Synthesis and Characteristics of PEDOT:PSS and PEDOT:Carrageenan

Subjects: Polymer Science

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Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) has been mostly used as a counter electrode to give a high performance of dye-sensitized solar cell (DSSC). PEDOT doped by carrageenan, namely PEDOT:Carrageenan, was introduced as a new material to be applied on DSSC as an electrolyte. PEDOT:Carrageenan has a similar synthesis process as PEDOT:PSS, owing to their similar ester sulphate (-SO_3H) groups in both PSS and carrageenan.

counter electrode DSSC electrolyte PEDOT-PSS PEDOT-Carrageenan

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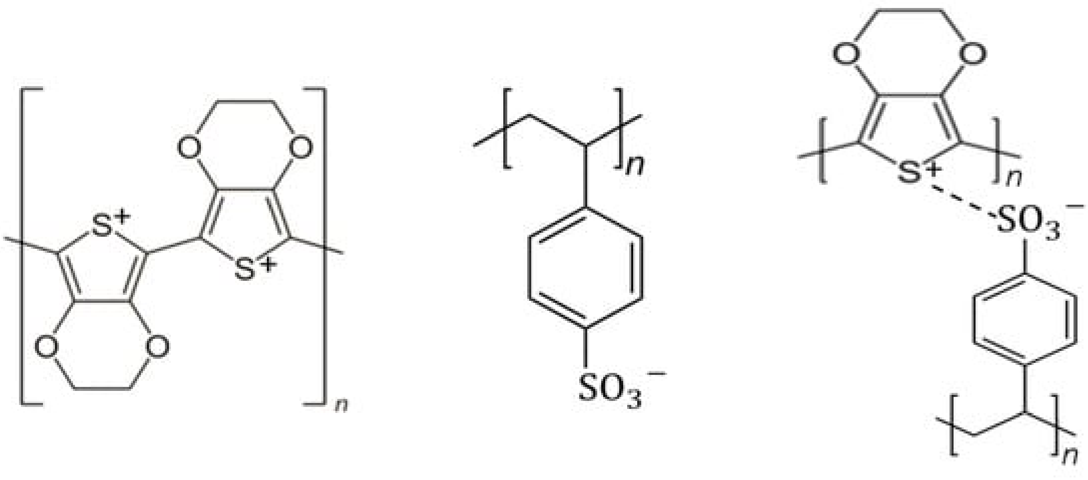
1. Synthesis and Characteristics of PEDOT:PSS

In 1988, PEDOT with cation of EDOT monomer (C2H4O2C4H2S)+ was first synthesized and commercialized by scientists in a German research laboratory [1]. PEDOT has succeeded in becoming one of the electronically conducting polymers (ECPs) that have immense potential applications. However, PEDOT was difficult to be synthesized by the standard chemo/electro-polymerization due to its insolubility and infusibility in many solvents. Therefore, PEDOT needs some materials as a dopant, which is a solvent-dispersible material, while maintaining the properties of PEDOT.

PSS with a chemical formula of C8H7SO3−, is a water-dispersible polyelectrolyte and a polymer surfactant that is able to be used as a dopant for PEDOT due to its -SO_3H functional group as the hydrophilic part. PEDOT and PSS formed a complex material as PEDOT:PSS, which is a poly–ion complex by electrostatic interaction between PEDOT cation and PSS anion. It consists of both positive charges conjugated PEDOT and negative charge saturated PSS. The chemical structure of PEDOT, PSS and PEDOT:PSS is shown in **Figure 1**, and the structure identification was completed with the FTIR analysis in **Table 1**. In PEDOT:PSS, PSS has two jobs: (i) it works as a counter ion for doped-PEDOT stability, and (ii) it supplies a matrix to form an aqueous dispersion [2].



(a) (b) (c)

Figure 1. The chemical structure of (**a**) PEDOT, (**b**) PSS and (**c**) PEDOT:PSS.

Table 1. FTIR analysis of PEDOT:PSS [3].

