

Review

Mechanochemical Synthesis of Polyanilines and Their Nanocomposites: A Critical Review

Cesar A. Barbero *  and Diego F. Acevedo 

Research Institute for Energy Technologies and Advanced Materials (IITEMA), National University of Río Cuarto (UNRC)-National Council of Scientific and Technical Research (CONICET), Río Cuarto 5800, Argentina
* Correspondence: cesarbarbero@gmail.com

Abstract: The mechanochemical synthesis of polyanilines (PANIs), made by oxidative polymerization of anilines, is reviewed. First, previous knowledge of the polymerization reaction in solution is discussed to understand the effect of different parameters: oxidant/monomer ratio, added acid, oxidant, temperature and water content on the properties of the conducting polymers (molecular weight, degradation, doping/oxidation level, conductivity, and nanostructure). The work on mechanochemical polymerization (MCP) of anilines is analyzed in view of previous data in solution, and published data are critically reconsidered to clarify the interpretation of experimental results. A key factor is the production of acids during polymerization, which is often overlooked. The production of gaseous HCl during MCP of aniline hydrochloride is experimentally observed. Since some experiments involve the addition of small amounts of water, the kinetics and heat balance of the reaction with concentrated solutions were simulated. A simple experiment shows fast (<2 min) heating of the reaction mixture to the boiling point of water and temperature increments are observed during MCP in a mortar. The form and sizes of PANI nanostructures made by MCP or solution are compared. The extensive work on the production of nanocomposites by MCP of anilines together with different nanomaterials (porous clays, graphene, carbon nanotubes, metal, and oxide nanoparticles) is also described.

Keywords: mechanochemistry; conductive polymers; polyanilines; nanocomposites



Citation: Barbero, C.A.; Acevedo, D.F. Mechanochemical Synthesis of Polyanilines and Their Nanocomposites: A Critical Review. *Polymers* **2023**, *15*, 133. <https://doi.org/10.3390/polym15010133>

Academic Editors: Ana Maria de Matos Charas and Hai-Feng (Frank) Ji

Received: 1 November 2022

Revised: 8 December 2022

Accepted: 16 December 2022

Published: 28 December 2022



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Polyanilines are conducting polymers [1], with a wide range of technological applications: electromagnetic shielding [2], electrochromics [3,4], photothermal antitumoral/antibacterial therapy [5], electromagnetic actuators [6], electrode materials of batteries [7,8], supercapacitors [9], flexible electronics [10], conducting hydrogels [11], electrochemically-driven ion exchangers [12], fluorescent nanoparticles [13], electrochemical sensors [14], etc. The synthesis of the polyanilines is usually made by oxidative polymerization of anilines in solution [15], at a relatively low concentration (0.1–0.2 M) [16]. Therefore, the synthesis of polymer uses a lot of water, which becomes contaminated with byproducts (e.g., ben-zidine which is a known carcinogen). This is a relevant matter in the chemical industry. For example, using the IUPAC standard procedure for polyaniline (PANI) synthesis [17], which uses a 0.2 M concentration of aniline chlorhydrate (AniHCl), ca. 54 liters of water (assuming 100% yield) have to be used to produce 1 kg of PANI (Emeraldine Base, EB). As we will see below, the maximum concentration cannot be increased because the reaction is highly exothermic, and relatively low (>50 °C) temperatures cause degradation. One way to avoid solvents is the use of mechanochemical synthesis where two solids are brought to a reaction under mechanical action (milling, grinding). Engineering and environmental considerations favor MC synthesis over the same reaction in solution. If the yield and conversion are high, reactor size is much smaller in MC, allowing large scale synthesis in small factories.

Mechanochemistry (MC) is a method with a long history [18], which has received renewed interest in recent years, especially in the field of polymer synthesis (MCP) [19].

Besides reacting solids, modern work in mechanochemical synthesis (MS) includes the use of small amounts of liquid (liquid assisted grinding, LAG [20]), solid diluents [21], or even additional polymers [22] to produce the reaction. Of great interest are those materials which cannot be made by a solution reaction but occur under MCP [23]. However, only one mechano-exclusive synthesis, that is, a conducting polymer only produced by MCP, has been reported [24]. On the other hand, oxidative polymerization of anilines is an exergonic reaction (exothermic) where no external energy input (e.g., mechanical) is required. Moreover, in the case of oxidative polymerization of aniline, to give polyaniline it is usually performed under cooling (0–5 °C) since at higher temperatures additional reactions occur which could degrade the conducting polymer. That is, energy is withdrawn from the reaction instead of introducing it. In MCP, the temperature is usually not controlled or measured [25], therefore, high temperature excursions could occur and the product could be degraded. The initial steps of aniline oxidation are well understood, but the details of polymer growth are unclear. The final product (conducting polymer) is insoluble in the solvent, and it is possible for the chains to grow in the solid state (a relevant point for solvent-free polymerization) or to grow in solution until it becomes insoluble and precipitate. Data on mechanochemical polymerization of anilines leading to conducting polymers are critically analyzed along with the effect of adding additives or changing the type or amount (relative to monomer) of reactants. The previously known mechanism in solution and the effect of parameters such as monomer/oxidant ratio, acidity, and the presence of precursor molecules (e.g., 4ADA) is used to analyze the mechanochemical data. A special case, widely studied in the field, involves the formation of composites with different solids. Here, the mechanical force could induce the milling of the solid (e.g., graphite to graphene), and the polymerization occurs in the exposed surface allowing producing nanocomposites. However, in some cases the polymer is already formed and the mechanical force allows the milling and mixing of both materials. In any case, the method is a simple way to produce nanocomposites containing PANIs. Finally, a future outlook in the field is discussed. IUPAC defines a mechanochemical (MC) reaction as a “chemical reaction that is induced by the direct absorption of mechanical energy” [26]. There are two ways to approach the MC technique. The physicochemical approach studies systems where mechanical energy (including static pressure) act at bond level to produce the reaction. On the other hand, the organic synthesis approach uses mechanical processes (grinding, milling, pressure, ultrasonic, etc.) as a tool to: (i) induce reactions not achievable by other methods (thermochemistry, photochemistry, and electrochemistry); (ii) improve the synthesis in terms of yield, reaction time, purity of the product, etc.; or (iii) make the synthesis more sustainable by eliminating (or diminishing drastically) the use of solvents. The synthetic approach, which is used in all the work reviewed here, is a practical one. The goal is the product, not the knowledge of the mechanism. In that sense, it is analogous to other modern tools of synthesis (microwave, ultrasound, radiofrequency, or hydrothermal) whose mechanism is still in discussion but are routinely used in organic chemistry. A better understanding of the parameters affecting the reaction should allow setting the best conditions to obtain desired outcomes: smaller time, highest yield, and absence of side reactions. Side reactions are more relevant in polymer than in general organic chemistry because the side products remain usually linked to the polymer. Experimental aids, such as the use of drops of liquid to aid the milling (LAG), have a profound effect on the synthetic output. The liquid could lubricate the grinding and transmit the pressure while being chemically inert. On the other hand, the liquid could dissolve one of the reactants, producing a heterogeneous (solution/solid) reaction. If all reactants are dissolved, the reaction is in solution but at a high local concentration. In both cases, the reaction rate obviously increases compared to a diluted solution. In the case of water, it not need to be added but could be present by absorption in hygroscopic reactants unless the reaction is performed in a dry box. The grinding process produces small (<1 μm) particles which have large surface areas. Therefore, water adsorption from the environment could be important. It is noteworthy that such considerations of the likely role of adventitious water were already

taken into account early on (1893) by Johnston and Adams [27], while discussing the effects of even and uneven pressure on inorganic reactions. Another reactant, which could exist in normal MCP, is oxygen from air. We will see that authors propose reactions (albeit catalyzed and taking several days) where oxygen from air is the only oxidant.

A novel way to do LAG involves using fused salts, ionic liquids (IL), or deep eutectic solvents (DES) as liquids [19]. As will be described in the review, some authors use fused salts, generally occurring by the heat of reaction, as an aid in MCP. Since the polymerization product is a solid polymer instead of a macromolecule dissolved in a solvent, the aggregation form (i.e., the nanostructure) produced in the synthesis remains in the final solid. It is noteworthy that the most often used method to produce PANI nanofibers involves oxidative polymerization at the interface of a solution of aniline in a solvent (immiscible with water, e.g., CHCl_3) and an aqueous (acid) solution of the oxidant (APS) [28]. The nanofibers grow towards the aqueous solution. The heterogeneous reaction between solid anilinium salt and solid oxidant resembles closely the liquid/liquid interphase. As will be seen, some authors indeed obtained PANI nanofibers by MCP.

The use of mechanical actions, being in a mortar/pestle, ball mill, tumble mill, or extruder, is known to influence the yield of product in synthetic chemistry. Moreover, experimental parameters, such as the number and size of balls, the hardness of them, and the effect of the ball/jar material (e.g., steel), could also affect the reactions. However, no comprehensive model exists to account for such effects, which have to be ascertained for each reaction. As will be seen below, the vast majority of polyanilines syntheses use mortar and pestle as MC. It is known that grinding in a mortar has low reproducibility, is limited to shorter times (although 6 h grinding times have been reported), and could endanger the operator through the release of toxic fumes/gases. On the other hand, if a visual confirmation of reaction exists (e.g., color change), it allows using only the necessary time. This is likely the reason that using mortar and pestle is the technique of choice in the synthesis of inorganic complexes, organic charge transfer complexes, and synthesis of conducting polymers, where clear color change occurs. In closed systems (e.g., ball mill jars), the reaction could be carried out for long times to assure complete conversion. However, polymer chain scission by mechanical action is well known [19], and ball milling of already formed polymers could decrease the molecular weight. On the other hand, closed milling devices allow for maintaining an inert (oxygen- and water-free) atmosphere, by filing the closed jar in a glove box. The closed container is also relevant when possible toxic and/or corrosive fumes are produced during reaction. There are several theories to explain mechanochemical effects in different areas of chemistry: (i) the hot spot theory, (ii) the magma-plasma model, and (iii) the pseudo-fluid model [19]. None of them is able to explain mechanochemical polymerization reactions completely [19]. Moreover, other processes occur during MC experiments that do not relate to mechanical energy input but influence the reaction. Milling/grinding achieves an intimate mixing of reactants at the nanometric scale (likely involving single or few macromolecules), allowing them to react. The process is dynamic, as size diminution creates fresh reactive surfaces, which allow reaction between solids and/or create small domains of highly concentrated solution in small amount of solvents (e.g., water). The later can be adsorbed from the reaction atmosphere or is added in LAG. Moreover, particle diminution decreases diffusion limitations, allowing movement of ions inside the solid during reaction time (min to h). Mechanical stress during milling/grinding generates heat at the interface between particles, and local temperature increases can lead to large increases of the reaction rate. While most reactions are endergonic and use the mechanical energy as input, the IUPAC definition of MC includes exothermic reactions between two solids where the reaction should occur spontaneously (if the reaction rate is large enough) but is inhibited by the absence of contact (i.e., occurs at the interface, which is small for macroscopic solids). Upon particle size decrease and/or pressuring in MC processes, the reaction occur. However, the reaction should stop when grinding is stopped. In fact, the well-known and thermodynamically favorable "termite" reaction of aluminum powder with Fe_2O_3 is initiated usually by external heating. The same reaction

became self-sustainable and controlled by grinding under MC conditions [29]. As we will see, the polymerization of ANIHCl with APS at high concentrations resembles the “termite” reaction (obviously at lower temperatures), and the models used to understand one reaction could be applied to the other.

