

Reaction analysis of 3,4-ethylenedioxythiophene with potassium persulfate in aqueous solution by using a calorimeter

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Abstract

A calorimeter was used to directly monitor the rate of emulsion polymerization of 3,4-ethylenedioxythiophene (EDOT) in aqueous solution for different concentrations of the initiator, potassium persulfate (KPS). The reaction involved polymerization and doping in one step, and yielded a poly(3,4-ethylenedioxythiophene) (PEDOT) with electrical conductivity. The electrical conductivity and yield of PEDOT increased as the molar ratio of KPS to EDOT increased until the molar ratio of unity. Then they decreased. The reaction rate was found to be governed by the concentration of the reactants: $R_p \propto [\text{KPS}]^{0.64} \times [\text{EDOT}]^{0.16}$. The exponent of EDOT concentration had so low value that the reaction was of approximately zero order, which could be explained by the presence of a so-called degradative addition. In addition, the effect of sulfuric acid on the polymerization rate of EDOT was also investigated. The reaction rate reached the maximum at pH 2.7. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymer; Poly(3,4-ethylenedioxythiophene); Potassium persulfate

1. Introduction

The conducting polymers produced by electrochemical techniques have a high conductivity [1–3], whereas the conducting polymers obtained by chemical methods are relatively poor conductors. In recent years there has been increasing interest in the synthesis of conducting polymers with high conductivity by chemical oxidation [4–7]. The chemical polymerization is more suitable for mass production than the electrochemical polymerization.

Poly(3,4-ethylenedioxythiophene) (PEDOT) has been attractive with a growing interest since it was first reported in 1992 [8] and has been produced commercially by Bayer AG. PEDOT can be synthesized chemically both in organic [8] and aqueous solutions [9]. Jonas et al. [9] reported the production of processable aqueous PEDOT solutions by oxidative polymerization in the presence of polystyrenesulfonic acid (PSSA) and potassium persulfate (KPS), an oxidizing agent. PEDOT can also be obtained electrochemically in either organic [10–12] or aqueous solutions [13,16].

Water is considered to be an unsuitable solvent because 3,4-ethylenedioxythiophene (EDOT) is hardly soluble [14]

and it inhibits the polymerization due to its reaction with thiophenyl cation radicals as initiating species [15]. Even in organic solvents such as ethanol, *n*-butanol and acetone, PEDOT shows the low yield and conductivity when the concentration of EDOT is low. To solve such problems, recently it has been proposed to add an anionic surfactant such as sodium dodecyl sulfate (SDS) to an aqueous solution of thiophene [16,17].

In spite of these disadvantages, water seems to be more attractive for the large scale synthesis of PEDOT than any other solvent from the viewpoint of cost, handling and safety. In this study, EDOT is oxidatively polymerized with KPS in water and the reaction rate is measured using a solution calorimeter. The reaction rate depends on the initial concentration of EDOT monomer, the concentration ratio of KPS/EDOT and pH.

2. Determination of polymerization rate

The basic for a calorimetry is an energy balance around the reactor. The detailed description of a calorimeter is elsewhere [18]. The energy balance is presented schematically in Fig. 1.

In this case, kinetic and potential energies are neglected. Reactor wall and jacket are considered to have the same

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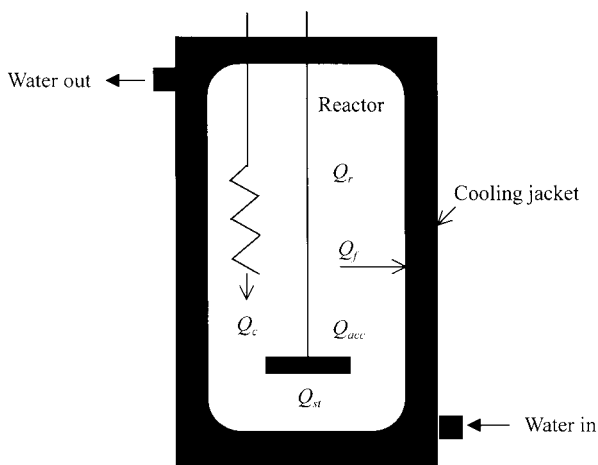


Fig. 1. Energy balance for a calorimeter where Q_r is heat of reaction, Q_c the heat of calibration or heater, Q_{acc} the heat accumulated in the reaction system, Q_f the heat flow through the reactor wall to the cooling system and Q_{st} is power input by stirrer.

