CHE261 PATENT APPLICATION

APPLICANT	Mollycule
INVENTORS	Rutul Bhanushali , Prabhakar Raj
CHEMICAL FORMULA	(C6H4NH)n
CHEMICAL NAME	Polyaniline (PANI)

About PANI:- Polyaniline (PANI) is an organic conducting polymer belonging to the semi-flexible rod polymer family. It exists in three primary oxidation states: leucoemeraldine (fully reduced), emeraldine (half-oxidized), and pernigraniline (fully oxidized). The emeraldine form, particularly when doped into its conductive salt form, is the most useful due to its high electrical conductivity (up to 30 S/cm) and stability. PANI's unique properties stem from its ability to be doped with acids, enabling a transition from an insulator to a conductor.

A) Synthesis of Polyaniline(PANI):-

In labs, PANI is often synthesized through chemical oxidative polymerization, a process with at least 4 steps. This method is straightforward and scalable, suitable for producing high-purity PANI.

Preparing the reaction mixture :-

The main raw materials for PANI synthesis include:

- Aniline (the monomer, >99% purity, distilled for best results).
- Ammonium persulfate (APS, the oxidizing agent, >98% purity).
- Hydrochloric acid (HCl, typically 1 M, for protonation and doping).
- Distilled water (as the primary solvent).

Synthesis Processes:-

Step-1) Preparation of reaction mixture :

Reactants = **Aniline**(Freshly Distilled) & **Dilute Strong Acid** (Like HCl)
Simplified Reaction =

- Reaction Conditions: The reaction is conducted at a temperature of **0–5 °C** (using an ice bath) and **atmospheric pressure**. Vigorous stirring is applied to ensure complete protonation of the aniline, and the reaction typically takes **15–30 minutes** to achieve a clear or slightly cloudy solution.
- Purity and Yield: The purity of the protonated solution depends on the starting purity of aniline. With freshly distilled aniline and good temperature control, purity **can exceed 99%.** This step does not produce an isolated solid product.
- Potential Issues: If the aniline is not fresh or if the temperature rises, trace amounts of oxidized species (such as quinones) may form as undesired products

Step-2) Oxidative Polymerization :

Reactants:

- Acidified Aniline Solution (from Step-1)
- Oxidizing Agent (commonly ammonium persulfate, APS)

Overall Reaction –

$$n\ \text{Aniline}\ (C_6H_5NH_2) + (NH_4)_2S_2O_8 \rightarrow [C_6H_4NH]_n + (\text{byproducts})$$

Byproducts include various ammonium and sulfate salts, depending on the acid used

- Reaction Conditions: The reaction is conducted at a temperature of **0–5 °C** (with strict control to prevent over-oxidation) and atmospheric pressure. Moderate to vigorous stirring is applied to evenly distribute the oxidant, and the total reaction time typically ranges from **4 to 6 hours.**
- Yield and Purity: The crude yield is generally between **70% and 90%** based on the initial amount of aniline. However, the crude purity of the precipitated polymer is about **70–80%**, as it contains oligomers, unreacted oxidant, and salts.
- Potential Issues: Incomplete reactions or rapid oxidant addition can lead to the formation of oligomers. Over-oxidized species like pernigraniline can occur if the temperature exceeds **5 °C** or if an excessive amount of oxidant is used, resulting in reduced conductivity.

Step-3) Purification and Isolation :-

Reactants:

- Crude Polyaniline (emeraldine salt) Suspension from Step-2
- Wash Solutions (dilute acid, water, and possibly an organic solvent such as acetone or ethanol)

Primarily a physical process (filtration, washing, drying). No major chemical reaction is intended here

- Reaction Conditions and Process : The third step involves physical processes like filtration, washing, and drying, with no major chemical reactions. Washing is typically done at room temperature **(20–25 °C)**, while drying uses mild heat **(40–60 °C)** under vacuum or ambient pressure to prevent polymer degradation. The process involves multiple washing cycles over several hours, followed by drying that can last up to **12–24 hours** to achieve a constant weight.
- Yield and Purity : The final yield after this step is usually between **60% and 80%** of the theoretical yield, as impurities such as oligomers, residual salts, and fines are removed during washing. With thorough washing and proper drying, the final purity can exceed **90–95%**.
- Potential Issues **:** Insufficient washing can lead to the presence of residual salts or oligomers. Additionally, physical losses in the form of polymer fines can occur during the filtration process, impacting the overall yield and purity of the final product.