2. Results

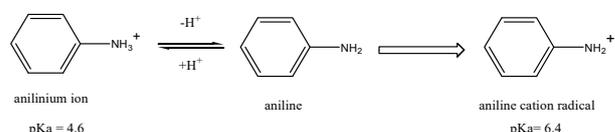
2.1. Synthesis of Polyanilines

2.1.1. Mechanochemical Polymerization of Aniline

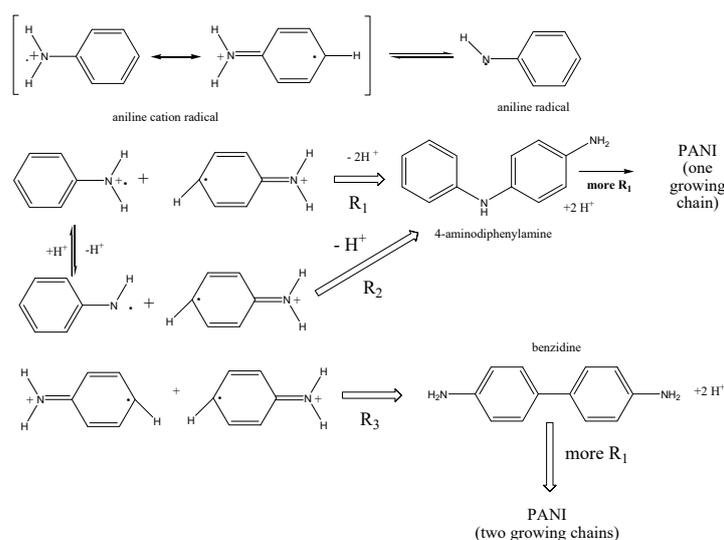
First, we discuss the state of the art in the polymerization of aniline in solution. Aniline is easily polymerized in an acid solution to produce PANI [30]. The formation of dyes and precipitates (likely polymers) was already produced by the oxidation of aniline even before Staudinger’s macromolecular hypothesis was defined. Therefore, they were considered compounds with only eight benzenoid rings. Wilstater and Dirogi [31], and Green and Woodhead [32], oxidized aniline (in acid media) using dichromate, persulfate, H_2O_2 (catalyzed by Fe^{+3}), and ClO_3^- (catalyzed by copper or vanadium salts). When metal containing ions were used, the product was heated with sulfuric acid to eliminate the metal ions [31], but cross-linking and/or degradation could occur. Josefowicz and coworkers [33] already recognized polyaniline as a semiconducting polymer, studied it, and built applications, all at least 9 years before the official discovery of conducting polymers [34]. They use ammonium persulfate to avoid metal contamination (or chlorination with chlorate), and it has become the most widely used oxidant [21]. The mechanism of aniline polymerization is supposed to involve three stages: an induction period, the growth of the polymer, and termination [35]. However, the stages occur simultaneously for all (or most) of the chains, and the termination occurs when the oxidant is consumed. This is unlike chain polymerization of vinyl compounds (radical, cationic, or anionic), where initiation, propagation, and termination occur along the whole polymerization time. Electrochemical (oxidative) polymerization involves similar steps, but the conditions are somewhat different [36]. The oxidant is the electrode, the oxidation occurs at the polymer/solution interface, and the mass transport conditions imply low concentration of the monomer. Indeed, when polyaniline is polymerized at high current densities, the polymer becomes degraded (showing the so-called “middle peak”) since oxidized polymer reacts with water. A similar situation exists when aniline is polymerized chemically (with oxidant) at ratios of oxidant/monomer larger than the stoichiometric amounts.

The initial stages of aniline oxidation are as follows:

The aniline cation radical is produced by oxidation of unprotonated aniline, which is produced by fast equilibria from the protonated aniline (anilinium ion) (Scheme 1). The initial condition is acidic (due to hydrolysis of the anilinium ion of added acid). Since the formation of the radical cation (oxidation) is fast and irreversible, all the anilinium could be converted to radical cation. The aniline radical cation suffer fast (<1 ms) follow-up irreversible reactions [36] to give 4-aminodiphenylamine (head-to-tail dimer) and benzidine (tail-to-tail dimer) (Scheme 2). A proton is produced in the dimerization process, furtherly decreasing the pH. A solution of 0.2 M anilinium ion (IUPAC, [21]) will have a pH of ca. 2.64, which will decrease with the reaction progress. In nonaqueous (and non-protic) media (e.g., DMSO), all aniline is available for oxidation, but the aniline will deprotonate the growing chain, converting it into emeraldine base (EB). Chemical polymerization could proceed, but electrochemical polymerization will stop since EB is non-conductive and no electrons can flow through. However, in protophobic media (e.g., ACN), the protons produced are able to protonate the PANI film, maintaining it in its ES (conductive) form [37].

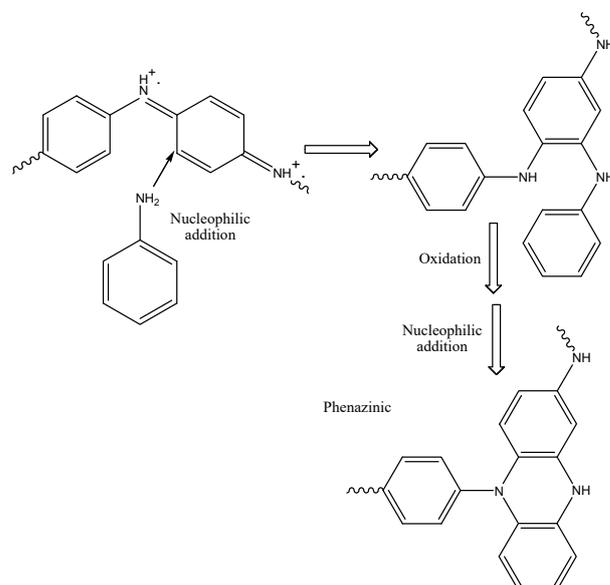


Scheme 1. Oxidation of anilinium ion.



Scheme 2. Polymerization: follow-up reactions of aniline cation radical.

There is spectroscopic (in situ FTIR) and electrochemical evidence of the occurrence of those reactions [38], in the same conditions (acid aqueous media) used for the electrochemical and chemical polymerization of aniline. Benzidine can be produced by tail-to-tail dimerization of cation radicals or by the reaction of an aniline radical (produced by deprotonation of the cation radical). Since the cation radical is less acidic than the anilinium ion, it will remain protonated in acid media, becoming deprotonated in neutral media. Therefore, benzidine concentration increases at a lower pH [35]. The polymerization is carried out in acid media to avoid head-to-head coupling, which gives rise to hydrazobenzene and azobenzene (in basic media) [39]. Unlike 4ADA and benzidine, PANI could not grow from azobenzene molecules, and the polymer does not grow in basic media. However, if the media is un-buffered (such as in solvent free polymerization) the production of protons could lower the pH (at least locally) and allow polymer grow. Additionally, nucleophilic addition of non-protonated (at higher pH values) aniline [40] gives rise to phenazine-like units (Scheme 3) [41]. Indeed, this reaction (using 4ADA as precursor and dichromate as oxidant) is the method to synthesize molecular dyes with phenazine units [42], related to the first organic synthetic dye, mauveine [43].



Scheme 3. Formation of phenylphenazine units in PANI.

The phenazine units localize the charges and lower its mobility, decreasing drastically the conductivity and acting as defects. The side chain could act as crosslinking points increasing the molecular weight of the polymer. Due to the existence of Peierls's transition [44,45], the charges could not move along the whole PANI chains. Therefore, long chains (with a polymerization degree larger than 30) do not show higher intrachain conductivity. Moreover, longer chains will be difficult to assemble in order, and the interchain conductivity would be smaller. Therefore, promoting the crosslinking does not produce a more conductive polymer. The long discussion in the early 1900s [31–33] about greenable aniline black (likely linear emeraldine) and ungreenable aniline black (likely a polymer containing a large amount of phenazine units) suggests that phenazine units are produced by the reaction of aniline with emeraldine, using dichromate as an oxidant. Since dichromate ion is a weaker oxidant ($E_0 = 1.33 V_{\text{NHE}}$) than persulfate ($E_0 = 2.01 V_{\text{NHE}}$), the reaction does not seem related to polymer overoxidation. It is noteworthy that electrochemical polymerization is usually performed at a lower potential of 1.0–1.05 V_{NHE} [46]. It is known that pernigraniline (produced at such electrode potentials) reacts easily with nucleophiles [47], including water (with degradation). It is surprising that the chemical oxidant most widely used to produce PANI has a redox potential ca. 1.0 V higher than the one used in electrochemical polymerization. Chloride is the most widely used counterion to produce PANI. On the other hand, the formation of Cl_2 by the oxidation of Cl^- with persulfate is thermodynamically favorable. Indeed, the usual polymerization procedure calls for APS to be dissolved in a small amount of water (maximum concentration = 3.5 M) and not in HCl solution (e.g., 1 M) because a strong chlorine smell is observed in the latter case. The Cl_2 formed could produce the electrophilic substitution of aniline and/or of PANI. Moreover, solution polymerization is carried out at low temperatures (0–5 °C) under cooling, since at higher temperatures the nucleophilic attack of water on the polymer leads to the hydrolysis of the quinonimine units, yielding carbonyl groups (quinone like) [48]. All reactants are in solution, but the actual growth of the polymer chain is a heterogeneous reaction because the polymer is insoluble in water. That is, the oxidant could oxidize the polymer chain not at the growing end but in other part of the polymer (not even of the same chain), which is electrically connected to PANI. On the other hand, Stejskal and coworkers [49] have demonstrated that aniline could polymerize even at low temperatures (–27 °C) with solvent (water) in the frozen state. This is a solid state polymerization, similar to mechanochemical synthesis, while the heat release could produce local melted regions. The polymerization reaction is highly exothermic, and it is often done in a reactor cooled by ice. Cavallo et al., simulate the polymerization kinetics of aniline in aqueous acid [50], using the kinetic model described by Tzou and Gregory [51]. Using the reaction enthalpy and the thermal transfer parameter of the reactor (extracted from the cooling profile after the reaction has finished), it is possible to extract the kinetic constants from the temperature–time profiles. Moreover, the model can be used to simulate the temperatures and reaction times. At high effective concentrations (>1 M), the model will predict high temperatures and fast reactions. We simulate the kinetics of aniline (as AnilHCl) polymerization with persulfate (equimolar to aniline) at the maximum concentration possible (3 M, due to solubility). The model suggests temperatures as large as 600 °C and initiation times of less than 10 s. To test the hypothesis, we experimentally mix 2 M solutions of AnilHCl and APS (ca. 15 mL each), while measuring the temperature. Since the reaction heat could project corrosive solution driven by the water vapor, small volumes (<20 mL) should be used, and the observation and temperature measuring should be performed away from the direction of possible projections. After 10 s, the clear solutions ($T_{\text{initial}} = 22.3 \text{ }^\circ\text{C}$) turn blue, and the temperature increases, reaching 30 °C (after the induction period) at 40 s. Then, the temperature reaches ca. 100 °C after 115 s (ca. 2 min). After that, the water evaporates, and the temperature remains constant but likely does not reflect the temperature of the whole polymer mass. (Figure 1). Vapor is seen coming out, and a bluish-violet porous mass of polymer remains in the beaker. After cooling, water is added, and the polymer filtered out. These results show that the reaction media of concentrated solutions produces large amount

