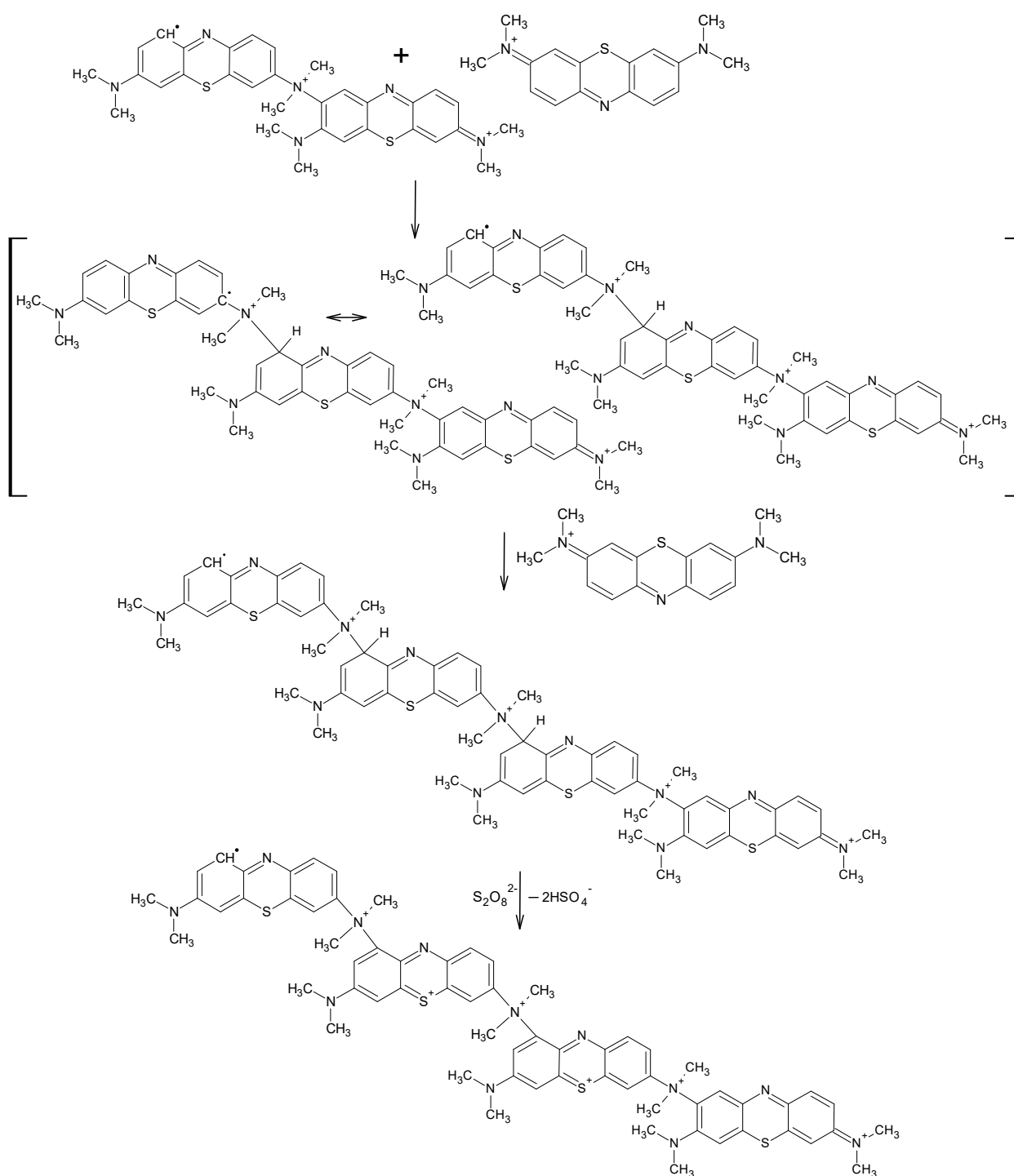
Figure 3. Temperature dependence of the rate constant of the oxidative polymerization of methylene blue in coordinates “ $\ln k$ vs. T^{-1} ”.