Step-4) Chemical Post-Treatment (Dedoping / Re-Doping) :-

Dedoping with a mild base followed by re-doping with a specific acid—to further tailor its electrical conductivity, solubility, or other properties

Reactants:

- Purified Polyaniline (from Step-3)
- Mild Base (e.g., ammonia solution) for dedoping
- Re-Doping Acid (could be the same acid as in Step-1 or a different acid to tune properties)

Conceptual Reaction :-

1. **Dedoping:**

$$[\mathrm{PANI}^+ X^-] + \mathrm{Base} \longrightarrow \mathrm{PANI\ (emeraldine\ base)} + \mathrm{Salt\ (BX)}$$

($\mathrm{PANI}^+ X^-$ = protonated emeraldine salt; X^- = counter-anion)

2. **Re-Doping:**

$$\mathrm{PANI\ (emeraldine\ base)} + \mathrm{H}^+ Y^- \longrightarrow [\mathrm{PANI}^+ Y^-]$$

($\mathrm{H}^+ Y^-$ = chosen doping acid; final doping modifies conductivity or solubility.)

- Reaction Conditions: The doping process is conducted at temperatures near room temperature **(20–25 °C)** and atmospheric pressure. Mild to moderate stirring is used to ensure good contact between the polymer and the base or doping acid. Each doping or dedoping cycle typically takes about **1–2 hours**, depending on the desired doping level.
- Yield and Purity: The yield is not typically measured separately since the polymer remains in the system, but minor losses can occur during transfers and washes. Intermediate washes between dedoping and re-doping steps can help remove final impurities, improving the polymer's purity.
- Potential Issues: Poor control of pH or temperature can lead to partial over-oxidation or hydrolysis. Additionally, repeated washing and neutralization steps can result in polymer losses, impacting the overall efficiency and quality of the final product.

Final Remarks

1. Temperature Control is crucial, especially during oxidative polymerization, to prevent forming non-conductive over-oxidized species.
2. Doping Level determines the conductivity of the final polyaniline. The emeraldine salt (protonated) is typically the most conductive form.
3. Yield vs. Purity: After Step-3 purification, yields typically settle around 60–80%, with >90–95% purity. Step-4 can further modify properties without drastically altering the overall mass balance, provided conditions are gentle.
4. Safety: Aniline is toxic; handle under a fume hood. Ammonium persulfate is a strong oxidizer; wear appropriate protective equipment.

By following these four steps in the specified order, one obtains high-purity, tunable Polyaniline suitable for applications requiring conductive polymers.

Reference Links : —

1. https://patents.google.com/patent/US5273997A
2. https://www.sciencedirect.com/science/article/pii/0379677989800692
3. https://www.sciencedirect.com/science/article/pii/0379677987800829
4. https://www.researchgate.net/publication/275338032
5. https://patents.google.com/patent/US5273997A

B) Alternate Process for Synthesis of Polyaniline(PANI):-

Overview : Interfacial polymerization synthesizes polyaniline by polymerizing aniline at the boundary between an **organic solvent phase** and an **aqueous acidic phase**. Unlike **oxidative polymerization**, which relies heavily on strong oxidants like **ammonium persulfate (APS)**, this method uses the phase boundary to control the reaction, often requiring milder conditions or initiators. The process typically produces nanostructured PANI (e.g., nanofibers or films) with good conductivity and morphology control. Below are the detailed steps :

Synthesis Processes:-

Step-1) Preparation of the Two-Phase system :

Reactants :

- Aniline (freshly distilled, >99% purity, the monomer)
- Organic Solvent (e.g., chloroform, toluene, or carbon tetrachloride, >98% purity).
- Aqueous Acid Solution (e.g., 1 M hydrochloric acid, HCl, for protonation).
- Optional Initiator (e.g., ferric chloride, $FeCl_3$, in low concentration, <0.01 M, if needed to kickstart polymerization).