of heat, as predicted by the model, being able to reach high temperatures (ca. 580 °C) in ca. 180 s (3 min) (Figure 1). The experimental data could not surpass the boiling point of water since it evaporates (absorbing heat), and the reaction was shut off for lack of solvent. The data are relevant to the analysis of mechanochemical synthesis where water is present since it is absorbed from the atmosphere or added as part of the experimental procedure. Obviously, in real conditions the reactants and products will decompose below 580 °C. However, the data suggest that high (even 100 °C) local temperatures can be attained.

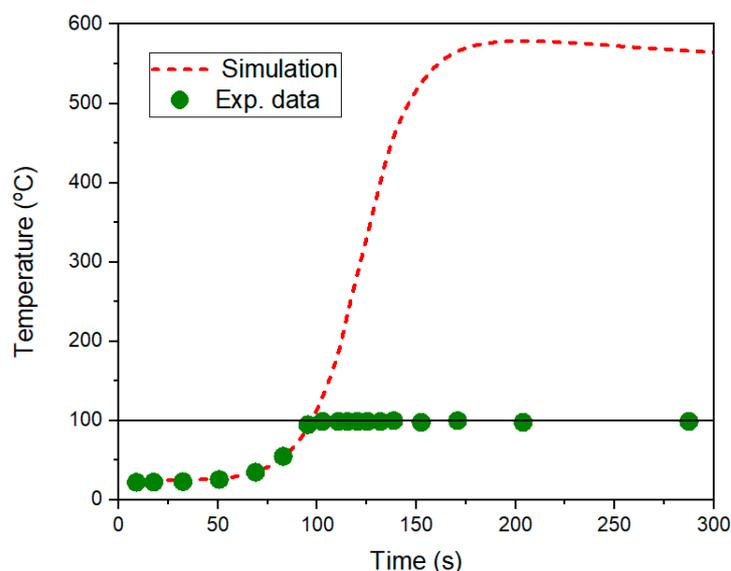


Figure 1. Comparison of experimental data (green circles) from the aniline polymerization at high (2 M) concentration of AnilHCl and APS with a simulation based on the kinetic model (dashed red line).

The large surface area of the powder allows for heat release by radiation, air convection, and transference to the reaction holder. In an open mortar, the most common device used (see Table 1), even local water evaporation could reduce the temperature. In some cases, the reaction holder (e.g., mortar) was cooled before grinding (see Table 1). Given the large mass ratio between the grinding media and the sample, this procedure should maintain a low temperature.

A simple test consisting the mixing of equimolar AnilHCl and APS (both dried in a desiccator after separate milling) is devised (see SI for experimental details). It is observed that 5 min of milling is enough to change the temperature, while the color of the powder changes from pale yellow to dark blue (Figure 2).

The temperature (measured by an infrared thermometer) changes from 27.3 °C to 31.2 °C. When only APS is grinded alone in the same mortar, no increasing trend is observed, suggesting that mechanical heat is not the cause of the increase of temperature. If the mortar is left still in a camera with a drying agent (anhydrous CaCl₂), the temperature only decays due to cooling (to 28.9 °C). On the other hand, if the mortar is then placed in a chamber with 100% humidity, the temperature increased again to 29.8 °C, suggesting that the absorbed water from the environment promotes further reaction.

While cryogenic grinders have the capability of cooling the grinding jar to low temperatures [52], ball mills were usually used at ambient temperatures to polymerize aniline. It is noteworthy that, in aqueous solution polymerization, relatively large temperatures (>50 °C) are usually precluded to avoid the nucleophilic attack of water [53]. On the other hand, it has been found that dry PANI backbone can withstand up to 500 °C without degradation [54]. Therefore, water-free MC polymerization of aniline should be better than that using liquid-assisted MC (Table 1). The stoichiometry of the reaction of oxidant (e.g., APS) and aniline (as anilinium salt) is shown in Scheme 4 [55]:

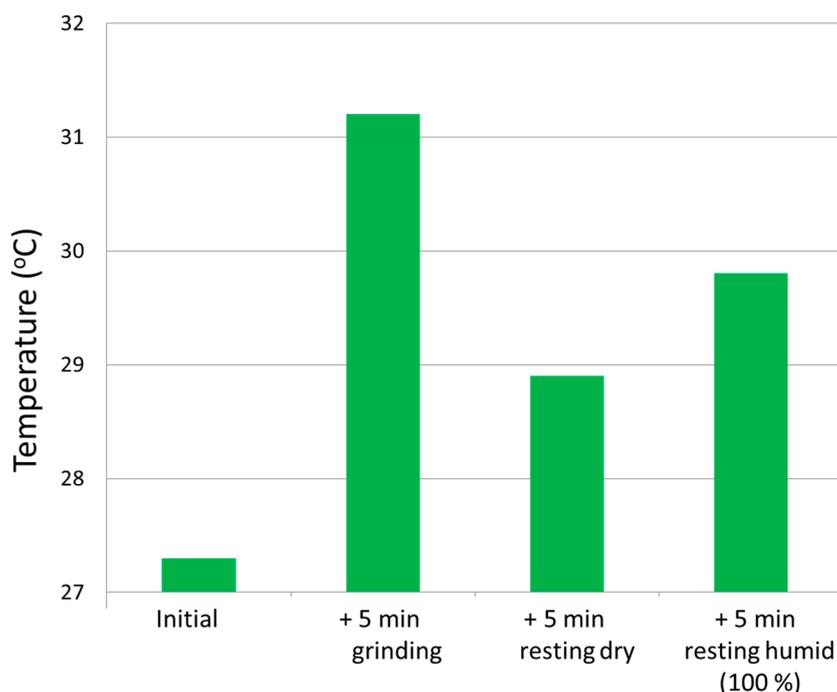
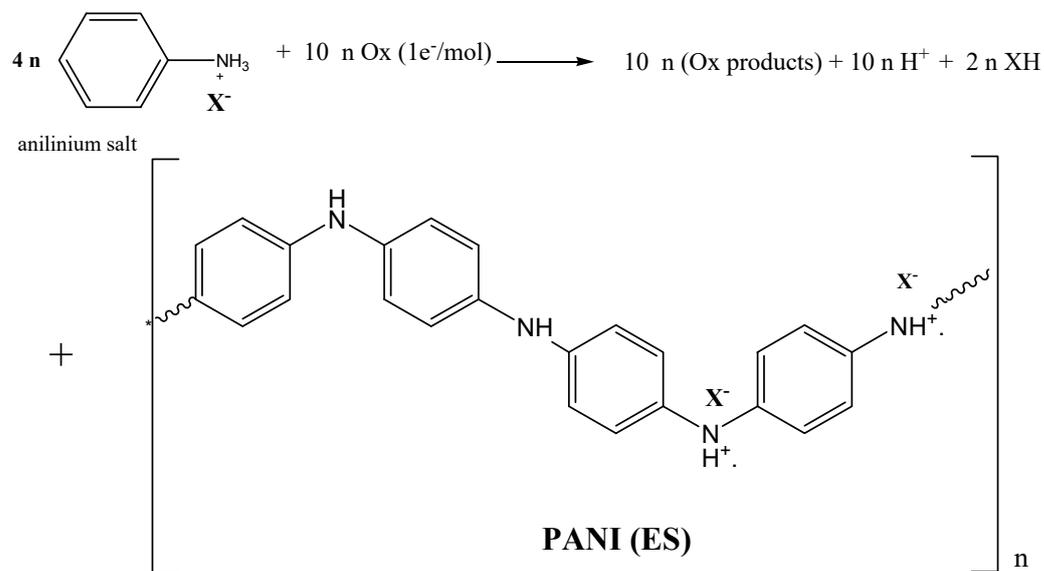


Figure 2. Evolution of temperature during grinding in a mortar and the effect of humidity on the polymerization process.



Scheme 4. Reaction of aniline salt with and oxidant to give doped PANI (ES form).

