Synthesis of polyaniline by chemical oxidative polymerization and characteristic of conductivity and reflection for various strong acid dopants

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Abstract. Herein, polyaniline (PANI) is synthesized via chemical oxidative polymerization of aniline monomer with ammonium persulfate as initiator by maintaining the flow rate and stirring for 8 h at room temperature. Particle sizes up to 54.716 μm are obtained, with a viscosity reaching 1.87 mPa-s at 270 min. The highest temperature during polymerization was 32 °C at 210 min. Thus, the polymer molecules undergo propagating process to form polymer chains. Fourier transform infrared spectroscopy confirms the presence of the PANI molecule, which reveals a complete reaction when the double-bond peak at 3442 cm\(^{-1}\) disappears from the spectrum and new peaks appear corresponding to benzoic and quinoid molecules at 1300–1600 cm\(^{-1}\). This ensures that all aniline molecules are converted to PANI with no residual. We conclude that PANI is synthesized via oxidative polymerization. The electrical conductivity of PANI is driven by protonic acids. The conductivity increases upon adding protonic acids as a strong acid-doping agent. Thus, PANI-HClO\(_4\) exhibits best conductivity. The best material candidate for a microwave-absorbing material is thus PANI-EB because it has the highest reflection loss at −29.69 dB at 11.812 GHz, whereas PANI-HClO\(_4\) has only −2.74 dB reflection loss at 12.400 GHz.

1. Introduction
Conducting polymers have been attracting significant research attention because of their unique properties [1]. Organic polymers normally form insulators; therefore, conducting polymers must have an unusual structure. Polymers with a conjugated \(\pi\)-electron backbone can have unusual electronic properties, such as low-energy optical transitions, low ionization potentials, and high electron affinities [2,3]. The result is a class of polymers that can be oxidized or reduced more easily and more reversibly than conventional polymers. Such oxidation or reduction of polymers is called “doping” and converts an insulating polymer to conduct polymer [2].

Polyaniline (PANI) is one of the more popular conducing polymers because of its high conductivity upon doping with acids, its well-behaved electrochemistry, its chemical, electrical, and environmental stability, and its easy preparation under reproducible conditions by both electro-polymerization and chemical oxidation of aniline [4,5].

One application of PANI is as an electromagnetic interface (EMI), which finds many uses, one of which is in the military, which has a use for materials that absorb electromagnetic waves. An example of this was the recent discovery that PANI could serve as a radar-absorbing material. When conductive PANI is used as a matrix for metals or oxide particles to form a composite system, some exciting physical and chemical properties can be expected from the system. Such materials can be used in modern technological applications, such as in new electronic devices or as materials for manipulating electromagnetic radiation (e.g., radar-absorbing material or electromagnetic interference shielding) [6]. PANI can be used to muffle reflections or absorb microwaves, thereby preventing the detection by radar of the surface that it covers.
exothermic, so the temperature of the system increases this phase, as shown in the experiments (discussed below). The temperature radical in the ion begins the polymerization. The bonds of the APS compound are broken, thereby constructing a free and termination. Oxidative polymerization of aniline may be divided into three main phases: initiation, propagation, and termination.

3.1. Synthesis of PANI

Oxidative polymerization of aniline may be divided into three main phases: initiation, propagation, and termination. Initiation is characterized by the radical construction of the APS initiator, which begins the polymerization. The bonds of the APS compound are broken, thereby constructing a free radical in the ion and the cation (or radical initiator).

The next phase is propagation, in which the polymer chain extends, as confirmed by the data from the experiments (discussed below). The temperature changes significantly during the early stages of this phase, as shown in figure 1. At 30 min. after the onset of polymerization, the temperature reaches 30 °C, and rises to 32.3 °C after 210 min. As detailed in previous experiments, the polymerization is exothermic, so the temperature of the system increases during the propagation phase [6,7].

The first 30 min. of polymerization is critical for the initiation and propagation processes. The rising temperature in the propagation phase is due to the construction of the polymer product, which

![Figure 1. Temperature as a function of time during oxidative polymerization of aniline.](image1)

![Figure 2. Particle size as a function of time during polymerization of aniline.](image2)
means the combination of radical aniline monomers with pure aniline monomers, releasing the enthalpy energy between the splitting of the bonds and the compound energy construction (i.e., enthalpy reactor with enthalpy product). The difference in energy $H = H_{\text{product}} - H_{\text{reactor}}$ is positive, so the system frees energy, which means it is an exothermic reaction that increases the temperature.

