Research Article

Synthesis and Physicochemical Characterization of Chitin Derivatives

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Firstly, chitin derivatives were synthesized. For this purpose, chitin was modified via ring-opening reaction with cyclic anhydrides in lithium chloride/*N,N*-dimethylacetamide. Then, chitin derivatives synthesized were characterized by FTIR, ¹H NMR, ¹³C NMR, and U-Vis spectroscopies and scanning electron microscopy. Thermogravimetric analysis was performed to investigate the thermal stability of chitin derivatives. Thermogravimetric analysis results showed that chitin modified with trimellitic anhydride is thermally more stable than chitin modified with phthalic anhydride. In addition, the electrical conductivity of chitin modified with phthalic anhydride and trimellitic anhydride was also measured. Electrical conductivity measurement results showed that the electrical conductivity of chitin modified with trimellitic anhydride ($1.2 \times 10^{-4} \text{ S cm}^{-1}$) is higher than that of chitin modified with phthalic anhydride ($9.2 \times 10^{-5} \text{ S cm}^{-1}$).

1. Introduction

Polymers have been considered as good electrical insulators for years, and they have widely been used as inactive packaging and insulating material. But this narrow perspective is rapidly changing as a new class of polymer known as intrinsically conducting polymers (CPs) or electroactive polymers (EAPs) is being discovered. Conjugated polymers are plastic semiconductors. They have band gaps that can be tuned by alternating the chemical nature of either polymer backbone or side groups present in chain. Conducting polymers contain conjugated π -electron system, responsible for their unusual electronic properties such as electrical conductivity, low-energy optical transitions, low ionization potential, and high electron affinity [1, 2]. CPs, such as polyacetylene [3, 4], polyaniline [5–13], polypyrrole [10, 14], polythiophene [10, 15], poly(*p*-phenylene) [16], and poly(*p*-phenylene vinylene) [17], have received a great deal of attention and constitute a class of materials that possess the properties of both organic polymers and inorganic conductors or semiconductors.

The preparation, characterization, and application of electrochemically active and electronically conducting polymeric systems are still in the foreground of research activity in electrochemistry. There are at least two major reasons for this intense interest. The first is the intellectual curiosity of scientists, which focuses on understanding the behavior of these systems, in particular on the mechanism of charge transfer and on charge transport processes that occur during the redox reactions of conducting polymers. The second is the wide range of promising applications of these compounds in the fields of energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, electrochromic displays, microsystem technologies, electronic devices, microwave screening, corrosion protection, and so forth. Many excellent monographs reviewing the knowledge accumulated regarding the development of conducting polymers, polymer film electrodes, and their applications have been published [18]. Studies for preparing alternative CPs or semiconductors from natural and/or low-cost materials have been rapidly continuing.

TABLE 1: Some important properties of chitin (Sigma C 9213).

Molecular formula	(C ₈ H ₁₃ NO ₅) _n [19]
Formula weight	~400.000 g mol ⁻¹ [19]
BET surface area	2.91 m ² g ⁻¹ [19]
Pore volume	0.0025 cm ³ g ⁻¹ [19]
Density	~0.45 g mL ⁻¹ [19]
pK _a	6.1 [19]
Appearance	Light yellow flakes
Solubility	Soluble in lithium chloride/N,N-dimethylacetamide, lithium chloride/N-methyl-2-pyrrolidone, trichloroacetic acid/formic acid, trichloroacetic acid/acetic acid, and dichloroacetic acid [20]

Chitin is a linear polymer composed of 2-acetamido-2-deoxy-D-glucopyranose (N-acetyl-D-glucosamine, GlcNAc) units linked by β -(1 $\rightarrow$ 4) linkage. It is distributed widely in nature as the skeletal material of crustaceans and insects and as a component of cell walls of bacteria and fungi. Chitin occurs naturally in three polymeric forms known as α -, β -, and γ -chitin [20]. α -chitin is arranged in an anti-parallel configuration while β -chitin is organized in a parallel configuration. However, γ -chitin has a parallel and anti-parallel structure, which is a combination of α -chitin and β -chitin [21]. Molecular structure and hydrogen bonding in α -chitin and β -chitin are shown in a paper [22]. α -Chitin is the most abundant form found in nature. Both α -chitin and β -chitin are crystalline [23]. Chitin has strong inter- and intramolecular hydrogen bonds between the polymer chains and is water insoluble due to its rigid crystalline structure [24]. It is the second most abundant organic compound, with 10¹¹ tons produced annually, after cellulose on earth [25]. In recent years important studies with respect to the electrical conductivity of some chitin derivatives are done [26–29].