The reason that more moles of oxidant (25% of APS ($2e^-/\text{mol}$)) are required to produce PANI is that 0.5 moles of e^- are required (per PANI unit of four rings) to oxidize PANI to its pernigraniline state (from the ES units). During each monomer addition cycle, the product is formed in the emeraldine state, which is less reactive towards aniline. Potentiometric measurements show that the chain grows in the pernigraniline state [56]. If the oxidant is present at a molar amount of less than or equal to 2.5 times the moles of aniline, the reaction stops when the oxidant (limiting reagent) is used up and the chains remain in the emeraldine state. On the other hand, if excess (>2.5 more moles of APS than aniline) oxidant is present, the polymerization stop when all aniline (limiting reagent) is used, but the chain stays in the pernigraniline state. In an aqueous solution, it suffers nucleophilic addition of water ($>55 \text{ M}$), forming $-\text{OH}$ terminated chains (aminophenol units) and/or

cutting the chain forming the same groups. The excess oxidant reoxidizes the aminophenol units to quinonimine, and the degradation continues until all excess oxidant is used up. In electrochemical driven oxidation, applying a potential where emeraldine is oxidized to pernigraniline ($>1.0 V_{\text{NHE}}$) induces the complete degradation of PANI into benzoquinone (detected by in situ FTIR in the solution [38]). One additional question regards the protonation state of the growing chain (i.e., present in the protonated state (pernigraniline salt, PNS) or an unprotonated state (pernigraniline, PN)). The electrochemical data of ion exchange suggest that PANI (PNS) deprotonates in 1 M monoprotic strong acid [57]. Since it is known that nucleophilic addition is faster in the protonated quinonimines than in the deprotonated ones [58], the nucleophilic attack of aniline to the growing chain (PN) will be faster at a higher acid concentration. This seems to be the case for $[\text{HCl}] > 1 \text{ M}$ [59].

The induction time occurs because dimers (4ADA and benzidine) are slowly formed from aniline to initiate the chains. The addition of the dimers or PANI eliminate the induction period [51]. Moreover, if other polymers containing aniline moieties are present in the polymer solution, the PANI chains grow linked to the polymer instead of becoming free chains [60].

The polymerization reaction produces protons, which form acid with the anions present [61]. Indeed, the release of a highly concentrated solution of acid has been observed during the solid state polymerization of aniline [62]. Usually, it is assumed that the anion in the anilinium salt is used as a counterion to dope the polymer. However, it is likely that both sulfate (from persulfate) and the anion (X^-) in anilinium salt are used. In the solution, this could be the situation if XH is as strong an acid as H_2SO_4 . However, if anilinium salts (e.g., $\text{CH}_3\text{COO}^- \text{AniH}^+$) of weak acids are used, the anions are protonated, and only sulfate will be the counterion of PANI (ES form). Moreover, it is known that a high concentration of chloride ion (2–6 M) favors the nucleophilic addition of Cl^- , leading to the formation of a polymer including 2-chloroaniline rings [63]. In a solution, such situation occurs at concentrations of HCl higher than 1 M. In a solid state reaction, pure HCl will be released, but in a wet reaction mixture the acid concentration could reach maximum solubility (ca. 12 M), then react with PANI.

While mechanochemistry can be traced back to prehistory, mechanochemical synthesis of PANI (called aniline blacks) also has a long history. Production of aniline black was a well-established process in the printing of cotton fabrics [64]. The process, discovered by J. Lightfoot, involves mixing AniHCl with chlorate salts and a catalyst (usually copper salts) [64]. The process was simple and provides a highly sought black color for inexpensive cotton cloth. The color was permanent and resistant to alkali (used in the 19th century to wash clothes) and light. The aniline blacks were specifically for cellulosic materials (cotton, paper, and wood) since they do not dye wool or silk well. It is likely that reducing groups (e.g., thiols) in the protein backbone of wool or silk inhibit the reaction. In our (UNRC) teaching labs, where wood is still used as counter material, Lightfoot's mixture (as a paste) was impregnated in the wood and left to react for 48 h, providing a black dye resistant to chemicals. Since a paste of solid salts is used, Lightfoot's recipe for dyeing cellulosic materials probably was the first industrial mechanochemical synthesis of (we know now) a conducting polymer.

Table 1 summarizes the research on the polymerization of anilines (without other components).

The first modern use of mechanochemical methods to synthesis of polyaniline was performed by Gong et al., who produce PANI in the presence of silicotungstic acid [65]. They react frozen aniline ($-20 \text{ }^\circ\text{C}$) with silicotungstic acid by MC, and then grind the product with APS in a mortar, producing PANI by MCP. They changed the ratio between the Keggin acid and APS, but they found an almost constant amount of anion (tungsten 50% in weight) and conductivity (ca. 0.3 S/cm), except in extreme values of the ratio.

Table 1. Summary of reaction conditions for MCP of aniline.

Monomer	Oxidant	Acid Added	Mechanochemical Device/Material	Assistant Liquid	Time Pol./Curing	Washing	Ref
ANI	APS	H ₄ SiW ₁₂ O ₄	Mortar/unknown	none	30 min	H ₂ O	[65]
AniH ₂ Sul AniCSA	APS	H ₂ SO ₄ CSA	PBM 600 rpm/SS jar and balls	none	1 h	EtOH/H ₂ O	[66]
Ani (added acid)	APS	TsOH DBSH MSH	Mortar	H ₂ O	30 min	DEE/EtOH /H ₂ O	[67]
Ani (added acid)	APS	HCl H ₂ SO ₄ H ₃ PO ₄	Mortar	H ₂ O	20 min	DEE/EtOH /H ₂ O	[68]
AniHCl ¹	APS	HCl	Mortar/agate	none	1.5–4 min/24 h	H ₂ O	[69]
AniH ₂ Sul	APS	H ₂ SO ₄	Pan mill(steel) Mortar	none	20 cycles 40 min	H ₂ O/EtOH	[70]
AniHCl	APS	H ₂ SO ₄	Mixing mortar + rest	none	5 min mix/24 h	EtOH	[62]
AniHCl	FeCl ₃	HCl	Mixing mortar + rest	none	5 min mix/1 week	EtOH	[62]
AniHCl	AgNO ₃	HCl NO ₃ H	Mixing mortar + rest	none	5 min mix/1 week	EtOH	[62]
AniHSu	SeO ₂	SeO ₃ H ₂	Mortar	none	1 h/ 24–48 h	H ₂ O/Acetone	[71]
AniH ₂ Sul	KPS	CSA CA	Mortar	none	30 min/ 24 h	H ₂ O/MeOH	[72]
AniHCl	APS	HCl	PBM 300 rpm/agate	none	1 h	EtOH/H ₂ O (pH = 2)	[73]
Ani ₂ SA	APS	CA	Mortar	none	30 min/24 h	H ₂ O/EtOH/MeOH	[74]
AniHCl	FeCl ₃ ·6H ₂ O	HCl	Mortar	none	50 min	H ₂ O	[75]
AniHCl	FeCl ₃ ·6H ₂ O	HCl	Mortar	none	42 min	H ₂ O/EtOH	[76]
Anit-PASA AniPAMPS	APS	t-PASA PAMPS	PBM 300 rpm/agate jar and balls	none	1 h	Dialysis	[77]

¹ The photographs in [69] show a light blue-green color of AniHCl, while it should be uncolored. Our own experience suggests that aged AniHCl spontaneously polymerizes in air, contaminating the salt with PANI.

The foundational study of mechanochemical polymerization of aniline was published by Kaner and coworkers [66]. They polymerize aniline sulfate with ammonium persulfate (APS) using a sealed ball mill (stainless steel balls and jar). After 3 h of milling, the anilinium salt converts into polyaniline and the ammonium persulfate into ammonium sulfate. As in any mechanochemical reaction, a stoichiometric balance is important because there is no solvent to dissolve the other products. Use of aniline salts is reasonable since they are solid, but the pH of the media will be only moderately acid since the pK_a of anilinium ion is 4.59 [78].

Therefore, even at a high concentration of 4.25 (solubility of the salt), the pH will be ca. 2. On the other hand, PANI in solution is usually polymerized in 1 M acid, with the pH close to zero. Kaner and coworkers studied the effect of Aniline/APS ratio on the yield of PANI (0.25 to 10). At a low ratio the yield is low (ca. 42%), and the maximum yield is obtained at a ratio 0.5 (65%) [66]. The yield decreases afterwards. The authors suggested that it is due to the formation of oligomers. However, it would imply that more than 80% of aniline was lost to secondary reactions, which is not detected experimentally during washing. The yield % should be calculated taking into account the limiting reagent (APS below ratio < 0.8 and anilinium for ratio > 0.8). Additionally, it has to be assumed that the mass of the polymer corresponds to the ES form of PANI (C₂₄H₂₄N)(SO₄H)₂. Otherwise, the yield will exceed 100%. The plot (Figure 3) gives a smooth variation where the highest yield % (for the limiting reagent) is 78.5% at a high anilinium/APS ratio (10).

Since no solvent is present and the PANI chain grow by adding aniline units to the chain, it seems that a large excess of aniline is required to grow the polymer around small APS grains [66]. Moreover, the authors find out that the molecular weight increases when the ratio is changed from 1:1 (11,220) to 2:1 (18,200) and 3:1 (45,700) in a similar fashion to the recalculated yield (Figure 3) but not related with the published yield (Figure 4 in [66]), where a growing amount of oligomers is produced. The larger molecular weight reported (45,700 g/mol) is higher than the one reported before for polyaniline made in solution (27,000 g/mol), but the high MW peak (501,200 g/mol) is lower than the one measured before for PANI produced in solution (210,000 g/mol) [79]. An interesting point is the

relatively large specific surface area (BET) of $69.7 \text{ m}^2/\text{g}$ obtained. It could be envisaged that oxidant (and/or ammonia sulfate product) crystals act as a pore former inside the polymer matrix. Another interesting result is the polymerization of aniline sulfate by simple hydrostatic pressure [66]. Monomer (aniline sulfate) and oxidant (ammonium persulfate) were finely milled and mixed by shaking. Then a high pressure (up to 16 kpsi) is applied between two steel rods. Since the product (PANI ES form) is electrically conductive and the reactants are not, the evolution of resistance (decreasing) shows the formation of the conducting polymer. The polymerization takes ca. 85 h but is only driven by pressure, not additional milling or local heating. The hydrostatic pressure system seems to be a very clean way to produce conducting polymers, but it has not been used after this work [66].

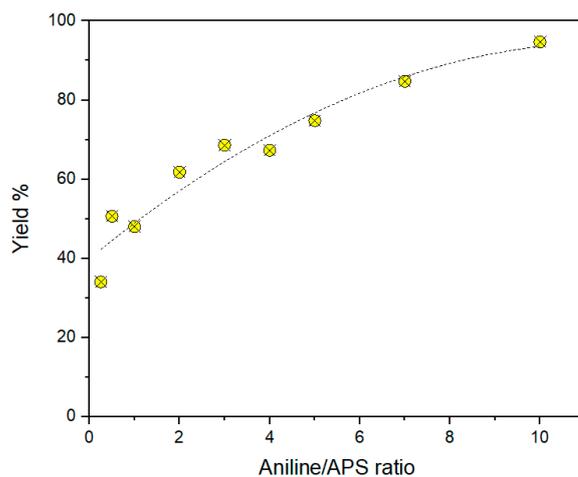


Figure 3. Effect of aniline/APS ratio on the yield% of PANI. (Recalculated using stoichiometry (Scheme 4) from data in [66]).