It is known that methylene blue is capable of forming molecular associates in aqueous solutions, among which the dimeric form predominates [20]. The first order of the initial stage of polymerization of methylene blue is probably a consequence of the transformation of molecular dimers of methylene blue, stabilized by charge transfer, into cation radicals of dye dimers built by covalent bonds (Scheme 1). Apparently, the reaction begins with the one-electron oxidation of the methylene blue dimer at the dimethylamino group. The proposed mechanism of the initial stage of the oxidative polymerization of methylene blue with the participation of the most stable resonance structures is shown in Scheme 1. The values of the enthalpy of activation and entropy of activation, calculated in accordance with the theory of the activated complex, are $46.5 \text{ kJ} \cdot \text{mol}^{-1}$ and $-140 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively. The negative value of the activation entropy of the initial stage of polymerization of methylene blue indicates the compactness of the transition state in comparison with the reagents and is consistent with the slow oxidation of methylene blue within the ion pair formed by the molecular dimer of the dye (doubly charged cation) and the peroxodisulfate anion. The calculated activation parameters are consistent with the rapid approach of these ions so that the ion pair actually functions as a monomer. A similar case was described earlier for the oxidation of dopamine hydrochloride by the action of ammonium peroxodisulfate [21].



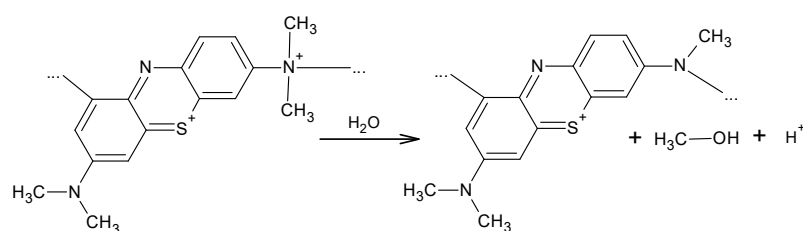
Scheme 1. The mechanism of the initial stage of the oxidative polymerization of methylene blue.

We assume that the subsequent formation of polymer chains is associated with the slow diffusion of methylene blue to the radical cations of methylene blue dimers, as shown in Scheme 2.



Scheme 2. Mechanism of chain growth under conditions of methylene blue polymerization.

Thus, considering the mechanism of methylene blue polymerization, one can expect the formation of dicationic units of the polymer chain, as well as monocationic fragments as a result of nucleophilic demethylation (Scheme 3).



Scheme 3. Possible structures of polymethylene blue chain links: nucleophilic demethylation.

The structure of the polymethylene blue chain is a subject of constant discussion in the literature and varies greatly in the works of various scientific teams [5,7,15–17]. Although the formation of quaternized nitrogen in the backbone seems to contradict the high electrical conductivity of polymethylene blue [15], the MALDI data indirectly indicate the presence of such units. In the MALDI of the starting methylene blue, under the conditions of detecting positively charged ions, signal 286.198 is observed (Figure 4), which, most likely, can be caused by the loss of sulfur and a hydrogen atom during laser desorption from the DHB matrix (Scheme 4).