temperature, and the reaction system in the reactor is regarded as perfectly mixed. The energy balance for a batch process is given by the following equation:

$$Q_r + Q_c + Q_{st} = Q_{acc} + Q_f \quad (1)$$

where the heat of reaction is calculated by

$$Q_r = V_{H_2O} \Delta H_p R_p \quad (2)$$

where V_{H_2O} is the volume of water in the system (l), ΔH_p is the molar heat of polymerization of monomer (J/mol) and is regarded as constant because the reaction is carried out in the same mechanism and in the narrow temperature range. And R_p is the rate of polymerization (mol/l s). The heat input by the stirrer is given by

$$Q_{st} = P_0 N^3 d^5 \rho \quad (3)$$

where P_0 is the power number, N the stirrer speed, d the diameter of the impeller, and ρ is the density of the solution. The accumulation of heat of reaction is calculated by

$$Q_{acc} = [(mC_p)_R + (mC_p)_i] \frac{dT_r}{dt} = (mC_p)_T \frac{dT_r}{dt} \quad (4)$$

where $(mC_p)_R$ and $(mC_p)_i$ are the product of mass by heat capacity for the reaction mixture and the inserts (stirrer and heater), respectively. dT_r/dt is the derivative of the reaction

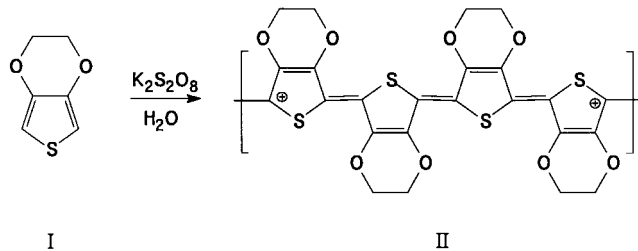


Fig. 2. Oxidative polymerization of 3,4-ethylenedioxythiophene (I) with potassium persulfate yielding the doped conducting polymer PEDOT (II).

temperature. The heat flow through the reactor wall to the water is given by

$$Q_f = UA\Delta T \quad (5)$$

where U is the overall heat transfer coefficient ($W/m^2 \text{ } ^\circ C$); A is the wet area (m^2); and $\Delta T = (T_r - T_j)$ is the difference between reaction and jacket temperatures.

Q_{st} is considered to be constant and contained in the baseline. U and $(mC_p)_T$ are measured by calibrating the calorimeter using a process of a known energy output for a certain period of time. Q_r is then calculated using the following equation:

$$Q_r = UA(T_r - T_j) + [mC_p]_T \frac{dT_r}{dt} - Q_{st} \quad (6)$$

Thus, the rate of polymerization can be calculated directly by measuring the parameters and combining Eq. (6) with Eq. (2).

Since Q_r is directly proportional to the polymerization rate $R_p = -d[M]/dt$, the thermogram reflects the change of R_p with time. For kinetic investigation, the initial reaction rate under (quasi) steady state conditions, $R_{p,0}$, is useful to determine reaction order, rate constant and activation parameters. In order to evaluate $R_{p,0}$ from a thermogram properly, it is generally necessary to follow the polymerization reaction until no heat evolution can be detected and subsequently to scan up to a higher temperature in order to get a complete conversion. It is time consuming, particularly for slow reactions.

Recently, it was shown that the maximum of a thermogram, which corresponds to the maximum rate $R_{p,max}$, may be taken as $R_{p,0}$ [19]. So $R_{p,0}$ is obtained directly from $R_{p,max}$ and the experiment can be interrupted as soon as the maximum is recorded.

3. Experimental

3.1. Polymerization

3,4-Ethylenedioxythiophene (EDOT) (Bayer) were used as received. All other chemicals were obtained from Aldrich and were used as received.

The polymerization of EDOT is depicted schematically in Fig. 2. It was carried out in a calorimeter (Calorimetry Sciences Co. Isoperibol Solution Calorimetry). KPS was dissolved in 25 g of an aqueous solution in a glass tube. EDOT was transferred into a sealed glass cell immersed in the KPS solution. After both reactants were warmed to $29.9^\circ C$ and reached the thermal equilibrium, the reactants were mixed and the polymerization reaction was started by pushing a rod and breaking the glass cell. The polymerization proceeded for a certain period under stirring action. The reaction temperature in the calorimeter was sensed by a thermocouple and recorded on a computer. The heat capacity of the calorimeter was calibrated prior to each

Table 1
Description of polymerization of EDOT and PEDOT yield

| Sample name | EDOT (mmol) | Oxidant | | Yield | |
|-------------|-------------|--|-------------|-------|------|
| | | Name | [Ox]/[EDOT] | g | % |
| PK0.5M1 | 7.04 | K ₂ S ₂ O ₈ | 0.5 | 0.004 | 0.4 |
| PK1M1 | 7.04 | K ₂ S ₂ O ₈ | 1 | 0.310 | 31.0 |
| PK2M1 | 7.04 | K ₂ S ₂ O ₈ | 2 | 0.237 | 23.7 |
| PK3M1 | 7.04 | K ₂ S ₂ O ₈ | 3 | 0.161 | 16.1 |
| PK4M1 | 7.04 | K ₂ S ₂ O ₈ | 4 | 0.123 | 12.3 |
| PF1M1 | 7.04 | FeCl ₃ | 1 | 0.008 | 0.8 |
| PF3M1 | 7.04 | FeCl ₃ | 3 | 0.050 | 5.0 |
| PF5M1 | 7.04 | FeCl ₃ | 5 | 0.135 | 13.5 |

experiment. To investigate the yield of polymer, PEDOT was synthesized chemically by oxidative polymerization of EDOT in an aqueous KPS solution. The mixtures were stirred continuously for desired reaction time at 30°C. The precipitates were collected by filtration and then washed with water and acetone successively, and dried under a dynamic vacuum at 40°C for 24 h. The yields of synthetic polymer were determined by weighing the solid powders. The reaction condition and yield are represented in Table 1. To investigate the effect of pH on the reaction, sulfuric acid (H₂SO₄) is added to control pH.