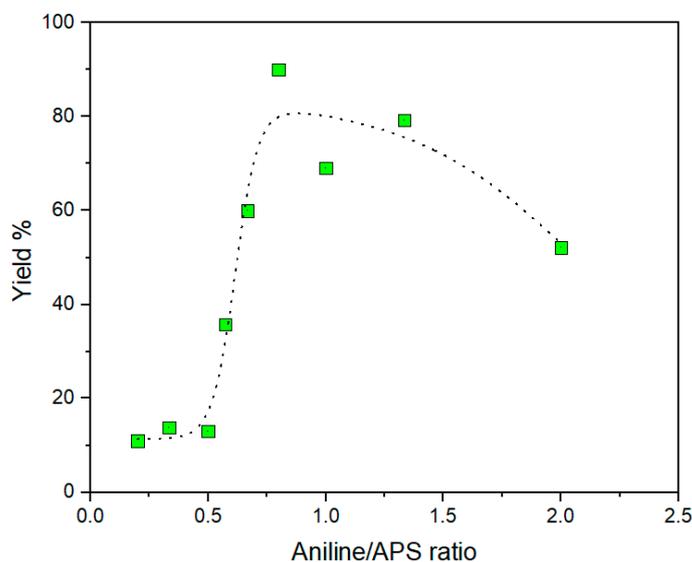


Figure 4. Effect of aniline/APS ratio on the yield% of PANI. Recalculated using stoichiometry (Scheme 4) from data in [69].

The reactants have to diffuse from the oxidant particle to the monomer particle and vice versa. The diffusion coefficients of ions inside crystals are in the order of $5 \times 10^{-13} \text{ cm}^2/\text{s}$ [80]. The time required to polymerize by hydrostatic pressure would be satisfied by interdiffusion between particles of ca. $7 \mu\text{m}$, which is a reasonable size of crystalline obtained by ball milling [81]. Moreover, in several published works on MC of PANI, a “rest” time period (1 day to 1 week) (Table 1) is applied after the grinding

procedure. One likely situation is that water acts as a liquid mediator in the polymerization (Figure 2). Anilinium salts and APS are highly hygroscopic, and hygroscopic acids (H_2SO_4 , HCl) are produced during the reaction. Therefore, water will be absorbed before, during, or after (the “rest” period) the reaction. In a particle of 10 μm , the ions should take 500 s (8.33 min) to interdiffuse (Fick’s law). This is much lower than the 1–3 h used in the ball milling [66], or the 83 h in the hydrostatic pressure experiment [66]. However, in another work (Table 1), the polymerization is performed in a mortar in less than 10 min. We try simple mortar grinding of dry AniHCl (1 g) and APS (1:1). The white powder mixture changes to green-blue after only 3 min of grinding, suggesting that the reaction occurs. Adding 50 mL of water (at the green-blue state) visibly induces a reaction showing a strong blue color of a solid dispersion. After 30 min a green solid appears, which, filtered, washed, and dried, shows the FTIR spectrum of PANI. However, after removing the solution with PANI, the flask (see supporting information in S1) shows a clear PANI film. It has been shown [82] that such film grows on the surface of the glass and cannot be produced by adsorption of solid PANI microparticles. Therefore, not all AniHCl and APS have reacted before water addition and the dilution converts the polymerization from a MCP to a solution/dispersion case. The point is relevant because when washing with water, a grinded mixture could induce a reaction.

Therefore, the solvent used in washing is quite important (See Table 1). Otherwise, the mixture should be diluted greatly or quenched by freezing. In this case, no reaction is observed after water addition, and no film is formed in the beaker where water was added. Therefore, it could be assumed that the solid state reaction is complete. In a solid state reaction, if a non-volatile acid is used (e.g., H_2SO_4), the acid will remain with PANI and can be washed out with water. On the other hand, other acids such as HCl are volatile and will be released during the reaction. As can be seen in Figure S2 (Supplementary Information), when AniHCl and APS are grinded in a glass mortar, the indicator paper shows a low pH (<1) since the wet indicator absorbs the HCl (gas) released by the polymerization reaction (Scheme 4).

The results suggest that the reactions in Scheme 4 should be taken into account when analyzing data on MCP of aniline. Huang et al. use AniH₂Sul as monomer salt and APS as oxidant [66]. Therefore, the only acid present is H_2SO_4 . In MCP studies of aniline polymerization, other acids are added (Table 1), and even it is claimed that adding a weak acid (e.g., citric acid) “dopes” the polymer. In the presence of sulfuric acid, citrate is not present and could not dope PANI. Abdiryim et al. studied the effect of different strong organic acids (TSA, MSA, and DBSA) on the properties of solid state synthesis of PANI [67]. The procedure is different than that of Kaner and coworkers [66]. One ml of water is placed on a mortar, then pure acid (0.015 mol, 15 M) is dissolved and aniline (0.01 mol, 10 M) is added. As can be seen, there is a ca. 50% excess of acid. A white precipitate is formed, which is the anilinium salt of the acid since the concentration is larger than the solubility of the salt. Then, persulfate (2.2 g, 0.0097 moles) is added and ground in the mortar for only 30 min until the reaction is carried out. The ratio of aniline/oxidant is close to 1:1. As discussed before, the reaction does not occur in a dry state but in a concentrated (unknown) solution of anilinium salt and persulfate (maximum solubility 3.5 M). Therefore, it will be very fast ($t_R = 60\text{--}100$ s) and with a large thermal heating. Indeed, the cyclic voltammograms of PANI produced using this method show a significant “middle peak”, which is usually assigned to redox groups (e.g., quinones [61]), produced during PANI degradation. The same group studied the effect of different inorganic strong acids on the mechanochemical polymerization of aniline [68]. The procedure is similar, using 1 mL of acid solution (37% HCl, 96% H_2SO_4 , and 87% H_3PO_4). The solid is filtered out and washed with diethyl ether (DEE), ethanol (EtOH), and water (W) and dried under vacuum. It should be mentioned that both APS, ammonium sulphate, and unreacted anilinium salts are insoluble in DEE; therefore, only oligomers could be removed. On the other hand, ethanol and water remove the organic salts, but usually ethanol is the last used. As can be seen, the

most conductive polymer is PANI/HCl, while the least conductive is PANI/DBSA. Those with the highest yield have the largest conductivity.

Bekri-Abbes and Srasra obtain a similar yield % (Figure 4) of AniHCl but lower ($6000\times$) conductivity [69]. The effect of the aniline/APS ratio on yield % is quite different than the one shown in Figure 3. It is likely that the different method of MCP (closed ball mill in [66] and open mortar/pestle in [69]) affect the MCP through the absorption of water from air in an open mortar.

Zhou et al. polymerize aniline sulphate with APS in a pan mill (600 rpm) and compared the polymer with one produced by 40 min of mortar grinding [70]. The molecular weight (estimated by viscosimetry) is lower for two pan mill cycles than for the mortar grinded mixture, becomes similar for 10 cycles, and is larger ($>2\times$) for 20 cycles. Unfortunately, the time for the cycle is not provided. Sedenkova et al. polymerize AniHCl using different oxidants (APS, FeCl_3 , and AgNO_3) [62]. The mechanochemical work is constrained to mixing the anilinium salt and the oxidant with a mortar (5 min). Then the powder is left to react in air (unknown humidity). Pellets are produced at 700 Mpa to measure conductivity, and a droplet of liquid is released. While APS produces PANI in 24 h, one week is required for Fe^{+3} and Ag^+ . While PANI is produced with APS, as expected, only oligomers and branched non-conductive polymers were obtained using Fe^{+3} or Ag^+ . The absence of polymerization was attributed to the low reduction potential of Fe^{+3} (0.77 V) or Ag^+ (0.799 V). However, PANI has been produced in solution using iron chloride [83,84] and silver nitrate [85]. Additionally, Fe^{+3} [86] and Ag^+ [87] can be used as oxidants to produce PANI in nanocomposites (see below). It is likely that longer (>5 min) grinding times are required to affect the polymerization. Posudievsky et al. oxidize AniHCl with APS in a PBM device (agate jar and mortar). They obtained a high conductive PANI (22.3 S/cm) and patented the procedure (see patents below) [73]. The procedure is quite similar to that used by Huang et al., except for using 300 rpm vs. 600 rpm in the ball mill and aniline hydrochloride instead of aniline sulfate [66]. The highly conductive PANI is obtained at a low APS/ANI ratio (0.5). The conductivity decreases when the ratio is increased and, at the stoichiometric ratio of 1.25, a polymer of relatively low conductivity (0.365 S/cm) is obtained. However, the conductivity for all materials is higher than the value reported by Huang et al. of ca. 0.01 S/cm [66]. Bhandari and Khastgir polymerize aniline in the presence and absence of citric acid (CA) to induce the formation of nanofibers of PANI [74]. While CA could have some effect on the morphology of PANI aggregates through hydrogen bonding, the authors claimed that PANI produced in the absence of CA is "undoped" when there are plenty of anions and acid to dope PANI. Moreover, the cyclic voltammogram (in 1 M H_2SO_4) for PANI produced in the presence or absence of CA show a broad peak with little separation between the first and second processes. This is not the typical behavior of "standard" PANI (synthesized in solution) and resembles PANI made electrochemically in nonaqueous solvent [88]. Du and coworkers polymerize aniline with $\text{Cl}_3\text{Fe}\cdot 6\text{H}_2\text{O}$ (1:2 moles, 20% defect of oxidant) and found that the hydrated salt melts upon grinding and act as a liquid assistant or solvent [75,76]. Extensive hand grinding (40–50 min) produces a low yield (8%) of PANI in the form of nanofibers, such as those produced by interfacial polymerization [28,89], but not requiring toxic organic solvents (e.g., chloroform). Interestingly, the authors do not find any contamination of the PANI NF with Fe. Gribkova et al. use MC (PBM) to polymerize aniline as salts of polymeric acids, PAMPS and t-PASA [77]. The results were compared with the same salts used as monomers in solution. The results are similar and relatively low conductivities were obtained (Table 2). However, TEM images of the polymer composites show that the MC procedure renders layered arrangements of PANI–polyacid while the polymerization in solution gives globular structures. Recently Peramal et al. used SeO_2 as an oxidant to polymerize aniline hydrogen sulfate [71]. They ground in a mortar for 1 h and let the material rest for 24–48 h, observing the effect on polymer properties. They also changed the ratio of SeO_2 /ANI, but the authors do not declare which is the product of SeO_2 reduction.