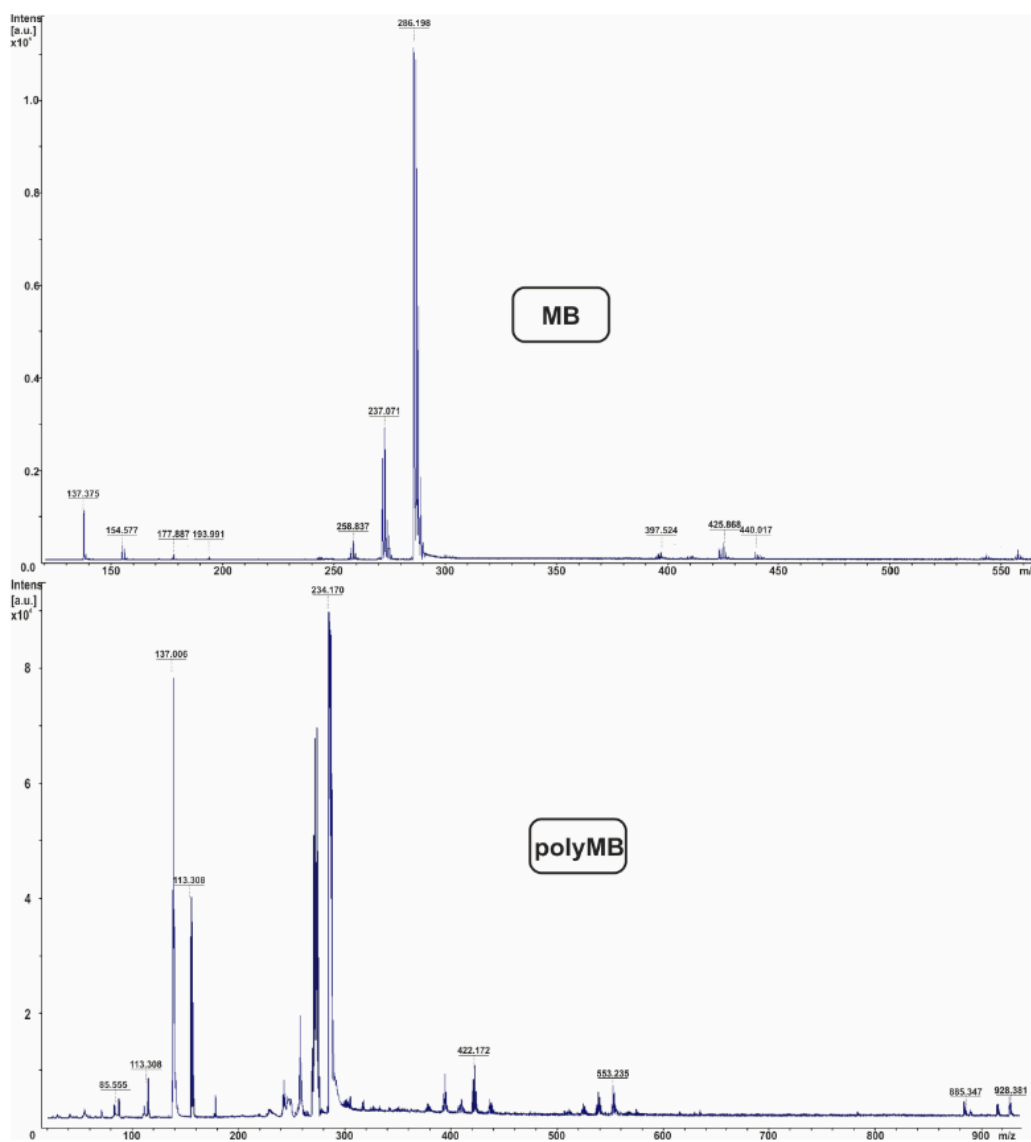
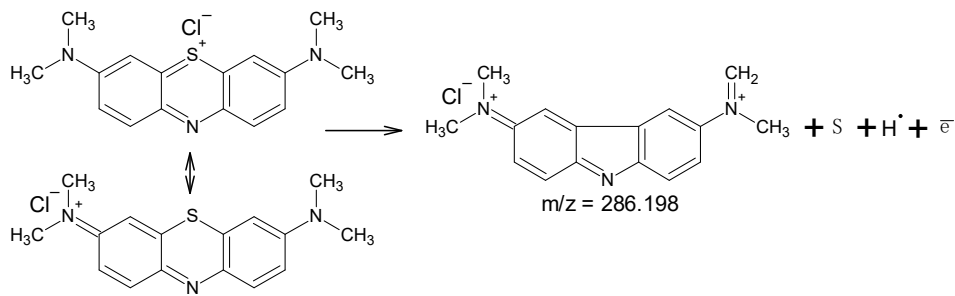
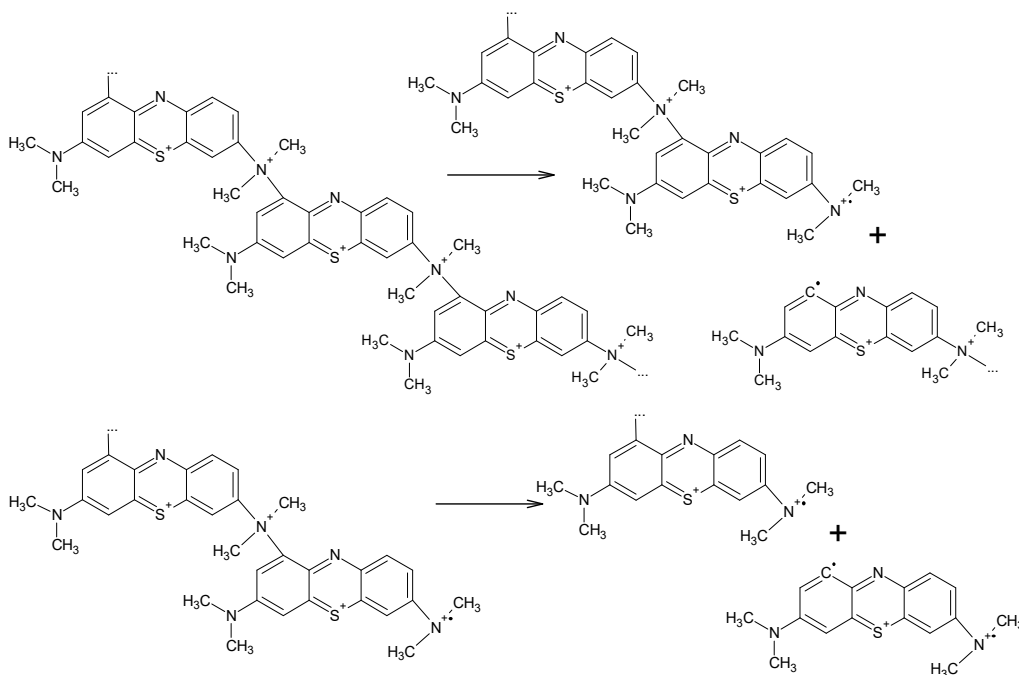