Phthalic anhydride is an important industrial chemical, especially for the large-scale production of plasticizers for plastics. It is presently obtained by the catalytic oxidation of *ortho*-xylene and naphthalene. Trimellitic anhydride is mainly used for producing polyester resin, polyimide resin, water-soluble alkyd resin, water-soluble polyurethane resin, plasticizer, water-soluble amino-alkyd resin, curing agent for epoxy resin, aeroengine oil, electric capacitor maceration oil, and so forth. The aim of this study was to synthesize chitin derivatives, to characterize physicochemically the derivatives to be synthesized and to compare them from the point of view of stability and conductivity.

2. Experimental

2.1. Materials. Chitin (Sigma C 9213, Germany), phthalic anhydride (Aldrich, Germany), trimellitic anhydride (Aldrich, Germany), lithium chloride (Fluka, Switzerland), N,N-dimethylacetamide (Fluka, Switzerland), and methanol

(Riedel-de Haën, Germany) were used as purchased. Molecular structures of phthalic anhydride and trimellitic anhydride are shown in Figure 1. Some important properties of chitin and anhydrides used are given in Tables 1 and 2, respectively. Besides, hydrochloric acid (Merck, Germany) was used for adjusting pH.

2.2. Synthesis of Chitin Derivatives. The 1.0% (w/v) chitin solution was prepared as follows: chitin (3.0 g) was added to 300 mL of 5% (w/v) LiCl/DMAc solution, and the mixture was stirred at room temperature for 3 h to give a clear solution. Cyclic anhydride (100 mmol) was added to 200 mL of the chitin solution (Scheme 1). After stirring for 24 h, reaction mixture (containing a gel) was poured into MeOH (100 mL). The precipitate was filtered, and then dispersed in 200 mL of water. The product was precipitated from the solution or suspension by adjusting the pH to 1-2 with 3 M HCl. The precipitate was filtered, washed with MeOH, and dried in vacua [30].

2.3. Characterization. FTIR spectra were recorded between 450 and 4400 cm⁻¹ with a resolution of 4 cm⁻¹ from KBr pellets on a PerkinElmer RXI FT-IR spectrometer (PerkinElmer Inc., USA). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded in DMSO on a BRUKER DPX-400 high-performance digital FT-NMR spectrometer (Bruker Corporation, Germany). Tetramethylsilane was used as an internal standard. UV-Vis absorption spectra were obtained with a PerkinElmer Lambda 25 UV/Vis spectrometer (PerkinElmer Inc., USA) working in the wavelength range of 190–1100 nm by using a quartz cell of 1 cm path length. SEM micrographs were taken with a VEGA-II LSU scanning electron microscope (Tescan Inc., USA). TGA thermograms were recorded by using a Pyris 1 thermogravimetric analyzer (PerkinElmer Inc., USA). Chitin modified with phthalic anhydride (CPA) and chitin modified with trimellitic anhydride (CTA) were heated from 25 to 900°C and from 35 to 900°C, respectively, at a heating rate of 10°C min⁻¹ under N₂ atmosphere. The direct current electrical conductivity of chitin derivatives was measured by the standard four-point probe method by using PCI-DAS6014 for a current source, voltmeter, and temperature controller. For this purpose, dry and powdered samples were transformed into pellets by using a steel die of 13 mm diameter under a pressure of 700 MPa.

3. Results and Discussion

3.1. Solubility. CPA and CTA such as chitin are soluble in 5% (w/v) LiCl/DMAc solution too. The solubility of chitin, CPA, and CTA in 5% (w/v) LiCl/DMAc solution has been changing in the order of CTA>CPA>chitin. Besides, chitin is being soluted as more gel according to CPA and CTA in 5% (w/v) LiCl/DMAc solution. There are no other solvents in Table 1 in our laboratory.

SCHEME 1: Route of the synthesis of chitin derivatives.

TABLE 2: Some important properties of phthalic anhydride and trimellitic anhydride.