SeO₂ (in acid media) has a reduction potential of 0.74 V_{NHE}, slightly lower than Fe⁺³ (0.77 V), which is able to polymerize aniline.

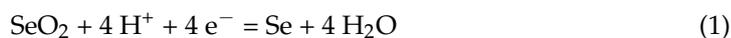


Table 2. Effect of anion dopant on the yield and conductivity of MC synthesized PANI.

Anion/Acid	Ratio Aniline/Oxidant	Ratio Acid/Aniline	Reaction Time (min)	Yield %	Conductivity (S/cm)	Ref.
C ₁₈ H ₂₇ SO ₃ ⁻ /DBSA	1.09	1.42	30	75	0.14	[67]
H ₂ PO ₄ ⁻ /PA	1.09	1.23	20	75	0.8	[68]
CH ₃ SO ₃ ⁻ /MSA	1.09	1.42	30	60	0.9	[67]
C ₆ H ₅ SO ₃ ⁻ /TSA	1.09	1.42	30	81	1.25	[67]
HSO ₄ ⁻ /SA	1.09	1.72	20	78	3.8	[68]
Cl ⁻ /HCl	1.09	1.14	20	82	12	[68]
Cl ⁻ /HCl	1	1	2	90	0.0025	[69]
SO ₄ ⁻² + Cl ⁻ / H ₂ SO ₄ + HCl	0.8	1	5 min + 24 h	ND	0.21	[62]
SiW ₁₂ O ₄₀ ⁻⁴	variable	0.1	30 min	16–40	0.32	[65]
t-PAS/t-PASA	APS	2	PBM 300 rpm/agate jar and balls	1 hr	0.024	[77]
PAMPS/PAMPSA	APS	2	PBM 300 rpm/agate jar and balls	1 hr	0.031	[77]

However, the reaction (Equation (1)) produces Se, which is insoluble in water and probably remains inside the polymer. Since metallic Se has been used to “dope” PANI [90], increasing the conductivity (by three orders of magnitude), the fate of the Se seems relevant. However, the higher conductivity obtained is 0.488 S/cm (ratio 1:1.5 when waiting 24 h), which is lower than other PANI obtained by MC (Table 2). Therefore, no clear effect of Se on conductivity is found. SeO₂ exchanges twice as many electrons/mol than APS. Therefore, if a 1:1 SeO₂/ANI ratio is used, some of the SeO₂ remains as SeO₃H₂ and is able to act as counterion dopant of PANI. However, since the first pK_a of SeO₃H₂ is 2.62 [91], and the pK_a of HSO₄⁻ (present from the monomer salt) is 1.99 [91], the acid will be neutral (protonated), and most likely hydrogen sulfate will be the counterion dopant. Using an SeO₂ ratio larger than 1 implies an excess of oxidant which could overoxidize the PANI.

From the experimental point of view, 80% of the published MCP of aniline were made using a mortar and pestle. As was discussed in the introduction, the mortar and pestle is a low cost device to produce PANI in small quantities. Since the pale mixture at the beginning becomes dark blue upon polymerization, it is possible to grind the mixture until full conversion is achieved, making it reproducible. Using a clear glass mortar, it can be seen that the dark color begins to appear in the contact region between the mortar surface and the head of the pestle. This result suggests that the reaction is induced by mechanical grinding and not by the effect of oxygen/water, which will act more in the upper layer of the powder. On the other hand, a warning seems in order. A strong odor can be smelled during mortar grinding of AniHCl + APS, which could be due to volatiles (e.g., aniline) or aerosols of powdered reactants. Placing a filter paper, wet with a solution of p-benzenediazonium salt, close to the mouth of the mortar produces a deep yellow color likely due to the formation of the diazoaminobenzene from the reaction of the diazonium ion with aniline. Since aniline is toxic and a carcinogen, protective breathing devices and face masks should be worn when MCP of aniline salts is performed by open by mortar grinding. Another point involves the reactor material. Usually mortars are made of agate, which is quite inert. However, several authors do not state the material from which the mortar is made. While glass mortars seem as inert as agate, porcelain enamel erodes under grinding, baring the underlying porous ceramic. The pores of the ceramic retain by-products, polymer, and even cleaning agents,

affecting following reactions. Stainless steel could corrode in concentrated acid, and soluble salts (e.g., Fe^{+2}) catalyze the MCP reaction.

As was discussed before, the aggregate form of PANI chains produced during polymerization create different shapes in the nanometer scale (nanostructures), which are preserved during washing/drying since the polymer remains insoluble. Figure 5 shows the SEM micrographs of PANI produced by solution polymerization and MCP (see experimental details in the Supplementary Information).

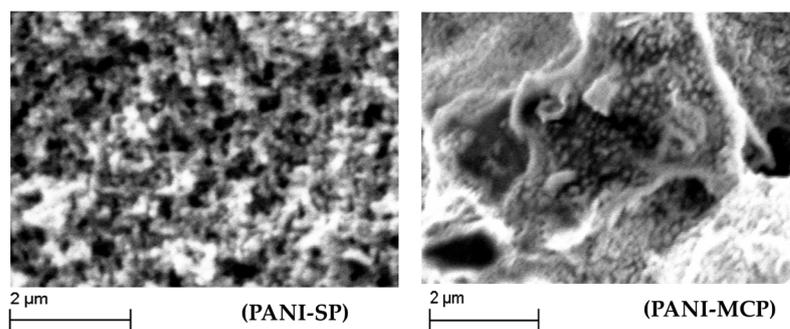


Figure 5. SEM micrographs (20,000 \times) of PANI powder, produced in solution (PANI-SP) or by mechanochemical polymerization (PANI-MCP). The experimental details are described in the Supplementary Information.

While solution polymerization produces a fiber-like intertwined structure, MCP-produced polymer shows small nanoparticles (ca 70 nm). A statistical analysis of the SEM image (dark center region) of MCP PANI (S3 Supplementary Information) allows one to obtain a distribution of nanoparticle sizes (S2 Supplementary Information). The mean size is 70 nm. A geometrical calculation of the surface area gives $62 \text{ m}^2/\text{g}$, which is close to the value ($69.7 \text{ m}^2/\text{g}$) measured by Huang et al. for MC-produced PANI [66]. If the particles could be deaggregated and stabilized, MCP could become a handy method to produce PANI nanoparticles.

2.1.2. Mechanochemical Polymerization of Substituted Anilines (with PANI-Like Linear Chains)

Anilines substituted in the *ortho* or *meta* position of the amino group could give head-to-tail and tail-to-tail coupling to produce dimers (similar to 4ADA and benzidine). From them, polyaniline-like chains can be grown Table 3 [61]. When the group is an electron donor, the reaction is faster than in the case of anilines. On the other hand, electron withdrawing groups slow down the chain growth, and only small oligomers (three to five rings) are formed. Therefore, copolymerization of aniline and the substituted (with electron withdrawing groups) aniline allows polymerization but with less than 100% of the rings substituted [92]. The incorporation of substituent groups in the ring has three effects: (i) to lower the conductivity, (ii) to increase solubility, and (iii) to increase the electrode potential for the oxidations: LE to ES and ES to PN. PANI is soluble only in concentrated acids (formic, acetic, and sulfuric) and some amides (NMP and DMF) when deprotonated or protonated with inorganic anions (e.g., Cl^-). Introduction of anionic groups (e.g., $-\text{SO}_3^-$) makes the polymer soluble in basic media [93], while linking organic groups makes it soluble in organic solvents (e.g., toluene) [94]. It seems that the attached groups sterically hinder the π - π interaction between electron rings in neighboring chains, making the solid less stable and more soluble. The drawback is that such interactions are the basis for electron hopping between chains (orbital overlapping), giving bulk conductivity. Therefore, increased solubility means lower conductivity. Additionally, the presence of bulky substituents in one side of the aniline rings introduces steric distortions of the diphenylamine unit, decreasing the conjugation and the conductivity. However, when two identical groups are attached, the symmetry of the steric effect restores the planarity and the conjugation, with a restoration of conductivity [95]. The change in the electrode potentials

of the LE-ES and ES-PN transitions is related to steric effects in the diphenylamine unit of PANI [96]. Small substituent groups (e.g., methyl) in the nitrogen (secondary amines) also allow dimerization, but benzidine-like dimer (tail-to-tail) formation is favored due to steric constraints of the head-to-tail attack [97].

Table 3. Summary of reaction conditions for MCP of substituted anilines (linear chains). The acids produced in the reaction are shown in italics.

Monomer/s	Oxidant (Ratio ox./mo)	Acid	MC Device/Material	Time Pol./Curing	Washing	Ref
oAS	APS (1:1)	MeSA TSA DBSA <i>H₂SO₄</i>	Mortar	30 min	DEE/EtOH/H ₂ O	[98]
2,5-DMOA	APS (1:1)	HCl <i>H₂SO₄</i> <i>H₃PO₄</i> <i>H₂SO₄</i>	Mortar/glass	20 min	H ₂ O/EtOH/DEE	[99]
N-(2-HEA)	APS	TSA <i>H₂SO₄</i>	Mortar/porcelain	10 min pol + (5 mL H ₂ O) 5 min mix)/24 h	85% EtOH centrifugation	[100]
oTOL	APS (1:1)	β -NSA, CSA, TSA <i>H₂SO₄</i>	Mortar	1 mL H ₂ O + Acid 20 min	DEE/EtOH/H ₂ O	[101]
3ASA	Cl ₃ Fe.6H ₂ O (5:1)	3ABSA <i>HCl</i>	Mortar/ (heated 40–45 °C)	1 h	H ₂ O	[28]

Khadijeva et al., polymerize aniline and poly[(N-2-hydroxyethyl)aniline by MCP [100]. They found that substituted aniline has lower conductivity. Abdiryim et al., polymerize o-toluidine by MCP using different organic sulfonic acids [101]. They found strong effect of the nature of the acid on conductivity

Large substituents in the nitrogen inhibit the formation of polymers. Table 3 summarizes the reaction conditions for the MC polymerization of substituted anilines. Jama et al. use different organic strong acids in the polymerization of o-methoxyaniline (o-anisidine) [98]. They found evidence of branched polymer chains, as observed before in electrochemically polymerized oAS [102]. The conductivity depends of the dopant anion, varying between 0.001 and 0.01 S/cm, which is lower than PANI produced in the same conditions. Palaniappan et al. use MCP to produce poly(2,6-dimethylaniline) and obtain a material with conductivity comparable with PANI [99] (Table 4), while the polymer of aniline with only one substituent (P(oAS)) shows smaller conductivity. The polymers bearing electron withdrawing groups show even smaller conductivity (Table 4). As mentioned in the introduction, Modarresi-Alam et al. produce a homopolymer of 3-aminobenzensulfonic acid [24]. This is the only case where a polymer that is not possible to produce in solution (likely due to the effect of the electron withdrawing group) was produced by MCP. Moreover, they use a fused salt (Cl₃Fe.6H₂O at T > 45 °C) both as oxidant and solvent. The method in general would lead to the synthesis of a large variety of polyanilines.