Figure 4. Spectra MALDI: MB—methylene blue; PolyMB—polymethylene blue.



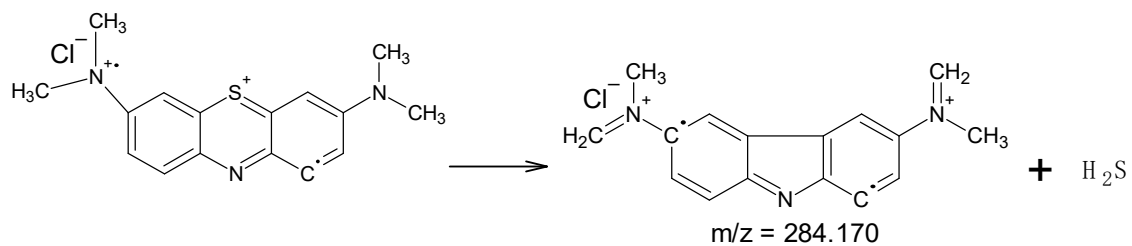
Scheme 4. Destruction of methylene blue under conditions of laser desorption from a DHB matrix.

For polymethylene blue under conditions of laser desorption from the DHB matrix, chain destruction can be expected in accordance with the mechanism presented in Scheme 5.



Scheme 5. Destruction of the polymethylene blue chain under conditions of laser desorption from the DHB matrix.

The pattern of the isotope distribution of the 284.17 signal (Figure 4) indicates the detection of ion pairs, which include the chloride anion. In this case, it can be expected that the reason for the most intense signal in MALDI is the loss of hydrogen sulfide by intermediates formed during chain destruction (Scheme 6).



Scheme 6. Extrusion of H_2S by an intermediate formed during the destruction of the polymethylene blue chain because of laser desorption from the DHB matrix.

The fraction of quaternized nitrogen in the main chain of polymethylene blue is probably small, and conjugation is realized in sections of the chain of considerable length.

At the same time, even a small number of dicationic units can lead to a dominant signal in MALDI (Figure 4), because these fragments are probably responsible for electrostatic destabilization of the chain.

The above assumptions are in indirect agreement with reports on the high electrical conductivity of polymethylene blue [15], as well as with the pronounced metallic luster of this polymer (Figure 5).