3.2. Instrumentation

FT-IR spectroscopy (Bomem, Model MB 100-C15) was used to identify the chemical structure of PEDOT. Solid specimens were prepared by grinding PEDOT with KBr powder and then pressing the mixture into a tablet. Elementary analyses were performed on an Elemental Analyzer (Carlo Erba). Electrical DC conductivity was measured with the conventional 4-point probe technique at room temperature, where the four points were in line on the

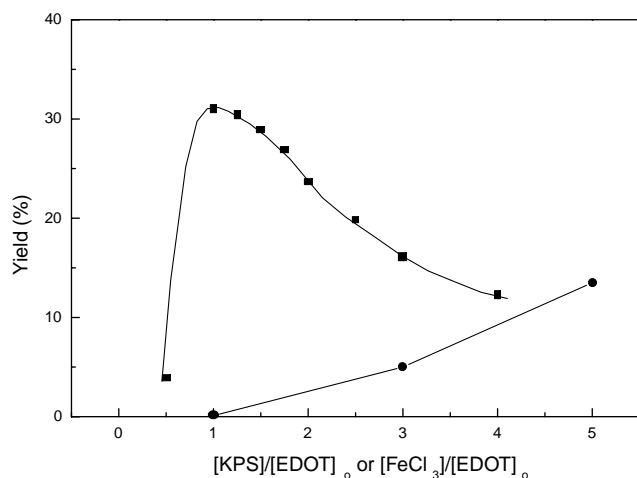


Fig. 3. Yield of PEDOT formed in the solution for 24 h as a function of the molar ratio of reactants: (■) using KPS; (●) using ferric chloride as an oxidant.

sample surface with an equal spacing of 1 mm. This sample was made as a pellet by pressing the powder up to 3000 psig utilizing an oil presser.

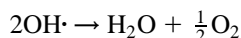
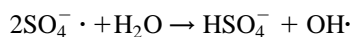
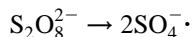
4. Results and discussion

4.1. Polymerization

The oxidative polymerization of EDOT has been reported in the literatures [7–9], after the first report on PEDOT in 1992 [8]. EDOT has a low solubility of 2.1 g/l in water at 20°C [17]. So an emulsion polymerization in water is used for the synthesis of PEDOT from EDOT using KPS as an initiator. The experimental results are listed in Table 1 and Fig. 3. It is clear that the yield is significantly low. The reason may be the extremely low solubility of EDOT in water [17].

The yield of PEDOT increases as the concentration of KPS in solution increases; it reaches a maximum at the ratio [KPS]/[EDOT] of unity, and then decreases. The color of supernatant liquids also changes from light yellow to greenish yellow as the initial concentration of KPS increases. It is recognized that the above results may be due to the presence of intermediate soluble products. The similar result was also obtained in the polymerization of pyrrole with KPS [20,21]. For the oxidant, FeCl₃, the yield of PEDOT increases as the ratio of oxidant to EDOT increases.

The atomic ratios of C/H, C/S and C/O were obtained from the elementary analysis and listed in Table 2. The theoretical formula for PEDOT appears C₆H₄O₂S₁. According to Table 2, the atomic ratios of C/S, C/H and C/O are lower than theoretical values in all products. In fact, a substantial proportion of polymer molecules has S-containing moieties as the initiating species. This initiating species can be SO₄^{•-} radical ion [20]. Thus if an amount of S is substantial, the excess amount of S in elementary analysis (Table 2) originates from SO₄^{•-} radical ion. In the absence of substances that can scavenge the SO₄^{•-} radicals formed initially the following reactions must take place in alkaline, neutral and dilute acid solution [24]:



At high concentration of KPS, hydroxyl radicals increase and these species initiate the reaction. Thus the excess amount of O could be classified with that of SO₄^{•-} radical ion and hydroxyl radical ion. Most of the oxygen atoms in the molecule give rise to >C=O group which is called an overoxidation [20]. Column 10 in Table 2 gives the amount of O due to the occurrence of overoxidation. It is recognized

Table 2
Atomic ratio of elements in the product

| Sample | [KPS]/[EDOT] | [C] ^a | [S] ^a | [O] ^a | C/S | C/H | C/O | Overoxidation | Wt% O |
|--------|---------------------|------------------|------------------|------------------|------|------|------|------------------|-------|
| | Theoretical formula | | | | 6.00 | 1.50 | 3.00 | [O] ^b | |
| PK1M1 | 1 | 3.661 | 0.678 | 1.703 | 5.40 | 1.20 | 2.15 | 0.209 | 3.34 |
| PK2M1 | 2 | 3.615 | 0.650 | 1.709 | 5.56 | 1.21 | 2.11 | 0.314 | 5.02 |
| PK3M1 | 3 | 3.564 | 0.662 | 1.790 | 5.38 | 1.17 | 1.99 | 0.330 | 5.28 |

^a Mole base of elements: [wt% of elements]/[MW of elements].