2.1.3. Other Conducting Polymers Obtained from Substituted Anilines

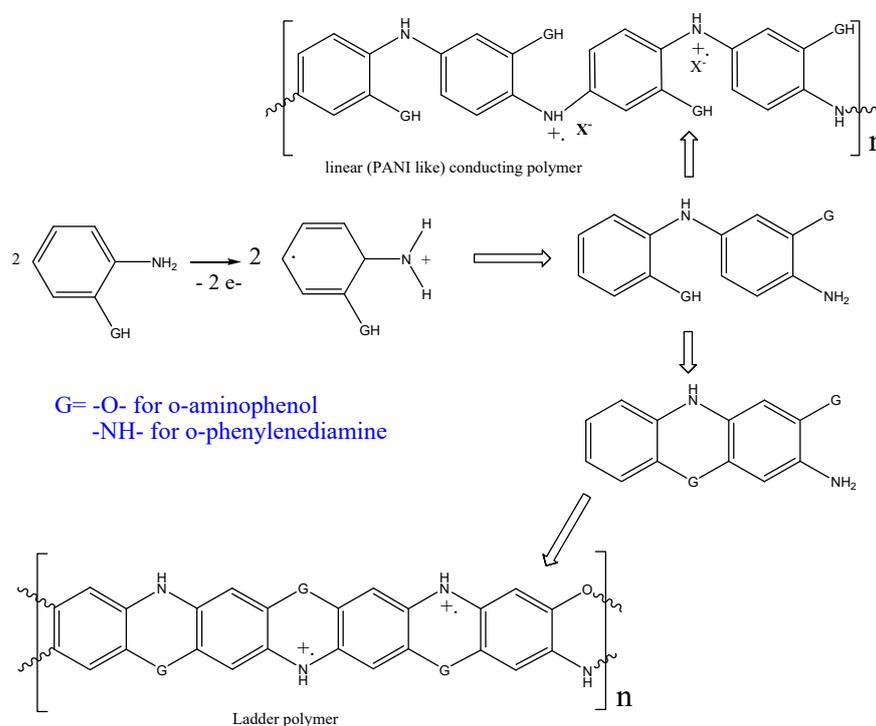
The MCP of substituted anilines discussed before occur in the reaction described in Schemes 1–4. However, some substituted anilines produce conducting polymers by other mechanisms. When aniline is substituted with –OH (aminophenols) or –NH₂ (phenylenediamines) in the *ortho* or *meta* positions, the dimerization and grow steps occur in a way similar to PANI, but the chains could react intramolecularly to give ladder polymers with phenoxazine (aminophenols) or phenazine moieties in the chain [103]. Two possible polymers can be formed: one with linear chains (e.g., oAS) and the other with ladder chains

made of phenoxazine (-O-) or phenazine rings (-N-) (Scheme 5). The linear polymer should have a response similar to that of PANI, with two separated electron transfer processes. The electrochemical behavior of poly(aminophenol) and poly(o-phenylenediamine) suggests that the polymer is made of rings (ladder polymer), although it is possible that blocks of each type exists in the material. Moreover, it is known that the cyclic dimer (e.g., 2,3-diaminophenazine, DAP) is the main product of the chemical oxidation (with APS or Cl_3Fe) of the substituted aniline (e.g., o-phenylenediamine) [104], and the electrochemical response of adsorbed DAP show the same electrode potential as the polymer. Therefore, even if a linear polymer is formed, it will form the ladder polymer by intramolecular cycle formation.

Table 4. Effect of acid added to MCP of substituted anilines on the yield and conductivity of the polymer.

Polymer	Oxidant (ox/mo)	Acid Added	Doping % (Method)	Yield %	Conductivity (S/cm)	Ref.
P(2,6-DMA)	APS (1:1)	HCl	29 (EA)	80	1.8	[99]
P(2,6-DMA)	APS (1:1)	H_2SO_4	25(EA)	76	1.02	[99]
P(2,6-DMA)	APS (1:1)	H_3PO_4	21 (EA)	72	0.42	[99]
P(oAS)	APS (1:1)	MeSA	42 (IR)	34	0.02	[98]
P(oAS)	APS (1:1)	p-TSA	41(EA)	41	0.081	[98]
P(oAS)	APS (1:1)	DBSA	44(EA)	28	0.0013	[98]
P(oTOL)	APS (1:1)	NSA	63 (EA)	66	0.0075	[101]
P(oTOL)	APS (1:1)	CSA	47 (EA)	61	0.0062	[101]
P(oTOL)	APS (1:1)	p-TSA	57 (EA)	51	0.003	[101]
P(3ASA)	Cl_3Fe (5:1)	HCl/ Cl_3Fe (Lewis)	46(EA)	46	0.00012	[24]

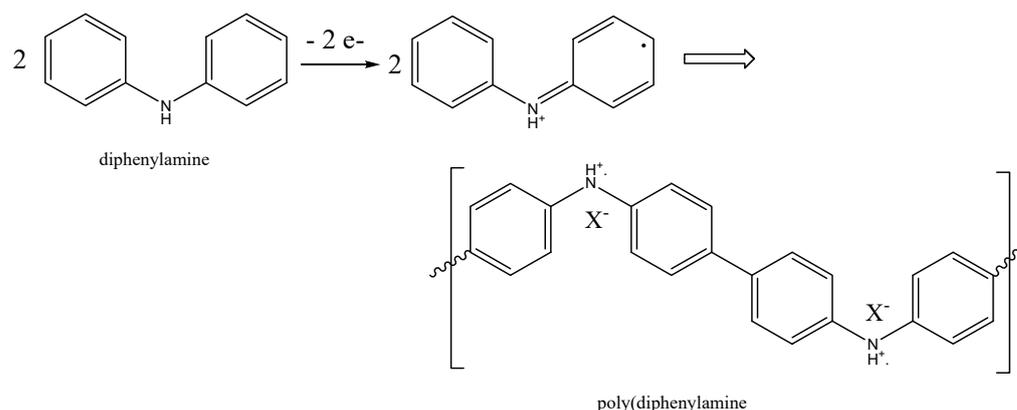
All polymers produced with APS as oxidant, contain sulfate as counterion, whatever the acid added to the polymerization mixture.



Scheme 5. Mechanism of polymerization of o-aminophenol and o-phenylenediamine.

It has been suggested in [103] that a tail-to-tail (similar to benzidine) could be produced. In a similar fashion to aniline polymerization, the tail-to-tail dimer could link to two additional molecules of the monomer and initiate the polymerization. However, the electrochemical response of o-aminophenol or o-phenylenediamine show no peak system that could be assigned to tail-to-tail dimers [103]. Such peak systems exist and have been

identified by IR spectroscopy in aniline oxidation [38]. While these ladder polymers show lower conductivity (2–5 orders of magnitude) than PANI [105], they are quite stable to degradation due to the ring chain structures [106]. Instead of the two separate electron transfers (LE→ES and ES→PN) of PANI, a single peak comprising two electron transfer is observed [107]. Diphenylamine (and triphenylamine [108]) could not produce head-to-tail chains but could polymerize by successive tail-to-tail reactions (such as dimerization to form benzidine) (Scheme 6) [109].



Scheme 6. Mechanism of diphenylamine polymerization.

In fact, diphenylamine is a well-known reactant for the detection of oxidants (e.g., dichromate), which, in diluted solutions, give tail-to-tail dimers with extended conjugations and visible colors [110]. The work on substituted anilines which show other polymerization mechanisms (Schemes 5 and 6) are summarized in Table 5.

Table 5. Summary of MCP conditions for aromatic amines, which give polymer chains different than the PANI backbone. The acids produced during the reaction are shown in italics.

Monomer/s	Oxidant (Ratio ox./mo)	Acid	MC Device/Material	Time pol./Curing	Washing	Ref
oAP	APS (1:0.81)	None <i>H₂SO₄</i>	Grinder RM 200/SS	10 min	H ₂ O/EtOH (1:1) EtOH	[111]
DPA	Cl ₃ Fe/(1.65:1)	None HCl H ₂ SO ₄ H ₃ PO ₄ HCl	Mortar/glass	20 min	H ₂ O/AC	[112]
oAP + mPD	APS (1:1.65)	None <i>H₂SO₄</i>	Grinder RM 200/SS	10 min	H ₂ O/EtOH (1:1) EtOH	[113]

Zoromba et al. use MCP to produce poly(o-aminophenol). They compare MCP with interfacial polymerization [113]. Since the chemical polymerization of oAP in solution with APS has been described [114], it should be most suited to the task. The ratio of oxidant to monomer (1:0.81) suggests an excess oxidant. However, the mechanism (Scheme 3) shows that double the amount of oxidant is required to produce ladder polymers. In the dimerization step, two moles of e⁻ (one mole of APS) are required per ring. But another 2 e⁻ are required for formation of the cycle, and 0.5 e⁻ to produce the polaron in the final polymer. On the other hand, both methods (MCP and IP) render a quite similar material. The same group pioneered the synthesis of a conducting copolymer: poly(o-

aminophenol-co-(m-phenylenediamine)) [113]. Here, the feed ratio (oxidant/monomer) is 1:1.65. Therefore, there is a large excess of monomers. Using the same comparison criteria, the copolymers produced by MCP and IP are similar. In both case, the solid state method does not require handling of a toxic solvent (chloroform) used in IP. Palaniappan et al. produce poly(diphenylamine) (pDPA) by MCP, using Cl_3Fe as the oxidant and diphenylamine as a monomer, using different acids (and none) added to the mixture [112]. The yield does not depend on the presence or kind of acid and is quite high (>70%). This is reasonable since the mechanism involves the dimerization of the radicals without a role for the nitrogen. The electrochemical response depends strongly on the acid used, suggesting different conductivity of the films.

2.1.4. Mechanochemical Synthesis of Nanocomposites

Mechanical mixing/grinding has been widely used to produce nanocomposites containing conducting polymers, being a dispersed component or a polymer matrix (Table 6). Since this review is focused on the MC synthesis of conducting polymers, we will discuss only the work where the conducting polymer is polymerized by MC, before or during the mixing with the other component of the nanocomposite. The fabrication of nanomaterials by MC have been reviewed before [115,116].