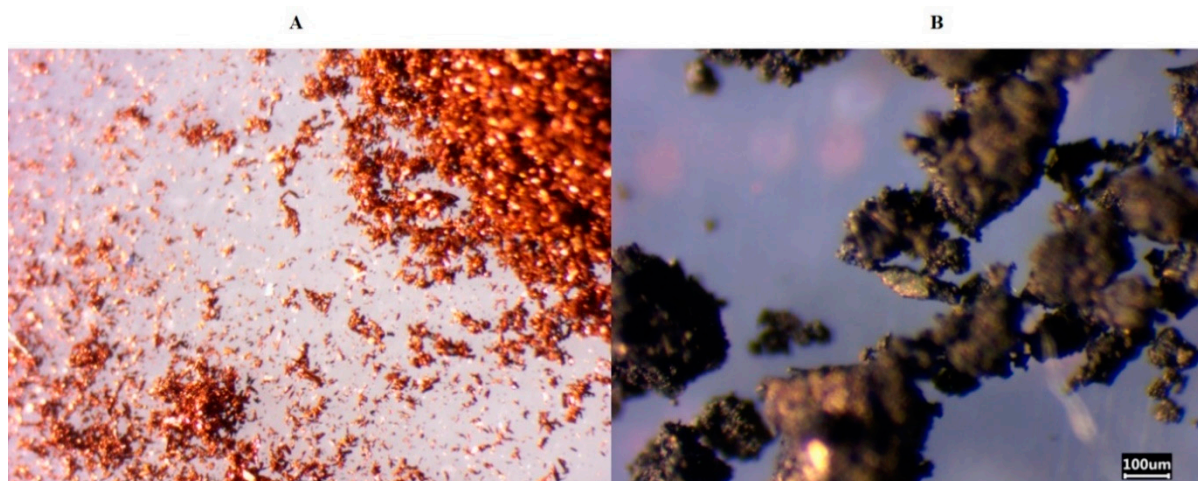


Figure 5. Photos of samples: (A)—methylene blue; (B)—polymethylene blue.

The mechanism of the onset of electrical conductivity may possibly also include the inter-chain contribution associated with the formation of complexes with charge transfer. EPR spectroscopic data are consistent with this assumption. First, methylene blue, used as a monomer, has an EPR signal with a line width of $\Delta H = 15.9$ G and a g-factor of ~ 2.0045 (Figure 6A). A polymethylene blue sample washed with five 100 mL portions of distilled water has an EPR signal with a width of $\Delta H = 16.6$ G and a g-factor of ~ 2.0050 (Figure 6B). The close EPR spectra of methylene blue and polymethylene blue suggest that, in both cases, the signal is caused by the formation of a charge transfer complex [18,22–25]. Taking into account the known ability of methylene blue to adsorb on various electrically conductive polymers [26–29], and the effectiveness of polymethylene blue as an adsorbent [13], we can assume chemisorption of methylene blue on polymethylene blue is a result of the formation of charge transfer complexes with the polymer chain links. The broadening of the EPR signal in this case is caused by the possibility of the formation of a number of different, but structurally related, complexes with charge transfer. Thorough purification of polymethylene blue with 25 portions of distilled water, 100 mL each, leads to a decrease in intensity and an increase in the width of the EPR signal to $\Delta H = 19.5$ G, which is consistent with the formation of complexes with charge transfer between the monomer and the links of the polymer chain (Figure 6C). In the latter case, the concentration of paramagnetic centers is about 5×10^{16} spin \cdot g $^{-1}$.

According to XRD data, polymethylene blue resulting from the chemical oxidative polymerization of methylene blue contains a significant amount of amorphous phase (Figure 7).