The other important indicator of chain propagation is the size of particles in the system [8]. Figure 2 shows, as a function of time, the particle size as determined by using a particle-size analyzer. The particle diameter rises rapidly to about 35 $\mu$m, and then grows more slowly until 270 min. have passed, reaching the size of about 55 $\mu$m. At the end of the measurement, the particle size is 55.890 $\mu$m.

The viscosity is another significant indicator that reflects the process of aniline polymerization. An increase in viscosity means that the system contains more PANI, with its higher molecular weight. This is caused by the propagation phase, which extends the PANI chain. The largest viscosity is 1.87 mPa-s at 270 min.

The termination phase is the final phase of polymerization. In this phase, radical aniline monomers combine with the end of the radical polymer chain in coupling and disproportionation. In the coupling termination process, two radicals combine to form a covalent bond, thereby connecting the system and the end of PANI polymer chain. Conversely, two radicals may emerge and construct two new molecules, which is known as disproportionation termination. The results shown in figure 2 confirm that the particle size is rather stable during the termination phase. This process stops if the radicals are all consumed by forming all of the bonds, so that no more radicals are available to trigger polymerization.

### 3.2. Fourier transform infrared characterization

Figure 3 shows the characteristic infrared (IR) absorption bands of the monomer aniline (C$_6$H$_5$NH$_2$). The peaks at 3426 and 3355 cm$^{-1}$ are from the vibration and stretching of the O–H bond, respectively. The peak at 3218 cm$^{-1}$ is the shoulder band that always emerges (especially on aniline) at smaller wavenumbers and is due to the N–H stretching vibration from the primary aniline monomer amine. The peaks at 1600 and 1273 cm$^{-1}$ are due to C–N stretching vibration. Finally, the peaks at 882 and 747 cm$^{-1}$ are due to C–H bending vibration and N–H wagging vibration from amine, respectively.

Figure 4 shows the IR transmission spectrum for PANI-ES. The peaks at 603 and 663 cm$^{-1}$ are due to C–Cl stretching vibration, that at 1647 cm$^{-1}$ is due to the N–H vibration from the primary amine, and that at 3248–3371 cm$^{-1}$ is due to the N–H stretching vibration from the amina, which is indicative of PANI.

Figure 5 shows the PANI-EB IR transmission spectrum. This material is formed by deprotonation (dedoping) of PANI by using the reductant NH$_4$OH. The peak at 833 cm$^{-1}$ is due to the C–H bending vibration and that at 1169 cm$^{-1}$ is due to the C=N stretching vibration within the quinoid ring. The peaks at 1289 and 1315 cm$^{-1}$ are due to the C–N stretching vibration. The peaks at 1491 cm$^{-1}$ and 1569 cm$^{-1}$ are due to the C=C stretching vibration from the benzenoid ring and the C=C stretching vibration from the quinoid ring, both of which are characteristic of PANI. The peak at 3229 cm$^{-1}$ is due to the N–H stretching vibration. No absorption is due to the bending vibration that is characteristic of PANI-EB, which shows that PANI-EB is no longer doped by protonic acid (HCl).
Figure 4. PANI-ES IR transmission spectrum showing the result of polymerization.

Figure 5. PANI-EB IR transmission spectrum.

Figure 6 shows the IR transmission spectra for PANI-HCOOH, PANI-HNO₃, PANI-HCL, and PANI-HClO₄. None of the four PANI spectra show any significant difference in the peak of the bending absorption, which is similar to that of PANI-EB. The IR transmission spectrum of PANI doped by HCl show two peaks, characteristic of the PANI bending absorption at 1568 and 1491 cm⁻¹, which are due to the C=C stretching vibration from the quinoid rings and benzenoid rings in the backbone of PANI. The same peaks appear at 1562 and 1485 cm⁻¹ for PANI doped by HClO₄, and at 1559 and 1483 cm⁻¹ for PANI doped by HCOOH. The absorption peaks at 1145, 1189, 1108, and 1044 cm⁻¹ of PANI doped by HCOOH, HNO₃, HCl, and HClO₄, respectively, show the C=O stretching vibration from the protonic quinoid that makes PANI a conducting polymer. These results show that doping PANI by a protonic acid as the source of the proton (H⁺) transforms the PANI into PANI-EB.