Wavenumber (cm^{-1})	Types of Atom Bonding	Identifications
691	C–S	Stretching of the thiophene ring in PEDOT
840		
936		
983	S–O	Stretching SO42− from oxide and the S-phenyl bond in PSS
1145		Stretching in PSS
1055	S=O	Stretching antisymmetric SO42− from oxidant
1198		Stretching symmetric in PSS
1092	C–O	Stretching in PEDOT
1144		
1340	C–C	Stretching in the thiophene rings of PEDOT
1518	C=C	Stretching in the thiophene rings of PEDOT
1640		Stretching in the aromatic rings in PSS
2921	C–H	Stretching of PEDOT and PSS
3415	O–H	Stretching in PSS

PEDOT:PSS was also first synthesized by scientists in German research laboratories. PEDOT:PSS is the most successful commercially available in the form of an aqueous dispersion with high water-dispersibility, excellent miscibility, good transparency, high electrical conductivity, excellent flexibility and satisfactory stretch-ability. PEDOT:PSS is typically synthesized via oxidative polymerization in two simple ways: in-situ and post-polymerization [4][5]. The synthesis process is shown in **Figure 2**. In-situ polymerization has several steps to do as follows: First, monomer powder EDOT was added to an aqueous of PSS solution. Then, the mixtures were stirred vigorously in a water bath at room temperature under nitrogen. The oxidant agents (e.g., sodium persulfate ($N_2S_2O_8$) and iron trichloride ($FeCl_3$) or iron tri-sulfate ($Fe_2(SO_4)_3$)) were immediately added to the mixture solution to produce a complex and stirred again at room temperature for 24 h. The precipitate was collected from the complex solution by centrifugation at a certain rpm and then rinsed with acetone and methanol at a certain ratio. The final result can be dispersed in water to be aqueous in a dark-blue solution or be dried in an oven at 60 °C for 24 h to get a black-powder. Post-polymerization includes the steps as follows: first, monomer powder EDOT was dispersed in water. The oxidant agents (e.g., $N_2S_2O_8$ and $FeCl_3$ or $Fe_2(SO_4)_3$) were immediately added to EDOT solution and stirred at room temperature for 24 h. Then, the mixture was purified by mixing water and ethanol at a certain ratio. The PEDOT powder as a result was added to the PSS solution. The PEDOT:PSS solution was stirred at room temperature for 24 h. The final result was the PEDOT:PSS aqueous in a dark-blue solution.