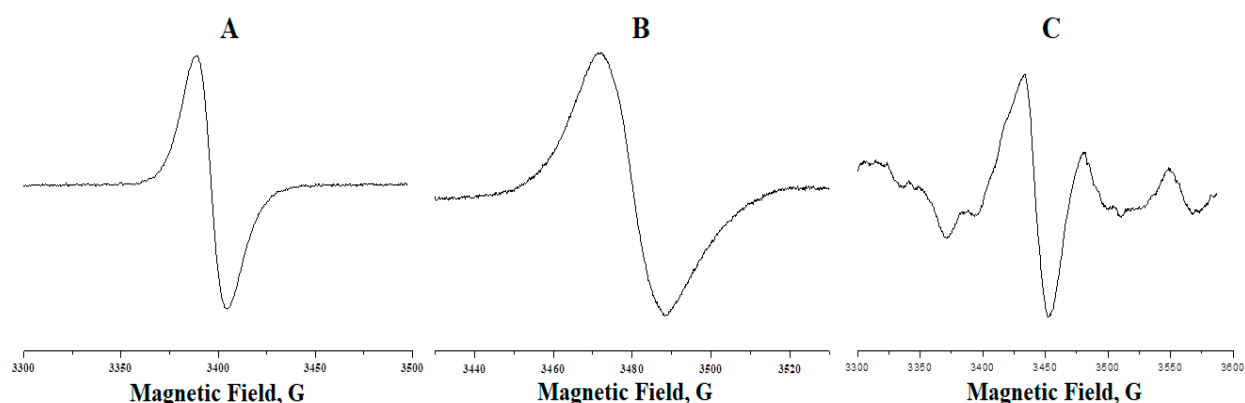


Figure 6. EPR spectra: (A)—methylene blue; (B)—polymethylene blue washed with five portions of distilled water, 100 mL each; (C)—washed with 25 portions of distilled water, 100 mL each.

