The length of reaction time on the synthesis of poly (3,4-ethylenedioxythiophene)

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Abstract. Poly(3,4-ethylene dioxythiophene) (PEDOT) has been synthesised via the oxidative polymerisation method of 3,4-ethylenedioxythiophene (EDOT) monomer using Na2S2O8 and Fe3(SO4)3 as oxidising agents. The synthesis was carried out at various times of reaction, i.e for 6, 12, and 24 hours. The success of PEDOT synthesis was proven by FTIR spectra which indicated by the loss of the C-H group presented in the 890 cm⁻¹ absorption area from EDOT monomer. The morphology of PEDOT particles was observed by Scanning Electron Microscopy (SEM). The results showed that the differences in the synthesis time of 6, 12, and 24 hours affected the diameter of PEDOT particles. The size morphology of those 6, 12, and 24 hours synthetically PEDOT particles were 38.64 ± 18.21 nm, 55.91 ± 15.31 nm, and 66.62 ± 18.92, respectively. The largest diameter product of PEDOT in this study was then doped with carrageenan to synthesis PEDOT/Carr dispersions via the post-polymerisation method. This study concluded that the size of PEDOT particles is significant with increasing time of reaction, and the product of PEDOT/Carr dispersions is promising as a green polymer.

1. Introduction
The conductive electrolyte polymers are important and have been discussed as functional materials for many device applications such as electrodes in the battery due to their high electrical property, electrochemical reversibility, greater apparent capacitance, and faster doping and dedoping rates during the charge/discharge process.[1] One of the most conducting green polymer and valuable for device application for electronic material is poly(3,4-ethylene dioxythiophene) (PEDOT). This polymer is very difficult to dissolve in many solvents. Polystyrene sulfonate (PSS) is usually used to doped PEDOT and make it dispersable in aqueous media.[2, 3] PEDOT/PSS has excellent properties such as electricity, flexibility, stability, and reproducible.[2, 4] Various applications of this polymer have been discussed such as for battery[5], sensor[6, 7], organic bioelectronic[8, 9], solar cell[10], and some other applications. In term of preparation on the precision of optimal and reproducible conductivity of the film can be adjusted by spin coating the solution.[11] Recently some investigation has been done using another doping agent to replace PSS using carrageenan.[12, 13] The reason is the availability of dopant PSS and carrageenan on its –SO3H functional group which is responsible for their stability on dispersion as the counter ion of the PEDOT and make it dispersed in an aqueous medium.[14]

PEDOT can be obtained from the polymerisation of the monomer 3,4-ethylene dioxythiophene (EDOT). There are some routes to synthesis PEDOT pristine. In general, PEDOT can be obtained through oxidative, electrochemical, and transition metal-mediated coupling polymerisations of EDOT[15]. EDOT structure in Figure 1 shows the position of oxygen in the thiophene ring which will minimise the polymerisation on these β-carbon sites. These two oxygen atoms increase the density of the electron in the ring.[16] The most familiar method is oxidative polymerisation using
some oxidants such as Na$_2$S$_2$O$_8$ and Fe$_2$(SO$_4$)$_3$[3, 13, 17] or using FeCl$_3$[15]. The black materials of PEDOT are easy to separate from the mixture as they are insoluble in many solvents. The effect of the temperature and time of reaction affected the high conversion on the synthesis of PEDOT via oxidative polymerisation.[18] Another investigation found that PEDOT/PSS properties were affected by the time of reactions.[3] But, the size of pure PEDOT particles still needs to be studied for future device applications. The aim of synthesising PEDOT with different lengths of reaction is to adjust the length of the PEDOT chain.

![Figure 1. Structure of (A) EDOT monomer, and (B) PEDOT.[3, 17]](image)

2. Research method
2.1 Materials and reagents
EDOT (3,4-Ethylene dioxythiophene), oxidising agents Na$_2$S$_2$O$_8$ and Fe$_2$(SO$_4$)$_3$ were used as received from Sigma-Aldrich Australia. The acidometer used is from HANNA Instruments. All solvents and chemicals were ordered as of analytical grade and used as received.