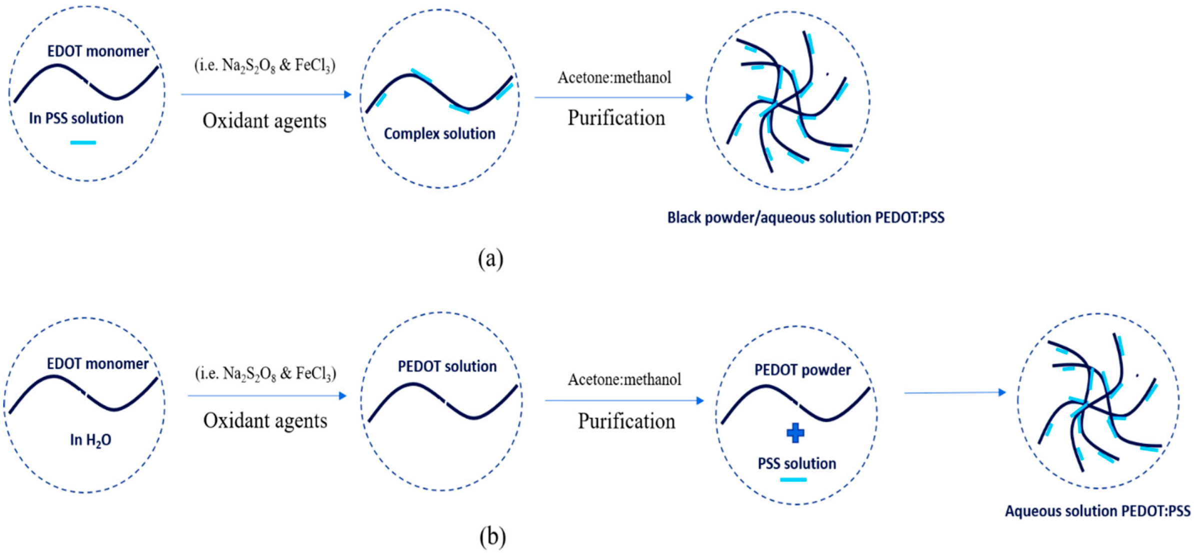


Figure 2. The synthesis process of PEDOT:PSS with (**a**) in-situ and (**b**) post-polymerization.

The properties of PEDOT:PSS are crucial things to consider in the synthesis process, especially for electrical conductivity. There are some factors that affect the electrical conductivity of PEDOT:PSS as shown in **Figure 3**. In the synthesis process, some parameters should be controlled, such as pH solution, temperature, humidity and polar solvent as additives or blending components. PSS has hygroscopic and corrosive properties due to its strong acid (pH < 2), which lowers the lifetime and performance of the application devices. The neutralizing of PSS can be attained by various alkaline, but this could change the structural and electrical conductivity resulting in PEDOT:PSS [6].

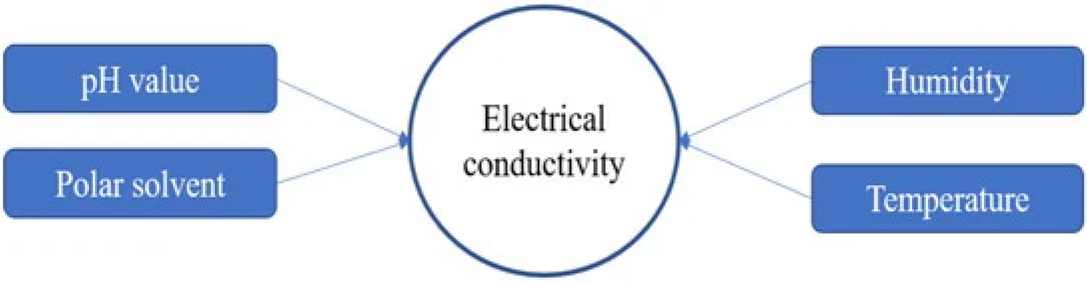


Figure 3. Factors affecting electrical conductivity.

Several studies showed that the higher the pH of the solution resulting from the synthesis process, for example, due to adding alkaline materials (e.g., sodium hydroxide (NaOH)), the more the electrical conductivity decreased and vice versa. If the resulting solution was in a lower pH, by adding acid materials (e.g., hydrochloride acid (HCl)) during the synthesis process, the electrical conductivity increased [1][6]. Mochizuki et al. have investigated the effect of adding NaOH concentration from 0.8 to 1.2 M with increasing pH of 2.5 to 11.7 to cause decreasing electrical conductivity of PEDOT:PSS from 10^{-2} to 10^{-4} $S{\cdot}cm^{-1}$ [6]. This is due to the removal of the insulting PSS from the surface of the colloidal particles and to the crystallization of the PEDOT molecule, which improves both intraparticle and interparticle transfer to charge carrier. The high electrical conductivity affected the higher carrier mobility and the structure of PEDOT:PSS. The lower pH and also adding polar solvents partially change PEDOT molecules with an amorphous form to a crystalline state by, i.e., ethylene glycol (EG), dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), etc. that were added during the synthesis process.

Besides pH and polar solvent, the humidity and temperature affected the electrical conductivity of PEDOT:PSS in thin layer form. The PEDOT:PSS can be applied in many application devices if it was made in thin layer form. Several methods, such as spin-coating, screen-printing, electrospinning, etc., are used as a technique for thin layer deposition. The electrical conductivity of PEDOT:PSS layer was changed in water. At first, the electrical conductivity initially increased significantly, but then it gradually decreased when its layer was slowly damaged, depending on the longer immersed time of PEDOT:PSS layer in water. Otherwise, when the temperature went down, the electrical conductivity of PEDOT:PSS layer started to decrease [1][2].