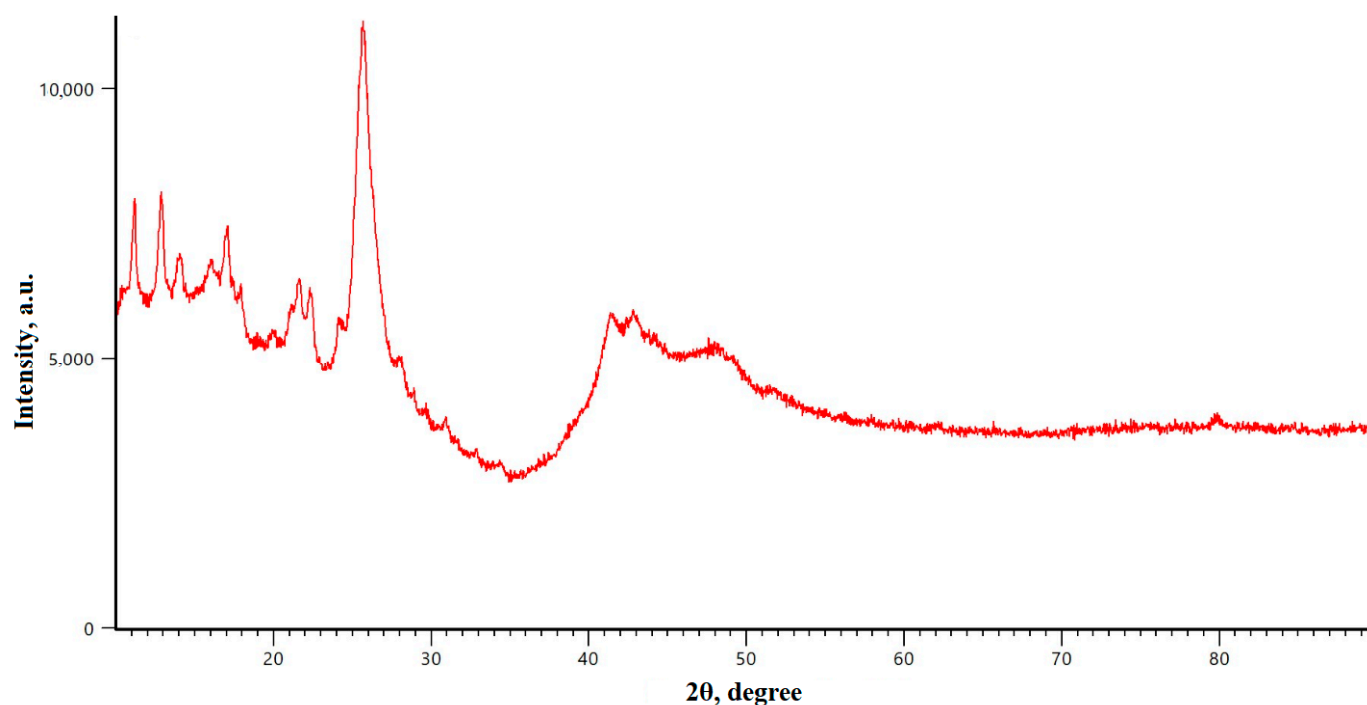


Figure 7. XRD of polymethylene blue synthesized by chemical oxidative polymerization of methylene blue.

IR spectroscopic data indicate an increase in wavenumbers by $10\text{--}50\text{ cm}^{-1}$ for most of the stretching and bending vibration bands in the range $1000\text{--}1700\text{ cm}^{-1}$ after polymerization of methylene blue (Figure 8). This circumstance is consistent with the more “rigid” structure of polymethylene blue compared to the initial methylene blue, which exists predominantly in the form of a molecular dimer stabilized by charge transfer [22–25]. The appearance of a shoulder of skeletal vibrations at 1600.2 cm^{-1} in the region of high wavenumbers, a change in the position of the bands of out-of-plane bending vibrations of C-H bonds, and a decrease in their number are consistent with an increase in the resonance energy and the participation of C-H bonds in the oxidative polymerization of methylene blue.

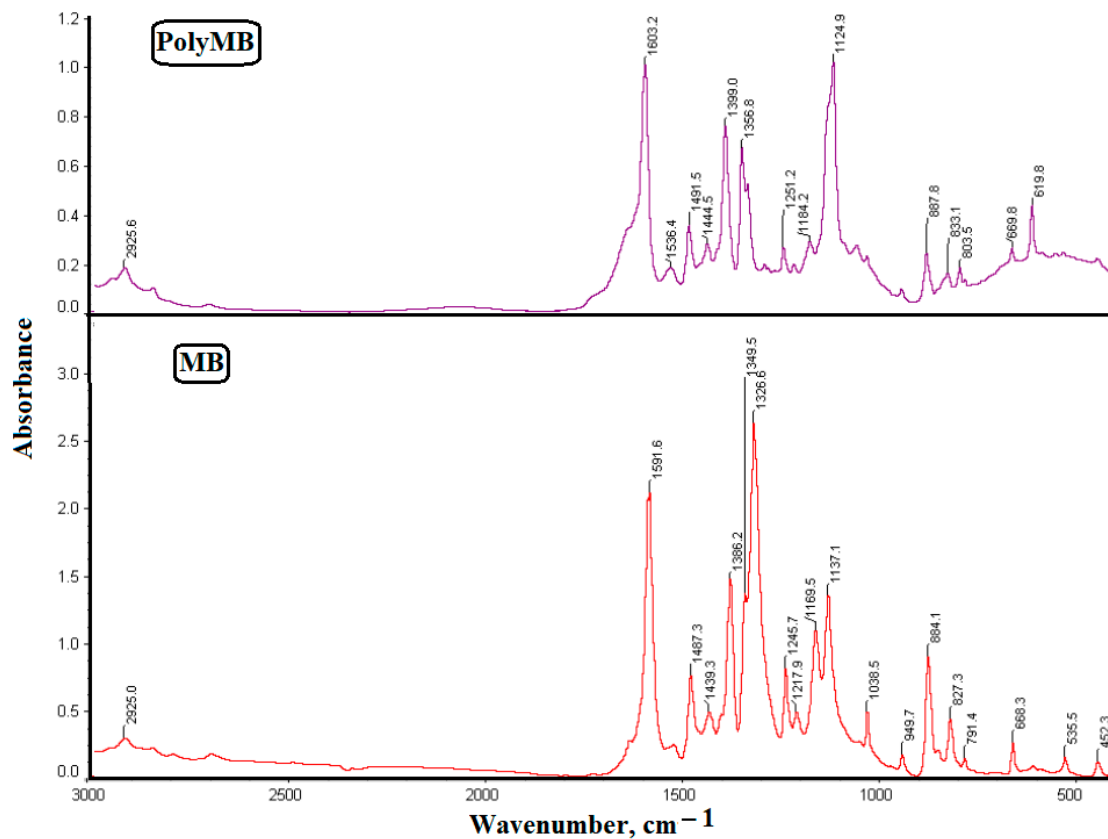


Figure 8. IR spectra: MB—methylene blue; PolyMB—polymethylene blue, recorded in potassium bromide tablets.