^b Mole base of oxygen for overoxidation: $[O] - [O]_p - [O]_l$ where $[O]_p$ is the oxygen in PEDOT ($[O]_p = [C]/(C/O \text{ for theoretical formula})$) and $[O]_l$ is the excess of oxygen obtained from the S containing moieties attached to PEDOT ($[O]_l = 4 \times ([S] - [C]) / (C/S \text{ for theoretical formula})$).

that the overoxidation of PEDOT increases as the concentration of KPS increases. In the case of chemically prepared polypyrrole, it was pointed out that the amount of O increased in a similar manner when an excess of initiator was added [20].

Fig. 4 shows the IR spectra of pristine PEDOT powders prepared with KPS and compares them with the spectrum of PEDOT powder made with $FeCl_3$. The main vibrations in the region $1600\text{--}600\text{ cm}^{-1}$ were proposed for the PEDOT obtained electrochemically [12].

Vibrations at 1520 and 1470 cm^{-1} (due to ring stretch of thiophene ring), and 1340 cm^{-1} (due to C–C and C=C stretch of quinoidal structure) originate from the thiophene ring [12,16,22]. Further vibrations from the C–S bond in the thiophene ring can be seen at 980 , 840 and 690 cm^{-1} [12,22]. Vibrations at 1190 , 1147 and $1090\text{--}1060\text{ cm}^{-1}$ are assigned to stretching in the C–O–C bond [12].

The doping process causes a profound change in IR spectra presumably due to the change in the electronic structure of the neutral polymer. The high background absorbance in the high-energy region above 2000 cm^{-1} is characteristic of conducting polymers and is attributed to the tailing of the electronic bipolaronic absorption from oxidatively doped regions in the polymer [23]. Therefore, the band at 1340 cm^{-1} and the high background absorbance indicate

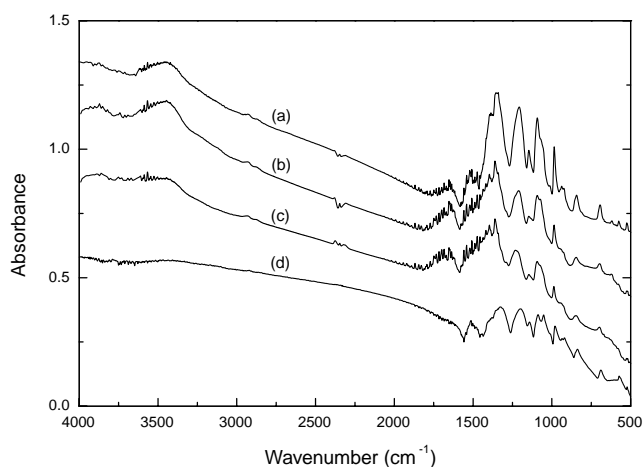


Fig. 4. FT-IR spectra of PEDOT: (a) PK1M1; (b) PK2M1; (c) PK3M1; and (d) PF3M1.

the simultaneous reaction of doping and polymerization of EDOT with KPS.

PEDOTs obtained by $FeCl_3$ and by KPS show similar spectra. However, the former shows no absorption bands in the frequency range between 1600 and 1800 cm^{-1} and the intense spectrum at $1550\text{--}1400\text{ cm}^{-1}$ due to ring stretching of thiophene ring. On the other hand, the latter shows the absorption band at 1640 cm^{-1} and the diminution of spectrum at 1520 cm^{-1} with increasing KPS in solution. The presence of a band at 1640 cm^{-1} indicates the presence of carbonyl group in the product. Also, absorption peaks in the region of $1500\text{--}1550\text{ cm}^{-1}$ disappear with the increase of KPS. These vibrations have been ascribed to the asymmetrical and symmetrical vibrations of the double bond in the EDOT ring. These bands become less sharp as the α -positions of EDOT are joined with other groups and double bonds are destroyed during reaction [20].

The disappearance of absorption peaks in $1500\text{--}1550\text{ cm}^{-1}$ is brought about by the excess oxidant and responsible for the decrease in conductivity [17]; Fig. 5 shows the electrical conductivity of pristine polymers versus molar ratio [KPS]/[EDOT]. It is seen that the electrical conductivity increases with the concentration of KPS up to the ratio of unity and decreases. The PEDOT obtained by a polymerization of EDOT using $FeCl_3$ shows almost no change of electrical conductivity and the high conductivity above the ratio [oxidant]/[EDOT] of 3.