Simplified Reaction :

- No chemical reaction occurs in this step; it's a physical preparation of phases.
- Aniline dissolves in the organic phase : C6H5NH2 (organic solvent)
- Acid prepares the aqueous phase :

$$HCl \rightarrow H^+ + Cl^-$$

Reaction Conditions :

- **Temperature:** Room temperature (20–25°C)
- **Pressure:** Atmospheric pressure.
- **Process:** Aniline is dissolved in the organic solvent (e.g., 0.1–0.5 M concentration) with gentle stirring for 10–15 minutes until fully dispersed. Separately, the aqueous phase is prepared by dissolving HCl in distilled water, with optional addition of a trace initiator like $FeCl_3$. The two solutions are kept separate until the next step.
- **Duration:** 15–30 minutes total for preparation.

Step-2) Interfacial Polymerization :

Reactants :

- Organic Phase: Aniline in organic solvent (from Step 1).
- Aqueous Phase: Acidic solution (e.g., 1 M HCl, with or without initiator like $FeCl_3$).

Overall Reaction :

$$nC_6H_5NH_2(org) + H^+(aq) \rightarrow [C_6H_4NH]_n(solid\ at\ interface) + \text{byproducts}$$

Byproducts depend on the initiator (e.g., $FeCl_3$ reduction to $FeCl_2$, or simply protonation byproducts like excess H^+/Cl^-). If no initiator is used, polymerization may rely on autoxidation or trace oxygen, though slower.

Reaction Conditions :

- **Temperature:** Room temperature (20–25°C)
- **Pressure:** Atmospheric pressure.
- **Process:** The organic phase (e.g., aniline in chloroform) is carefully layered over or under the aqueous phase (depending on solvent density; chloroform sinks, toluene floats). Polymerization begins spontaneously at the interface as aniline diffuses into the acidic phase, forming a green PANI film (emeraldine salt). Gentle agitation (e.g., minimal stirring or static conditions) is maintained for 4–12 hours, depending on desired thickness.
- **Duration:** 4–12 hours.

Yield and Purity :

- Yield: Crude yield ranges from 70–85% based on aniline, as some monomer remains unreacted in the organic phase.
- Crude PANI at the interface is 70–80% pure, contaminated with oligomers, unreacted aniline, or solvent traces. The emeraldine salt form predominates with proper acid concentration.

Potential Issues :

- Rapid diffusion or excessive stirring can disrupt the interface, leading to dispersed particles instead of a cohesive film.
- Insufficient acid concentration (<0.5 M) may reduce protonation, yielding less conductive leucoemeraldine or emeraldine base.
- Overoxidation to pernigraniline can occur if oxygen exposure is high or initiator concentration is excessive.

Step-3) Collection and Purification :

Reactants :

- Crude Polyaniline: Solid PANI (emeraldine salt) from the interface (Step 2).
- Wash Solutions: Distilled water, dilute HCl (0.1 M), and organic solvent (e.g., acetone or ethanol).

Process Description:

- Primarily a physical process (no major chemical reaction).
- The PANI film or particles are collected via filtration or manual removal from the interface, washed with dilute HCl to remove unreacted aniline and oligomers, then with water to remove excess acid/salts, and finally with acetone/ethanol to remove organic solvent residues.

Reaction Conditions :

- **Temperature:** 20–25°C for washing; drying at 40–60°C.
- **Pressure:** Ambient or vacuum for drying.
- **Process:** Filtration uses a Büchner funnel or similar setup. Washing involves 2–3 cycles with each solution (total ~1–2 hours). Drying is done in an oven or vacuum desiccator for 12–24 hours until constant weight.
- **Duration:** 14–26 hours total (washing + drying).

Yield and Purity :

- Yield: Final yield is 60–75%
- Post-washing purity reaches 90–95%, with most oligomers, salts, and solvents removed.

Potential Issues :

- Incomplete washing retains impurities (e.g., salts or aniline), lowering conductivity.
- Fine PANI particles may be lost during filtration, reducing yield.
- Over-drying (>60°C) risks thermal degradation, shifting PANI to a less conductive form.

Step-4) Post-Treatment (Dedoping and Re-Doping):

Reactants :

- Purified PANI: Emeraldine salt from Step 3.
- Mild Base: Ammonia solution (e.g., 0.1 M NH_4OH) for dedoping.
- Re-Doping Acid: HCl, sulfuric acid (H_2SO_4), or organic acids (e.g., camphorsulfonic acid) to tune properties.