	Phthalic anhydride	Trimellitic anhydride
Molecular formula	$C_8H_4O_3$	$C_9H_4O_5$
Formula weight ($g\ mol^{-1}$)	148.1	192.13
Melting point ($^{\circ}C$)	131	164–169
Boiling point ($^{\circ}C$)	295	390
Density ($g\ mL^{-1}$)	1.53	1.54
Appearance	White flakes	White flakes
Vapor pressure (torr)	5.14×10^{-4} at $25^{\circ}C$	7.50×10^{-3} at $20^{\circ}C$
Solubility	0.62 g in 100 g water (reacts slowly)	Decomposes in water

FIGURE 1: Molecular structures of (a) phthalic anhydride and (b) trimellitic anhydride.

3.2. FTIR Spectra. Figure 2 shows the FTIR spectra of CPA and CTA. Characteristic absorption bands of CPA and CTA are given in Table 3. Carbonyl stretching vibrations ($1739\ cm^{-1}$ for CPA and $1712\ cm^{-1}$ for CTA) related to ester and/or carboxylic acid and aromatic $C=C$ stretching vibrations ($1493\text{--}1451\ cm^{-1}$ for CPA and $1503\text{--}1476\ cm^{-1}$ for CTA) related to benzene ring in the FTIR spectra of CPA (Figure 2(a)) and of CTA (Figure 2(b)) confirmed that chitin was successfully modified with phthalic anhydride and trimellitic anhydride.

3.3. 1H and ^{13}C NMR Spectra. Figures 3 and 4 display the 1H and ^{13}C NMR spectra of CPA and CTA, respectively.

1H NMR (DMSO) for CPA: δ (ppm) 2.04 (s, 3H), 2.59–2.60 (m, 2H), 2.77–2.80 (m, 2H), 2.87–3.04 (m, 5H for ring protons), 3.12–3.14 (m, 2H), 3.55 (bs, 1H), 8.02–8.15 (m, 4H), 8.69 (d, 1H), 10.62 (bs, 1H). ^{13}C NMR (DMSO) for CPA: δ (ppm) 9.54, 22.20, 35.10, 38.40, 39.17, 41.50, 45.78, 130.77, 131.30, 132.97, 135.45, 168.51. The peaks related to ester and carboxylic acid carbonyls and to the tertiary carbons of aromatic ring were not observed. 1H NMR (DMSO) for CTA: δ (ppm) 1.96 (s, 3H), 2.46–2.55 (m, 2H), 2.78–2.79 (m, 2H), 2.88–2.94 (m, 2H for ester and 5H for ring protons), 3.53 (bs, 1H), 7.49 (d, 1H), 8.16 (d, 1H), 8.55 (s, 1H). The peaks of carboxylic acid and amide protons were not observed. ^{13}C NMR (DMSO) for CTA: δ (ppm) 8.84, 21.88, 34.97, 38.20, 40.10, 40.70, 45.71, 131.30, 132.70, 133.39, 134.90, 138.30, 166.96, 167.71, 167.91, 170.12.

Broad singlet at 3.55 ppm with 1H intensity related to the secondary hydroxyl groups of CPA and broad singlet at 3.53 ppm with 1H intensity related to the secondary hydroxyl groups of CTA in their 1H NMR spectra show that esterification reaction occurred with only or usually primary hydroxyl groups. The primary hydroxyl groups according to the secondary hydroxyl groups in chitin react easier to form an ester because the nucleophilic attack of the secondary hydroxyl groups gets difficult due to the steric hindrance of chitin ring. Scheme 1 in [30] is confirming this idea.

TABLE 3: Characteristic absorption bands of CPA and CTA.