It is obvious from Figs. 3 and 5 that the conductivity of PEDOT polymerized using KPS has the maximum value like the yield versus molar ratio of the reactants. It is related to side reactions of PEDOT such as overoxidation depending on the concentration of KPS.

Fig. 6 shows the yield and conductivity of PEDOT prepared in the aqueous medium as a function of polymerization time. The yield increases steeply with polymerization time whereas the conductivity decreases slowly. The reason of decreasing conductivity seems to be the unfavorable reactions such as overoxidation [17].

4.2. Kinetics

Kinetic studies on EDOT polymerization with KPS

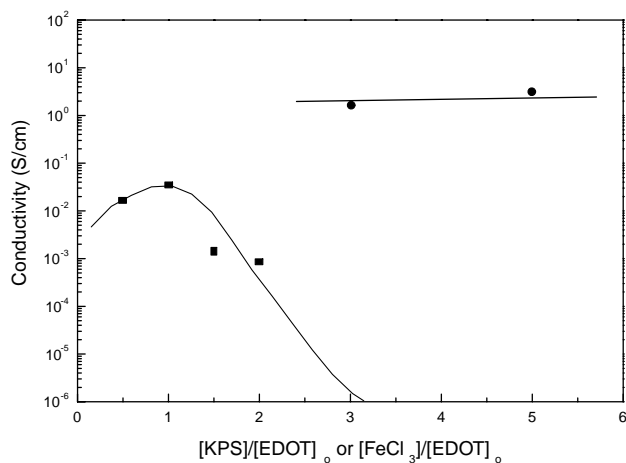


Fig. 5. Electrical conductivity of PEDOT powders as a function of the molar ratio of reactants for $[\text{EDOT}]_0 = 0.0704 \text{ M}$: (■) using KPS; (●) using ferric chloride as an oxidant.

were carried out by calorimetry method. The typical temperature versus time curves are shown in Fig. 7(a). Also, the heat rate of reaction, Q_r , is calculated by using Eq. (6) and plotted in Fig. 7(b). Since Q_r is directly proportional to the reaction rate, the rate of polymerization R_p , can be determined from the initial maximum part of the Q_r profile [19].

According to Fig. 7(b), three intervals have been described from this polymerization process such as the typical type of an emulsion polymerization [25]: R_p increases with time in Interval I. R_p remains constant or increases with time in Interval II. R_p decreases in Interval III because the monomer concentration decreases with time.

It is observed that these reactions have a lower R_p

in a whole process, when compared with the polymerization of aniline [32] and pyrrole [20,21], and can complete over 24 h in some cases. Another remarkable feature is the second maximum in R_p at the end of Interval II. It may be explained by the occlusion polymerization (gel effect) [25].

4.2.1. Effect of KPS concentration

The second maximum becomes lower as the concentration of KPS increases as shown in Fig. 7(b). As the KPS concentration decreases, the Q_r curves become flatter in a long period of reaction time, and the gel effect appears to be more significant.

When the first maximum value of Q_r proportional to the rate of polymerization, is plotted against the initiator concentration on a log–log plot, the linear relationship is obtained as in Fig. 8. The slope is calculated to give the following dependence:

$$R_p \propto [\text{KPS}]^{0.64} \quad (7)$$

If the polymerization of EDOT with KPS describes the common case of radical polymerization, the polymerization rate depends on the square root of the initiator concentration [25]. In Eq. (7), the reaction rate has the exponent of 0.64, which is close to 0.5. However, we cannot explain the reaction by the radical mechanism with the exponent value of initiator concentration because we need other experiments to verify the reaction mechanism.

In recent years attention has been paid to the mechanistic features of the intriguing transformation of benzene and heterocyclic monomers such as thiophene, pyrrole, etc. on exposure to oxidants. Two mechanisms are proposed for polymerization [26–28]: one propagation with the involvement of radical species [27] and another with carbocation

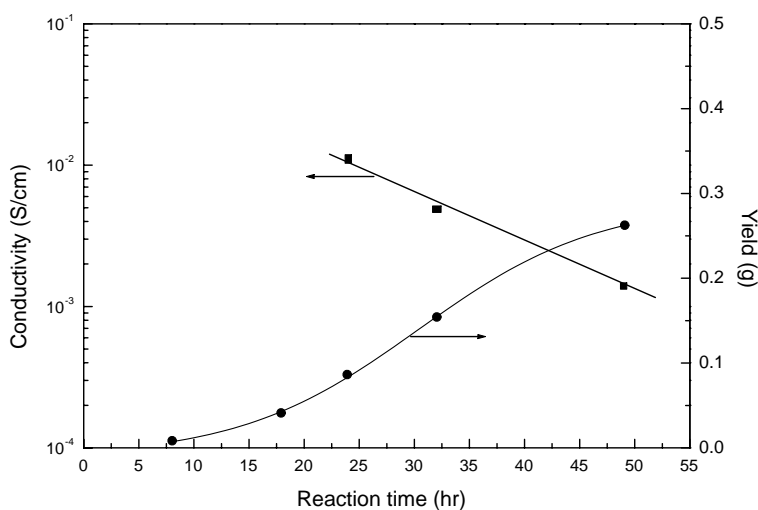


Fig. 6. Electrical conductivity and yield of PEDOT as a function of the reaction time for $[\text{EDOT}]_0$ and $[\text{KPS}] = 0.0352 \text{ M}$: (■) the electrical conductivity; (●) the yield of polymer.