2. Synthesis and Characteristics of PEDOT:Carrageenan

Carrageenan comes from various forms of red algae (*Rhodophyta*) and is used as a general name for a poly-saccharides (sulphated galactans) family. Chemically, carrageenan is a linear polymer, which is arranged of alternating *disaccharide* repeating units of 3-linked β-D-*galactopyranose* (G-units) and 4-linked α-D-*galactopyranose* (D-Units) or 4-linked 3,6-*anhydrogalactose* (DA-Units) [7][8]. In 1862, the British pharmacist Stanford found the first called *phycocolloid carrageenin* by extracting it from Irish moss (*Chandrus crispus*) [8]. The name was later changed to *carrageenan* so as to fulfill with the “-an” suffix the names of polysaccharides that were accepted in the industry dates from the 1940s [9].

Carrageenan has three commercially important types according to the position and number of sulphate groups: *kappa (κ)-*, *iota (ι)-* and *lambda (λ)-carrageenan*. The *κ-carrageenan* with the chemical formula of C12H17O9SO3− is produced from the seaweed *Kappaphycus alvarezii*, known as *Euchema cottonii* (or simply *cottonii*). The *ι-carrageenan* with the chemical formula of C12H16O9(SO3−)2 is largely produced from *Euchema denticulum*, known as *Euchemaspinosum* (or simply *spinosum* species). The *λ-carrageenan* with the chemical formula of C12H17O10(SO3−)3 is extracted from the species of *Gigantana* and *Chondrus ginera*. There are also several other *carrageenan* repeating units, e.g., *mu (μ)-*, *nu (υ)-*, *xi(ξ)-*, *theta (θ)- and beta (β)-carrageenans* [9][10][11]. **Figure 4** shows all types of *carrageenan.* Based on IUPAC and the letter codes of carrageenans, which are shown in **Table 2**, their corresponding names of *κ-*, *ι-* and *λ-carrageenan* are *carrageenase 2,40-disulphate* (G4S-DA2S), *carrageenase 40-sulphate* (G4S-DA) and *carrageenan 2,6,20-trisulphate* (G2S-D2S,6S), respectively [9][10].