If methylene blue begins to decompose slowly at temperatures above 373–383 K [30], then polymethylene blue, when heated to a temperature of about 440 K, undergoes only a loss of adsorbed water (Figure 9). It is not excluded that the exothermic peak in the temperature range 440–480 K, which corresponds to the constant mass of the sample, may be associated with rearrangements in the polymer chain, leading to the disappearance of energetically unfavorable dication units.

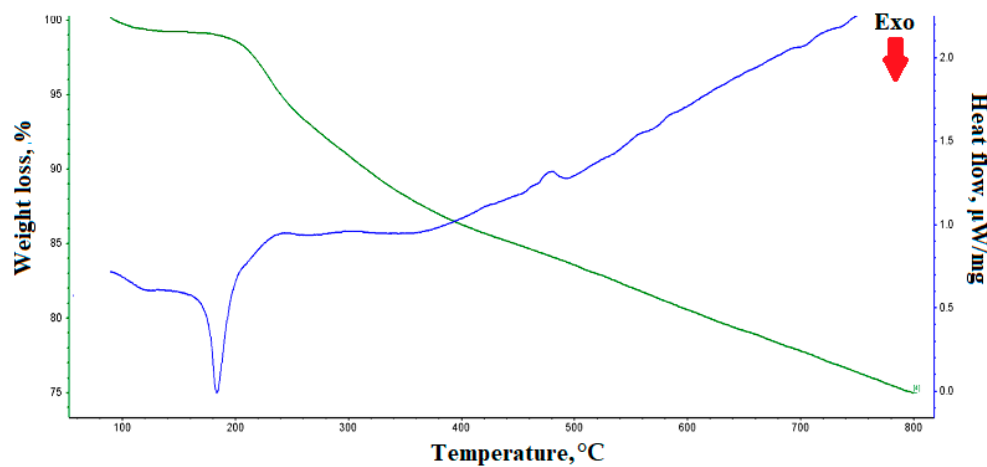


Figure 9. TGA and DSC of polymethylene blue.

Although polymethylene blue is unstable when heated above 440 K, low-volatility compounds predominate among its decomposition products. Thus, when heated to 1000 K, the sample retains about 75 wt% of the initial mass.

4. Conclusions

It is shown that the rate of the initial stage of chemical oxidative polymerization of methylene blue obeys a first-order kinetic equation with an activation energy of $49 \text{ kJ} \cdot \text{mol}^{-1}$. The first kinetic order is presumably a consequence of the rapid convergence of the molecular dimer of methylene blue, stabilized by charge transfer, and the peroxodisulfate anion, followed by a slow one-electron transfer within the ion pair. The implementation of one-electron transfer within the ion pair is also indicated by the low value of the preexponential factor $7.9 \cdot 10^5 \text{ s}^{-1}$ and the negative value of the activation entropy $-140 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. As a result, at the initiation stage, a radical cation of the covalent methylene blue dimer is formed, which is capable of subsequent addition of monomer molecules. Taking into account electronic and spatial factors, as well as kinetic data, a mechanism for the polymerization of methylene blue is proposed, which implies the formation of a chain linked through position 8 of the ring and quaternized nitrogen atoms, and the possibility of nucleophilic demethylation of the initially formed polymer is considered. The proposed structure of the polymethylene blue chain assumes the presence of extended conjugated sections of the chains and is consistent with its metallic luster and the data of MALDI, EPR, and IR spectroscopy methods. It was found that polymethylene blue can maintain stability up to 440 K; however, with a further increase in temperature up to 1000 K in an inert atmosphere, only 25 wt% of products are formed, subject to entrainment.

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