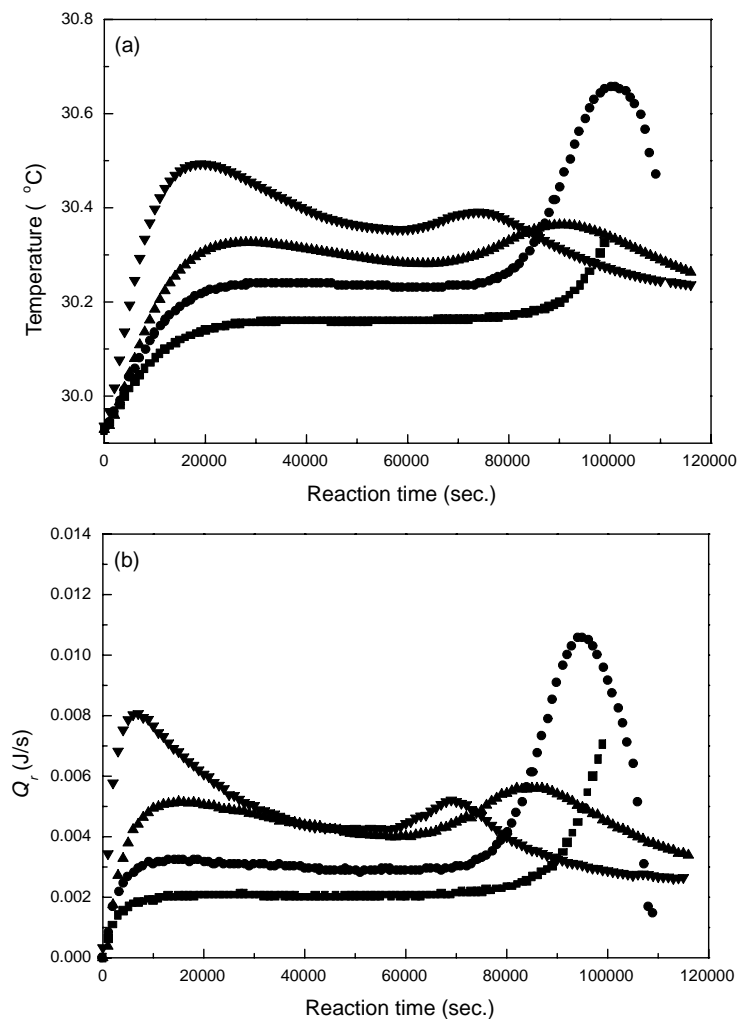


Fig. 7. Typical thermograms of polymerization of EDOT in the Isoperibol calorimeter for different KPS concentrations with $[\text{EDOT}]_0 = 0.0352 \text{ M}$ at $T_j = 30.00^\circ\text{C}$: (a) reaction temperature profiles versus time and (b) heat rate of reaction versus time. (■) PK05M1; (●) PK1M1; (▲) PK2M1; (▼) PK4M1.

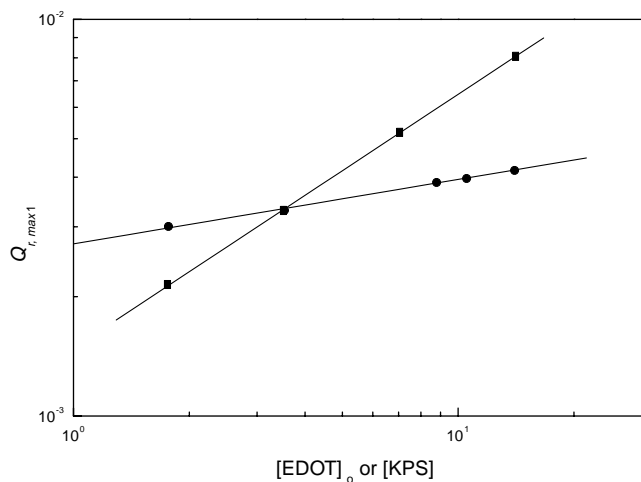
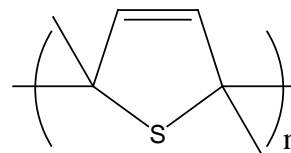


Fig. 8. Influence of reactants concentration on R_p at $T_j = 30.00^\circ\text{C}$: (■) $\log Q_{r,max1}$ versus $\log[\text{KPS}]$ for $[\text{EDOT}]_0 = 0.0352 \text{ M}$; (●) $\log Q_{r,max1}$ versus $\log[\text{EDOT}]_0$ for $[\text{KPS}] = 0.0352 \text{ M}$.

type species [28]. Regardless of the polymerization mechanism, the reaction is initiated by radical cation species [26] and propagates with structures such as dihydro structure III [26–28,33], which are subsequently oxidized to a polymer such as polythiophene [33].