FTIR spectral (cm^{-1})	Assignment
CPA	
3600–3150	O–H stretching vibrations
3070	Aromatic C–H stretching vibrations
2975	
2939	
2878	
2802	Aliphatic C–H stretching vibrations
2756	
2739	
2677	
2491	Hydrogen bond stretching vibrations
1739	C=O stretching vibrations (for ester and carboxylic acid)
1631	C=O stretching vibrations (amide I band)
1584	N–H stretching vibrations (amide II band)
1493–1451	Aromatic C=C stretching vibrations
1412	C–N stretching vibrations (amide III band)
1332	Aliphatic C–H in-plane bending vibrations (for CH_3)
1265	C–O–C symmetric stretching vibrations (for ester)
1171	C–O–C asymmetric stretching vibrations (for ester)
1079	C–O–C asymmetric stretching vibrations (for ether)
1036	C–O–C symmetric stretching vibrations (for ether)
CTA	
3600–3150	O–H stretching vibrations
~3071	Aromatic C–H stretching vibrations
2976	
2941	
2879	
2803	Aliphatic C–H stretching vibrations
2757	
2739	
2677	
2492	Hydrogen bond stretching vibrations
1712	C=O stretching vibrations (for ester and carboxylic acid)
1605	C=O stretching vibrations (amide I band)
~1570	N–H stretching vibrations (amide II band)
1503–1476	Aromatic C=C stretching vibrations
1433	C–N stretching vibrations (amide III band)
1312	Aliphatic C–H in-plane bending vibrations (for CH_3)
1246	C–O–C symmetric stretching vibrations (for ester)
1156	C–O–C asymmetric stretching vibrations (for ester)
1069	C–O–C asymmetric stretching vibrations (for ether)
1036	C–O–C symmetric stretching vibrations (for ether)

FIGURE 2: FTIR spectra of (a) CPA and (b) CTA.

3.4. UV-Vis Absorption Spectra. Figure 5 shows the UV-Vis absorption spectra of CPA and CTA. As it is known, UV-Vis spectroscopy is the measurement of the wavelength and intensity of absorption of near-ultraviolet and visible light by a sample. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels [31]. As can be seen from Figures 5(a) and 5(b), CPA has one absorption band but CTA has two absorption bands. The absorption band at about 259 nm in Figure 5(a) may be due to $n \rightarrow \pi^*$ transition (R band). As for the absorption bands at about 265 nm and about 293 nm in Figure 5(b) that may be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions (R band), respectively.

3.5. SEM Micrographs. Figure 6 displays the SEM micrographs of CPA and CTA. The SEM micrographs of CPA and CTA show that CPA has more ordered and bigger macropores according to CTA. As it is known, pores decrease the electrical conductivity of material. This effect becomes more while it is gone from micropore to macropore.

FIGURE 5: UV-Vis absorption spectra of (a) CPA and (b) CTA.

- (2) aromatic C=C stretching vibrations (at $1493\text{--}1451\text{ cm}^{-1}$ for CPA and at $1503\text{--}1476\text{ cm}^{-1}$ for CTA) related to benzene ring in the FTIR spectra of CPA (Figure 2(a)) and CTA (Figure 2(b)),
- (3) the multiplet peaks at $8.02\text{--}8.15\text{ ppm}$ related to the protons of aromatic ring and the broad singlet at 10.62 ppm related to the proton of carboxylic acid in ^1H NMR spectrum (Figure 3(a)) of CPA,
- (4) the peaks at $7.49\text{--}8.55\text{ ppm}$ related to the protons of aromatic ring in ^1H NMR spectrum (Figure 3(b)) of CTA,
- (5) the peaks at 130.77 ppm , 132.97 ppm , and 135.45 ppm related to the carbons of aromatic ring in ^{13}C NMR spectrum (Figure 4(a)) of CPA,
- (6) the peaks at 167.71 ppm and 167.91 ppm related to carboxyl carbon of carboxylic acids, the peak at 170.12 ppm related to carbonyl carbon of ester, and the peaks at 131.30 ppm , 132.70 ppm , 133.39 ppm , 134.90 ppm , and 138.30 ppm related to the carbons of aromatic ring in ^{13}C NMR spectrum (Figure 4(b)) of CTA.

CPA has one absorption band, but CTA has two absorption bands. The absorption band at about 259 nm in Figure 5(a) may be due to $n \rightarrow \pi^*$ transition (R band). As for the absorption bands at about 265 nm and about 293 nm in Figure 5(b) that may be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$

(a)

(b)

FIGURE 6: SEM micrographs of (a) CPA and (b) CTA.

transitions (R band), respectively. The SEM micrographs of CPA and CTA show that CPA has more ordered and bigger macropores according to CTA. Besides, CTA is thermally more stable and more conductive than CPA.

As a conclusion, the modification of chitin with phthalic anhydride and trimellitic anhydride is of low cost, and the electrical conductivity of especially CTA is higher than the electrical conductivities of previous synthesized chitin derivatives. It can be said that CTA can be used as an alternative semiconductor.

FIGURE 7: TGA curves (—) of (a) CPA and (b) CTA.

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