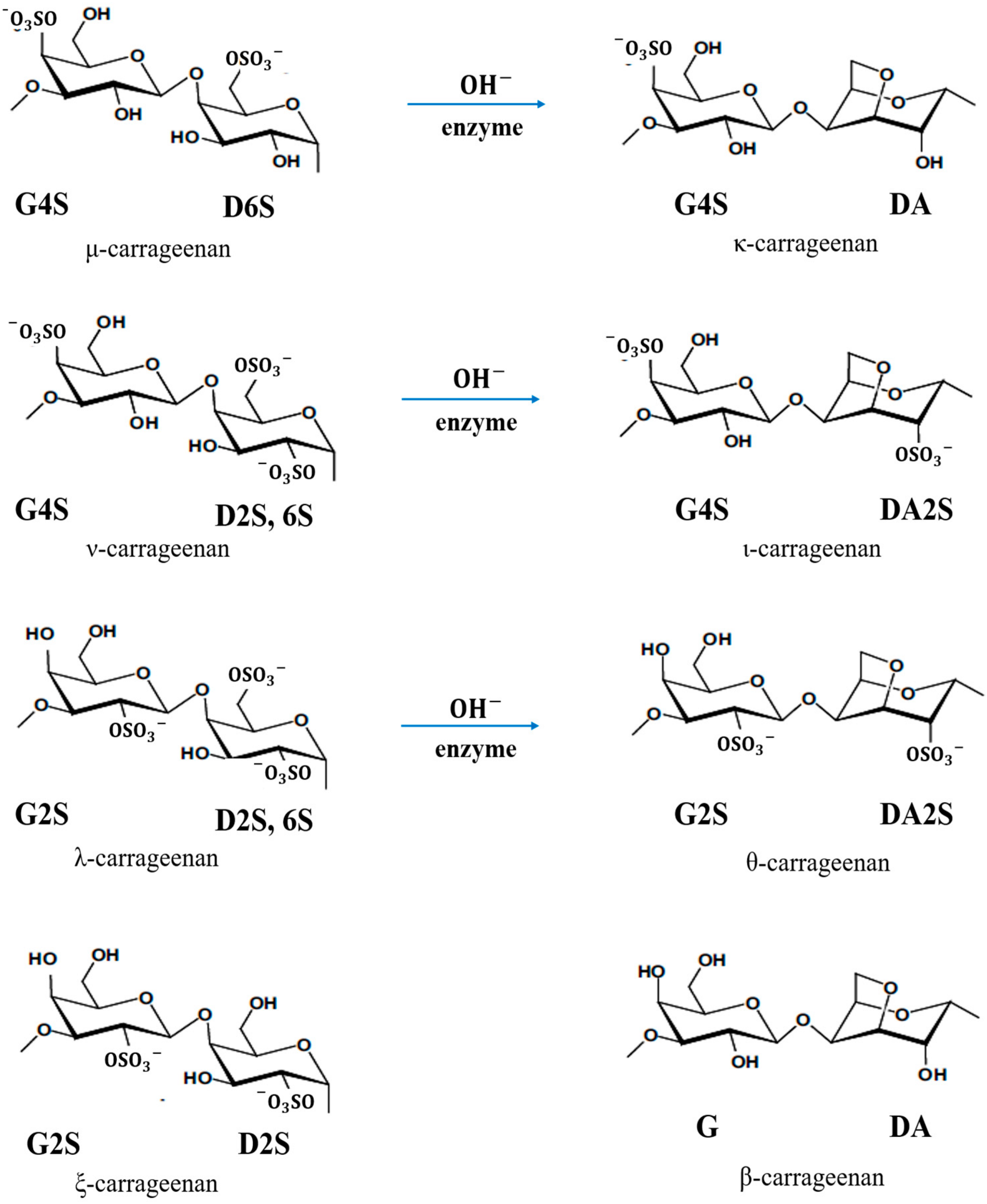


Figure 4. Chemical structure of all types of *carrageenan*.

Table 2. The letter code for the different sugar units found in *carrageenan* [9][10].

Letter Code	Carrageenan	IUPAC Name
D	Not Found	4-Linked α-D-galactopyranose
D2S	ξ	4-Linked α-D-galactopyranose 2-sulphate

Letter Code	Carrageenan	IUPAC Name
D2S, 6S	*λ, υ*	4-Linked α-D-galactopyranose 2,6-disulphate
D6S	*μ*	4-Linked α-D-galactopyranose 6-sulphate
DA	*κ, β*	4-Linked 3,6-anhydro-α-D-galactopyranose
DA2S	*ι, θ*	4-Linked 3,6-anhydro-α-D-galactopyranose 2-sulphate
G	*β*	3-Linked β-D-galactopyranose
G2S	*λ, θ*	3-Linked β-D-galactopyranose 2-sulphate
G4S	*κ, ι, μ, υ*	3-Linked β-D-galactopyranose 4-sulphate
S	*κ, ι, λ, μ, υ, θ, ξ*	Sulphate ester (O-SO3−)

Carrageenan is one of the natural polymers, with ester sulphate (-SO_3H) groups, that has the capability to produce thermo-reversible gels or high viscous solution. In a number of foods and pharmaceutical and cosmetic products, it is commonly used as gellifier, stabilizer and emulsifying agent [12]. Carrageenan has the similarity of ester sulphate (-SO_3H) groups to PSS. PSS has been used as a dopant in complex material PEDOT:PSS; then, carrageenan also has the potential to be used as dopant to form a complex material PEDOT:Carrageenan. **Figure 5** shows the complete chemical structure of PEDOT:Carrageenan, and the structure identification was completed with FTIR analysis in **Table 3**.