<III>

An earlier investigation showed that thiophene, when it was treated with aluminum chloride or trifluoroacetic acid, was converted to a higher molecular weight material with the structure IV [30].

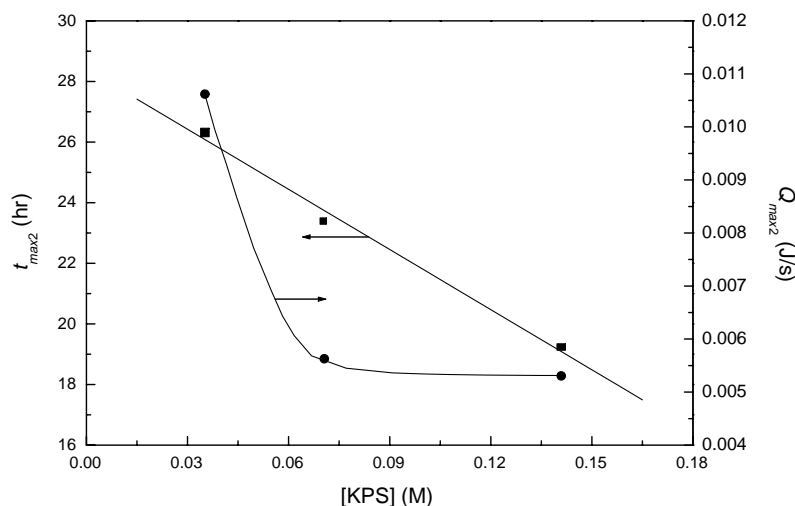
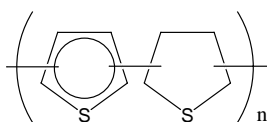
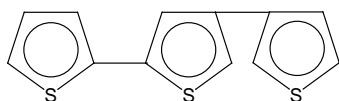


Fig. 9. The variation in reaction time (■) and $Q_{r,max2}$ (●) when the heat rate reached the second maximum using different KPS concentration for $[EDOT]_0 = 0.0352$ M at $T_j = 30.00^\circ\text{C}$.



<IV>

The structure IV suggests that polythiophene polymerized under cationic conditions may have an alternating aromatic and nonaromatic structure. Hartough and co-workers [31] found that phosphoric acid or silica–alumina catalyst converted thiophene to liquid oligomers. They identified the major product as the trimer V.



<V>

Although the above reaction mechanisms represent the reaction of thiophene, it is suggested that EDOT has a similar reaction mechanism. Thus there are some side reactions in which the α -positions of EDOT are joined with other groups and double bonds are destroyed. The side reactions occur more frequently as the concentration of KPS increases. As a result, the absorption peaks in the region of $1500\text{--}1550\text{ cm}^{-1}$ diminish and the amount of oxygen atom due to the overoxidation increases.

As the concentrations of KPS increases, the second maximum of reaction rate occurs faster as shown in Fig. 9. The second maximum means the occlusion polymerization (gel effect) [25]. This gel effect is caused by the termination rate rather than the propagation rate. The growing polymeric

species become coiled up, since they are essentially insoluble or on the verge of insolubility in the solvent. Termination occurs progressively more slowly, while propagation proceeds with a reasonable rate.

4.2.2. Effect of monomer concentration

The rate of polymerization is plotted against the monomer concentration on a log–log plot; the linear relationship is obtained as shown in Fig. 8. The slope in Fig. 8 was calculated to determine the exponent value of EDOT concentration:

$$R_p \propto [EDOT]^{0.16} \quad (8)$$

This small value of exponent may be explained by the degradative addition [25,29]. In the cases of the free-radical polymerization, the retarded polymerization is caused by the low reactivity of propagating species which is produced by the interaction of a propagating chain with some other species (maybe the monomers) [29]. In general, degradative chain transfer to monomers is represented by two possibilities: abstraction of a hydrogen atom from the monomer by the propagating species or addition of propagating species to the monomer (in a manner other than that in the propagation step) to give the ‘inactive’ species.

As the polymerization of thiophene, there is the possibility of alkylation of EDOT and the formation of liquid oligomer. The hydrogenation mechanism for the formation of the structure IV with aluminum chloride has been proposed by Kovacic et al. [30]. However, in the case of EDOT it is unnecessary to consider irregular bonds, such as α – β and β – β bonds (the structure V) because the β -positions of the thiophene ring are blocked by the ethylenedioxy group.