Conceptual Reaction :-

1. **Dedoping:**

$$[\mathrm{PANI}^+ X^-] + \mathrm{Base} \longrightarrow \mathrm{PANI\ (emeraldine\ base)} + \mathrm{Salt\ (BX)}$$

($\mathrm{PANI}^+ X^-$ = protonated emeraldine salt; X^- = counter-anion)

2. **Re-Doping:**

$$\mathrm{PANI\ (emeraldine\ base)} + \mathrm{H}^+ Y^- \longrightarrow [\mathrm{PANI}^+ Y^-]$$

($\mathrm{H}^+ Y^-$ = chosen doping acid; final doping modifies conductivity or solubility.)

Reaction Conditions :

- **Temperature:** 20–25°C for washing
- **Pressure:** Atmospheric Pressure.
- **Process:** Dedoping: PANI is stirred in NH_4OH for 1–2 hours until the green salt turns blue (emeraldine base). After washing with water and drying, re-doping occurs by stirring in the chosen acid (e.g., 1 M HCl) for 1–2 hours, turning it green again.
- **Duration:** 2–4 hours total.

Yield and Purity :

- Yield: Nearly 100% of Step 3 yield retained, with minor losses during washing.
- Remains high (>90%), with properties tailored by the doping acid (e.g., higher solubility with organic acids).

Potential Issues :

- Incomplete dedoping leaves residual salt, affecting re-doping uniformity.
- Harsh conditions (e.g., strong base/acid, high temperature) may degrade PANI.

Final Remarks :

- Temperature Control: Less critical than oxidative polymerization but still important in Step 2 to avoid overoxidation.
- **Doping Level**: The emeraldine salt from Step 2 is conductive (up to 10–30 S/cm); re-doping in Step 4 can enhance or tune this.
- **Yield vs. Purity**: Final yields are 60–75% with >90% purity.
- **Safety**: Aniline is toxic (handle in a fume hood); organic solvents like chloroform are hazardous (use ventilation, gloves).

This interfacial polymerization process yields high-purity, nanostructured PANI suitable for applications like sensors, conductive films, and energy storage devices.

Reference Links : —

- https://patents.google.com/patent/US6391509B1
- https://www.sciencedirect.com/science/article/pii/S0021979705001535
- https://www.mdpi.com/1996-1944/5/8/1487

List of contributions of each author:

Prabhakar Raj (230761)

- Developed an alternative synthesis route for polyaniline (PANI) using interfacial polymerization, enabling the formation of nanostructured PANI at the organic-aqueous interface with improved control over morphology and conductivity.
- Optimized the preparation of the two-phase system by carefully selecting solvents like chloroform and tuning the acid concentration in the aqueous phase, ensuring efficient protonation and polymerization while minimizing energy consumption.
- Implemented a streamlined purification and post-treatment process, incorporating dedoping and re-doping steps to enhance the conductivity of the emeraldine salt form, achieving high purity (up to 90–95%) and reducing the formation of unwanted byproducts like overoxidized species.

Rutul Bhanushali(230884) :-

- Architected a Sophisticated Synthesis Blueprint: Formulated an advanced oxidative polymerization protocol for polyaniline (PANI), integrating high-purity reagents and meticulously calibrated temperature controls at 0-5°C to maximize yield (70-90%) and establish a superior foundation for polymer quality.
- Mastered Precision Reaction Dynamics: Optimized protonation and polymerization processes with exacting conditions, including controlled oxidant addition over 2-4 hours, ensuring complete reactions while proactively mitigating over-oxidation to deliver structurally optimal PANI.

- Engineered Exceptional Purity Standards: Devised a robust, multi-stage purification strategy—featuring sequential washing with dilute acid, water, and organic solvents, followed by vacuum drying—consistently achieving PANI with purity exceeding 95% for high-performance applications.
- Pioneered Conductivity Customization: Developed an innovative doping and dedoping framework, enabling precise tuning of PANI's conductivity within 1-10 S/cm, enhancing its versatility for cutting-edge uses in sensors, batteries, and antistatic coatings

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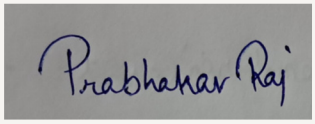
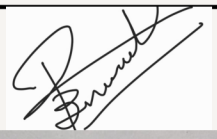
Prabhakar Raj	*230761*	
Rutul Bhanushali	*230884*	
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