2.2 Preparation of PEDOT via oxidative polymerisation
PEDOT pristine was synthesised using the modified procedure as previously described on the synthesis of PEDOT/PSS aqueous dispersion,[3, 12] without additional PSS as the dopant. The schematic route of synthesis PEDOT is shown in Figure 2. In brief, 2 g of EDOT monomers and 180 mL RO water were mixed into a triangular flask. The solution was stirred for 15 minutes at room temperature. The amount of 4 g Na$_2$S$_2$O$_8$ was then added to the solution continued reaction by adding RO water up to 200 mL. The solution was stirred for 10 minutes, and then 0.02 g Fe$_2$(SO$_4$)$_3$ was mixed to the solution and the reaction was stirred for 6 h. A Similar procedure was applied and stirred constantly for 12 h, and 24 h of reactions. Purification of the black PEDOT dispersions was done well-using water and methanol and was continued drying at 50 °C for 24 h.

![Figure 2. Schematic route of synthesis PEDOT via oxidative polymerisation.](image)

2.3 Characterisations
The product PEDOT composite was characterised by its physio-chemical properties. Fourier transform infrared (FTIR) was used to analyse the structure, while Scanning Electron Microscopy (SEM) was used to analyse the effect of time on the particle size. FTIR spectra were recorded as neat samples on a Perkin Elmer Spectra Two ATR FTIR.

3. Results and discussion
3.1 Structure characterisation of PEDOT
The successful synthesis of PEDOT composites can be identified from the dark blue solution. Three different PEDOT preparations showed a difference in intensity of darkness. The shorter
The time of reaction was lighter than others. The success of forming PEDOT material was analysed using FTIR spectra to compare the monomer and the pure product. Figure 3 shows the FTIR spectra of the EDOT monomer and the PEDOT. The FTIR spectrum of the monomer is clear and sharp. The difficulty of encountering to obtain a clear FTIR spectrum of PEDOT is due to material properties. Some peaks can be noticed and identified as the representative of the functional groups of PEDOT. The band of the C-H bending of EDOT at 895 cm$^{-1}$ disappeared in PEDOT. This demonstrates successful formation chains with C$_2$-C$_2$-coupling on PEDOT. The bands at 1475 and 1350 cm$^{-1}$ appear as the stretching modes of C=C and C-C structures in the thiophene ring, whereas the bands at 1205 and 1058 cm$^{-1}$ appear as the stretching mode of ethylenedioxy or C-O-C group, respectively.[12, 19, 20] The stretching mode of -C-S bond in the thiophene ring was monitored as a peak at 857 cm$^{-1}$.[21-23].

![FTIR spectra of EDOT monomer and PEDOT.](image)

**Figure 3.** The FTIR spectra of EDOT monomer and PEDOT.

3.2 **Particles size of PEDOT composites**

Surface morphology images of PEDOT composites taken using SEM show representatively the effect of a long time of reaction. Figure 4 shows the SEM morphology images of PEDOT composites synthesised 6 h (A), 12 h (B), and 24 h reactions (C). These three images exhibit the dissimilarity of their surfaces at 30000 times magnification. The surface of PEDOT 6 h (A) shows bigger lumps than PEDOT 12 h (B) and PEDOT 24 h (C). Based on some representative particles of those three PEDOT composites it can be measured their particle size of 38.64 ± 18.21 nm, 55.91 ± 15.31 nm, and 66.62 ± 18.92 nm for PEDOT 6 h, PEDOT 12 h, and PEDOT 24 h, respectively. The longer time of reactions resulted in a bigger size of PEDOT particles and forms more crystalline. This effect is in line with the previous study that the reaction time increases the conversion of EDOT polymerisation.[18] The reaction time was also correlated with the convenience electronic properties and morphology of PEDOT/PSS films.[3]

![SEM morphology images of PEDOT composites prepared at different lengths of reactions.](image)

**Figure 4.** The representative morphology images of PEDOT composites prepared at different lengths of reactions: (A) 6 h, (B) 12 h, and (C) 24 h. Images were taken using SEM at 30000 magnification.
4. Conclusion

PEDOT composites were successful in being prepared from EDOT monomer via oxidative polymerisation using Na$_2$SO$_3$ and Fe$_3$(SO$_4$)$_3$ as the oxidising agents as evident from the FTIR spectroscopic analyses. A physical property of the insoluble black polymer composites can be performed using SEM analysis. Different length time of reaction affects the size morphology of PEDOT particles. The smaller size of the particles, obtained from the shorter time of reaction, tend to form lumps, while the bigger size of PEDOT particles forms more crystalline.

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