On the other hand, the side reaction may make the reactivity of propagating species low, give rise to the degradative addition and destroy the conjugation structure of

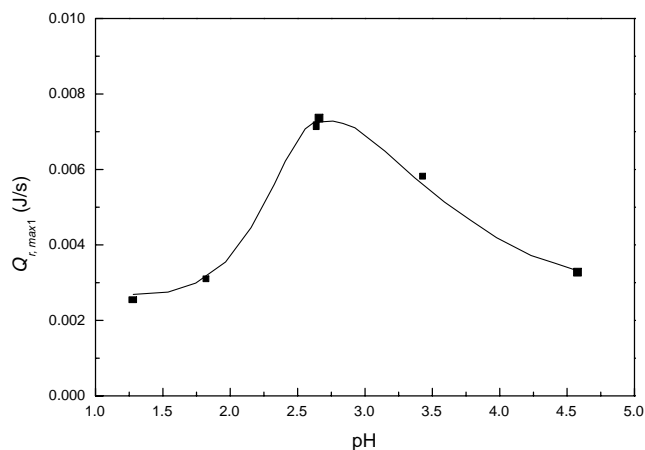


Fig. 10. Heat rate of reaction, $Q_{r,max1}$, as a function of pH at a constant $[EDOT]_0$ and $[KPS]$ of 0.0352 M, $T_j = 30.00^\circ\text{C}$.

EDOT. Thus PEDOT formed with KPS has the lower electrical conductivity than that formed with ferric chloride or other oxidants as shown in Fig. 5 [7,17].

4.2.3. Effect of pH in solution

It is known that the polymerization of benzene or heterocyclic species such as pyrrole and thiophene is sensitive not only to oxidant concentration but also to pH changes [21,31,32]. Fig. 10 shows the results of a set of experiments carried out for solutions having a constant concentration of EDOT (0.0352 M) and the molar ratio of KPS to EDOT equals to 1 at various sulfuric acid concentrations. FT-IR spectra of the polymer formed in acidic media are shown in Fig. 11. Although FT-IR spectra indicate that the polymers have similar structures, the heat rates of polymerization are very different. It can be shown from Fig. 10 that the $Q_{r,max1}$ depends largely on pH. The reaction rate increases as pH decreases from 4.3 to 2.7 and then decreases as pH

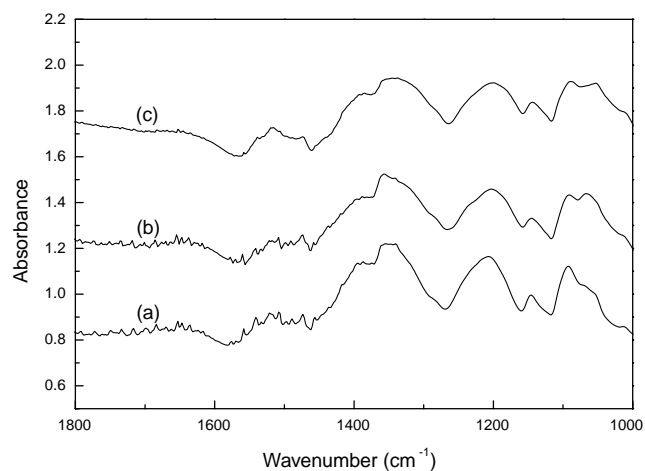


Fig. 11. FT-IR spectra of PEDOT formed for 24 h at a constant $[EDOT]_0$ and $[KPS]$ of 0.0352 M as a function of pH: (a) pH 4.6; (b) pH 2.6 and (c) pH 1.8.

decreases from 2.7. Therefore, these polymerization kinetics are different for different pHs.

Various reagent systems are known to act as initiator for the oxidation of benzene or heterocyclic species [26]: sulfuric acid, hydrogen fluoride, ferric chloride, aluminum chloride, trifluoroacetic acid. Thus when pH is controlled with sulfuric acid the rate elevation can be attributed to the initiating interaction of sulfuric acid with EDOT monomer. However, the alkylation of thiophene ring makes the degradative addition more active in strong acidic medium, as has been suggested by Hartough and co-workers [31] and the reaction rate decreases.

5. Conclusions

3,4-Ethylenedioxythiophene with potassium persulfate in aqueous solution was polymerized and doped in one step. PEDOT had an electrical conductivity. The yield and conductivity of PEDOT increased and reached the maximum at the ratio $[KPS]/[EDOT]$ of unity. Then it decreased as the concentration of KPS increased. As fixed concentrations of EDOT and KPS, the conductivity decreased and the yield increased with the reaction time. It would indicate that a side reaction occurred more actively as the reaction time increased.

The thermograms of polymerization of EDOT showed that the reaction rate was heavily dependent on the reaction condition. The first maximum value in the heat rate of reaction (rate of polymerization) curve was dependent on the potassium persulfate concentration and of the acid concentration whereas it was almost independent of the monomer concentration. As the concentration of KPS increased, the first peak appeared earlier with higher peak height whereas the second peak appeared with lower peak height.

The thermograms from 3,4-ethylenedioxythiophene polymerization at various acid concentrations were dramatically different. The reaction rate was elevated by the initiating action of sulfuric acid and dropped by the degradative addition in strong acidic medium. Work on the effect of sulfuric acid is now in the progress in our laboratory and will be reported in the near future.

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