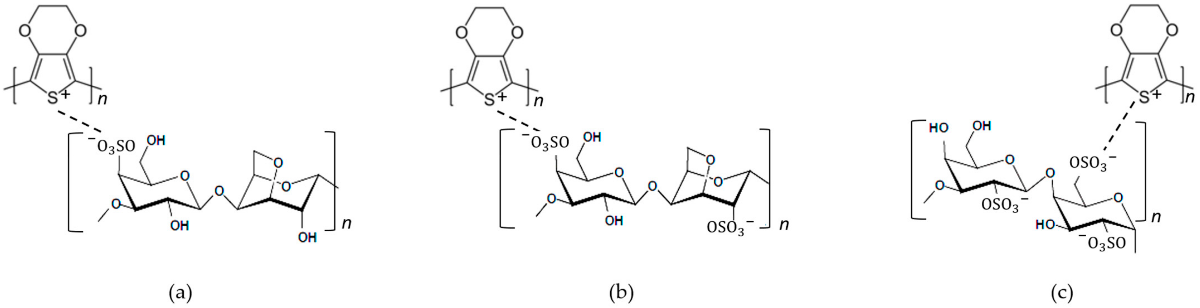


Figure 5. The chemical structure of (**a**) PEDOT:κ-Carrageenan, (**b**) PEDOT:ι-Carrageenan and (**c**) PEDOT:λ-Carrageenan.

Table 3. FTIR analysis of PEDOT:Carrageenan [9][13][14].

Wavenumber (cm^{-1})	Bond(s)/Group(s)	Letter Code	Type of Carrageenan
1495	C = C of thiophene ring	-	-
1371	C–C of thiophene ring	-	-
1198, 1060	C–O–C of stretching mode of the ethylene groups	-	-

Wavenumber (cm^{-1})	Bond(s)/Group(s)	Letter Code	Type of Carrageenan
892	C–H of PEDOT chains	-	-
1210–1260	S = O of sulphate ester	S	κ, ι, λ, μ, υ, θ, ξ
970–975	Galactose	G/D	κ, ι, μ, υ, θ, β
928–933, 1070 (shoulder)	C–O of 3,6-anhydro-D-galactose	DA	κ, ι, θ, β
890–900	Unsulphated β-D-galactose	G/D	β
840–850	C–O–SO_3 of D-galactose-4-sulphate	G4S	κ, ι, μ, υ
825–830	C–O–SO_3 of D-galactose-4-sulphate	G/D2S	λ, υ, θ, ξ
820, 825 (shoulder)	C–O–SO_3 of D-galactose-2,6-sulphate	D2S,6S	λ, υ
810–820, 867 (shoulder)	C–O–SO_3 of D-galactose-6-sulphate	G/D6S	μ
800–805, 905 (shoulder)	C–O–SO_3 of 3,6-anhydro-D-galactose-2-sulphate	DA2S	ι, θ

[13][14] PSS. The oxidative polymerization was done in two simple ways: in-situ and post-polymerization. The procedures of both two ways as similar as PEDOT:PSS, but the carrageenan powder was first diluted in water under stirring at 70 °C. Then, monomer EDOT, oxidant agents and surfactant were mixed together until the PEDOT:Carrageenan solution was obtained in homogenous solution. The process synthesis of PEDOT:Carrageenan is shown in **Figure 6**.