The IR absorption peak further show the C–N stretching vibration from amina aromatic and the transferring π electron for PANI doped by HCOOH (PANI-HCOOH) at 1288 cm⁻¹, for PANI doped by HNO₃ (PANI-HNO₃) at 1357 and 1288 cm⁻¹, for PANI doped by HCl (PANI-HCl) at 1285 and 1241 cm⁻¹, and for PANI doped by HClO₄ (PANI-HClO₄) at 1286 and 1254 cm⁻¹. The absorption of the N–H stretching vibration appears for all dopants: for PANI-HCOOH at 3233 cm⁻¹, for PANI-HNO₃, at 3231 cm⁻¹, for PANI-HCl at 3222 cm⁻¹, and for PANI-HClO₄, at 3226 cm⁻¹.

3.3 Characterization of conductivity
Table 1 summarizes the results of conductivity measurements of PANI with various dopants. The
Table 1. Conductivity of various PANI-EB, PANI-ES, and PANI doped with various dopants.

| Sample                  | Conductivity ($\mu$S/cm) |
|-------------------------|--------------------------|
| PANI-ES (from polymerization) | 4479.9371                |
| PANI-EB (from deprotonation)   | 0.00099                  |
| PANI-HCOOH               | 0.1023                   |
| PANI-HNO.                | 0.1220                   |
| PANI-HCl                 | 291.7690                 |
| PANI-HClO.               | 13496.5003               |

Figure 6. IR transmission spectra of PANI with different dopants.

Figure 7. Microwave absorption of PANI-EB, PANI-ES, and various doped forms of PANI.

conductivity was acquired after the oxidative polymerization of aniline, which for PANI-ES gives $4479.9371 \times 10^{-3}$ S/cm. PANI-ES is the result of oxidative polymerization of aniline and yields a semiconducting PANI. Deprotonation (dedoping) gives PANI-EB with a conductivity of $0.00099 \times 10^{-10}$ S/cm. Thus, PANI-EB is an electrical isolator.

The conductivities of the various doped forms of PANI-EB (PANI-HCOOH, PANI-HNO3, PANI-HCl, PANI-HClO) are greater than that of PANI-EB. Specifically, the conductivities are $0.1023$, $0.1220$, $291.7690$, and $13496.5003$ µS/cm, respectively. Converted to S/cm gives $1.023 \times 10^{-5}$ S/cm for PANI-HCOOH and $1350 \times 10^{-5}$ S/cm for PANI-HClO. The results show that PANI-EB doped with HClO has the highest conductivity of all samples tested, including the semiconductor.
3.4. Characterization by vector network analyzer

Consider now figure 7, which shows the microwave absorption of different forms of PANI as a function of frequency. The highest microwave absorption of $-29.69$ dB is for PANI-EB at 11.812 GHz. PANI-EB also has the lowest conductivity aside from other PANI. The smallest absorption of $2.74$ dB is for PANI-HClO$_4$ at 12.400 GHz, despite PANI-HClO$_4$ having the highest conductivity.

PANI-HNO$_3$, PANI-ES, and PANI-HCl have maximum microwave absorptions of $-14.20$ dB at 12.316 GHz, $-3.13$ dB at 12.4 GHz, and $-2.12$ dB at 11.644 GHz, respectively. The widening of the microwave absorption peak is due to the dielectric, which also contributes to the absorption.

4. Conclusions

The results and discussion above indicate that, during the oxidative polymerization reaction, the solution is characterized by an increase in temperature to 32 $^\circ$C, which is associated with the formation of polymer chains. The mean particle size of the polymer chains reaches $\sim$54.72 $\mu$m, and the viscosity of the solution increases to 1.87 mPa s after 270 min of polymerization. After treating PANI-EB, a conductive PANE-ES is obtained with an electrical conductivity of 4479.9371 $\mu$S/cm, which can be enhanced to 13,496.5003 $\mu$S/cm by doping with HClO$_4$. The largest microwave absorption of $-29.69$ dB is obtained for PANI-EB at 11.812 GHz, although PANI-EB has the lowest conductivity aside from other PANI. Thus, the higher the conductivity, the lower the absorption and vice versa.

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