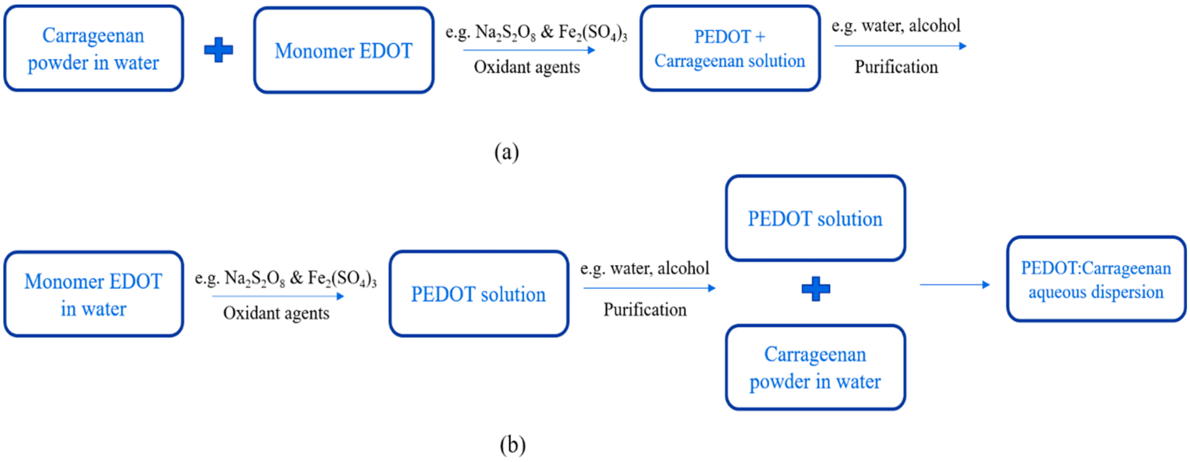


Figure 6. Synthesis process of PEDOT:Carrageenan with (**a**) in-situ and (**b**) post-polymerization.

In summary, PEDOT:PSS and PEDOT:Carrageenan has similar synthesis process because both PSS and Carrageenan has ester sulphate (-SO_3H) functional group that cause them as a dopant for PEDOT. However, PSS and Carrageenan have different polymer structure that affects the molecular weight of both PEDOT:PSS and

PEDOT:Carrageenan. By analyzing the chemical structure of their monomer as shown in **Figure 1** and **Figure 5**, the molecular weight of both PEDOT:PSS and PEDOT:Carrageenan could be calculated by adding up the molecular weight of their monomer. It depends on their chain numbers (n). PEDOT:PSS has EDOT monomer and styrene sulfonate (SS) monomer with a molecular weight of 142 and 183 g/mol, respectively. Three types of PEDOT:Carrageenan, namely PEDOT:κ-Carrageenan, PEDOT:ι-Carrageenan and PEDOT:λ-Carrageenan, consist of EDOT monomer and carrageenan monomer (κ-, ι- and λ-carrageenan). Molecular weight of κ-, ι- and λ-carrageenan monomer is 385, 464 and 561 g/mol, respectively.

Table 4 shows the difference in the electrical and optical properties of PEDOT:PSS and PEDOT:Carrageenan. PEDOT:PSS has excellent conductivity of >4000 $S·cm^{-1}$ with a low sheet resistance of <100 $Ω·sq^{-1}$ and high transparency of 80–95% [1]. With high conductivity, PEDOT:PSS has ionic and electronic mobility of 2.2×10^{-3} and 1.3 $cm^2v^{-1}s^{-1}$, respectively [15], with carrier density of 4×10^{20} cm^{-3} at approximately +0.5 Volt [16]. However, PEDOT:Carrageenan has conductivity of 16.23 $S·cm^{-1}$, and it was measured for PEDOT:κ-Carrageenan [17]. The value of sheet resistance, transparency, ionic and electron mobility and carrier density of PEDOT:Carrageenan has not been available since the research of PEDOT:Carrageenan is still very limited, especially in analyzing the electrical and optical properties that are the basis for the application of a material in electronic devices.

Table 4. Electrical and optical properties of PEDOT:PSS and PEDOT:Carrageenan.

Properties	PEDOT:PSS	PEDOT:Carrageenan
Conductivity ($S·cm^{-1}$)	>4000 [1]	16.23 [17]
Sheet resistance ($Ω·sq^{-1}$)	<100 [1]	N/A
Transparency (%)	80–95 [1]	N/A
Ionic mobility ($cm^2v^{-1}s^{-1}$)	2.2×10^{-3} [15]	N/A
Electronic mobility ($cm^2v^{-1}s^{-1}$)	1.3 [15]	N/A
Carrier density (cm^{-3})	4×10^{20} [16]	N/A

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