Table 6. Summary of conditions used for mechanochemical synthesis of nanocomposites.

Monomer	Oxidant	Other Component	Acid Added	MC Device/Material	Liquid Assistant	Time	Ref.
AniHCl	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	TiO_2 NP	Cl_3Fe (Lewis)	Mortar/ceramic	$\text{Cl}_3\text{Fe} \cdot 6\text{H}_2\text{O}$ (melt)	100 min	[117]
AniHCl	APS	MT	None	Mortar/agate	None	10 min AniHCl + MT + 24 H w/APS	[118]
Ani	APS	β -CD	HCl	Mortar	H_2O (63%)	20 min	[119]
AniHCl	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	CNTs	None	OBM/Steel	H_2O	20–60 min	[120]
Ani	APS	TiO_2 NPs Graphene	p-TSA	Mortar	None	30 min	[121]
Ani	FeCl_3	CNF	None	Mortar	None	1 mixing CNF + Ani 10 milling with FeCl_3 .	[122]
AniHCl	Cu^{+2}	MT	None	Mortar/agate	None	6–20 min	[123]
AniHCl	Fe^{+3} /Air	MT	None	Mortar	None	120 min grind + 10 days rest in air	[124]
AniHCl	APS	MT	None	Mortar	None	30 min 72 h rest	[125]
AniSul	APS	MT	None	Mortar	None	30 min 72 h rest	[126]
Ani	APS	MT	p-TSA	Mortar	None	10 min 72 h rest	[127]
Ani	APS	KAO	None	Mortar	None	–	[128]
Ani oTOL oAS	APS	MT	None	Mortar	None	10 min 72 h rest	[129]
Ani	APS	MT	p-TSA	Mortar	None	10 min 72 h rest	[130]
Ani	MT	MT	none	Motorized Mortar/ss	None	120 min 14–54 d rest	[131]
Ani	FeCl_3	SiO_2	FeCl_3 (Lewis)	Mortar	None	12 h	[132]
Ani	APS	Graphene	H_2SO_4	PBM/ss	None	2 h Ani+G 2 h MCP	[133]
Ani	APS	Fe_2O_3 NP + TAPcZn	None	Mortar/agate	None	15 min + 1 h rest	[134]
oTOL	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	WO_3 NPs	None	Mortar/ceramic	None	75 min	[135]

Table 6. Cont.

Monomer	Oxidant	Other Component	Acid Added	MC Device/Material	Liquid Assistant	Time	Ref.
Ani	APS	MWNT	p-TSA	Mortar	None	40 min	[136]
Ani	APS	SWNT MWNT	p-TSA	Mortar	None	40 min	[137]
AniH ₂ Sul	AgNO ₃	Ag NPs	None	–	None	–	[87]
oPDHCl	AgNO ₃	Ag NPs	None	Mortar/agate	None	2 h	[138]
oASH ₂ Sul	AgNO ₃	Ag NPs	None	Mortar	None	45 min	[139]

- Nanocomposites with clays

Bekri-Abbes and Srasra use MC (with APS) to polymerize clay (montmorillonite), where anilinium ions have been intercalated by cation exchange (using MC grinding) [118]. During the 20 min of MC grinding (clay + AniHCl), Mg⁺², Al⁺³, and Fe⁺³ are exchanged by the anilinium ion. The ratio of AniHCl to the cation exchange capacity (CEC) of the clay was varied. The intercalation is verified by XRD. They found the oxidant/aniline ratio that gives the largest yield (86%). The material where the AniHCl amount used was equal to three times the CEC with an oxidant/aniline ratio of 0.75 gives the best results. It shows a low frequency conductivity of 5.7×10^{-3} S/cm, which is higher than an effective medium approximation of conductive PANI ($\sigma = 3$ S/cm) and dielectric MT would have predicted. It seems that aniline polymerizes in an ordered way inside the clay, being the lamellar structure of MT a template for the polymer. Bekri-Abbes and Srasra load montmorillonite with Cu⁺² and grind for up to 20 min with AniHCl (depending on the ratio of Cu⁺²/MT to aniline) [123]. The highest DC conductivity of the NCs is 1.37×10^{-5} . The same authors load MT with Fe⁺³ ions, and then grind the Fe⁺³/clay with AniHCl (120 min). However, to finish the polymerization, the mixture has to be left in the air for 10 days. The nanocomposite shows a DC conductivity of 0.058 S/cm, much higher than Cu⁺²/clay. The comparison of both publications supports the idea that the redox potential of the oxidant is not determinant in the chemical oxidation. While Cu⁺²/Cu⁰ redox potential is +0.34 V_{NHE}, the Fe⁺³/Fe⁺² redox potential is +0.77 V_{NHE}. If the standard potential for oxidation of pernigraniline (the redox form during growing of PANI) is 1.05 V_{NHE}, the polymerization should not occur ($\Delta E < 0$ implies $\Delta G > 0$). However, it is known that the emeraldine salt form is less reactive than pernigraniline towards aniline, but it could react [140]. Therefore, the chain could slowly grow at low electrode potentials. In fact, it has been shown that PANI can be synthesized by interfacial polymerization using air as an oxidant ($E_{O_2/H_2O} = 1.23$ V_{NHE}), albeit with catalysis by Cu⁺² [141,142]. In a following work, Bekri-Abbes and Srasra use non-intercalated MT, which contains 6.3% Fe, as a catalyst for air polymerization of aniline [123]. AniHCl and virgin MT were grinded for 120 min and left to stand in the air for 14 days. The DC conductivity is 0.0016 S/cm. The relationship between conductivity and PANI content measured by Shakoor et al. [130] implies that the PANI content is below 15%, which is similar to other NC produced using Fe⁺³ as oxidant. Zheng et al. produce a NC of PANI and clay (kaolinite, KAO) using MCP [128]. Aniline was loaded inside the lamellar clay and then polymerized with APS by grinding. The basal spacing of the clay (measured by XRD) increases ca. 100% due to the intercalation of PANI chains. The thermal stability of intercalated PANI is higher than free polymer. The NC is applied as an anti-corrosion agent, dispersed in epoxy resin coatings. Yoshimoto et al. intercalate excess anilinium cations (from anilinium chloride) inside MT by MC. The basal spacing of MT increases ca. 157% [125]. Then, they use MCP (with APS) to produce a PANI(Cl⁻)/MT nanocomposite. The basal spacing of MT decreases to 38%, indicating the polymerization of aniline produces flat PANI chains. The thermal stability of PANI improves upon intercalation. The same group studied the formation by MCP of a PANI(SO₄⁻²)/MT [126] and a PANI(p-TSO⁻)/MT [127] nanocomposite. In all cases, the thermal stability improves, and, in the case of PANI(p-TSO⁻)/MT [127], electronic conductivities of up to 0.01 S/cm are obtained. Kalaivasan et al. applied the same procedure

to the synthesis of nanocomposites of MT with Ani, oTOL, and oAS [129]. The EPR studies indicate radical cations are present in the three NCs. Shakoor et al. [130] use a similar method to fabricate a PANI(TSO-)/MT nanocomposite. They found that conductivity of the NC increases proportionally to the amount of PANI in the NC where 99% PANI has a conductivity of ca 80% of a pure polymer. This value is reasonable since the electrons should percolate through the nanocomposite, where only PANI is conductive.

- Nanocomposites with carbon materials

Garcia-Gallegos et al. use MCP to produce nanocomposites of PANI and carbon nanotubes (CNTs, plain carbon (MWNT), and doped carbon (CNx)) [112]. They vary the amount of water added to the solid and the amount of CNTs. Very low yields (<3.15%) were obtained, and even lower yields (0.3%) were reported without liquid aid (water). It is noteworthy that Du et al., using FeCl₃ to MCP aniline, also obtain low yields of PANI NFs (<8%) [75]. The electrical conductivity of the nanocomposites is similar to those NCs prepared by other methods, while the conductivity of pure PANI (using the same method) is quite low (ca. 10⁻⁴ S/cm) compared with other PANI prepared by MCP (see Table 2). The authors claim that they use an stoichiometric excess of oxidant (2:1), but the reaction stoichiometry (Scheme 2) requires a 2.5:1 (Cl₃Fe/AniHCl) molar ratio for complete conversion (equivalent to 1.25 in the case of APS). Jiang et al., uses mechanical grinding (2 h) to exfoliate graphite (using aniline as stripping agent) into graphene and then MCP (with APS) to produce PANI/G composites [133]. The TEM images show small nanoparticles of PANI (<20 nm) adsorbed on graphene plates. The content of PANI is up to 11.2%. The NC shows the characteristic cyclic voltammetry response of PANI, with a negligible “middle peak” revealing little degradation/crosslinking. The material shows a specific capacitance is up to 886 F/g. The capacitance has contributions of graphene (double layer capacitance) and PANI (pseudocapacitance). The method seems promising to fabricate supercapacitors, where graphene contributes with conductivity and surface area (double layer) and PANI with pseudocapacitance. PANI NPs (<20 nm) will have a surface area of more than 200 m²/g, contributing also to the double layer capacitance. Moreover, such small particles will switch in μs, even assuming a low diffusion coefficient (10⁻¹⁰ cm²/s) of ions inside PANI. Therefore, the material will have a large specific capacitance and fast response time. The MC technique is able to disperse the CNTs, and the presence of AniHCl protects the CNTs from mechanical damage due to the grinding, which occurs when the mixture (without monomer) is milled. Interestingly, the authors detect steel particles in the composite, coming from the milling jar. Jamal et al. synthesize PANI/TiO₂/G and PANI/G by MCP of aniline [121]. The properties of the different composites are very similar. Du et al. use MCP to synthesize a NC of PANI and CNFs [122]. The CNFs become decorated with branched nanofibers as those reported before by MCP of Ani with FeCl₃ [75]. The presence of PANI nanofibers in the surface of the CNFs aid the dispersion of the NC in ethanol. From the amount of CNF in the final solid (50%) and the mass ratio of aniline/CNF (1:0.2), it is possible to calculate a yield of ca. 8.3%, similar to the one reported before with the same oxidant [75]. It seems that MCP of PANI with FeCl₃ as oxidant gives low yields [62,75,121,122]. Moreover, Modarresi-Alam et al. also obtain low yields of a substituted aniline (3ASA) in the same conditions [28]. Only using the melted (>37–45 °C) salt (FeCl₃·6H₂O) as oxidant allows them to obtain higher yields (46%). On the other hand, Koosheh et al. produce NC of silica with PANI using MCP (with FeCl₃) [132]. They obtain large yields (up to 91%), confirming that in situ formation of NC is not equivalent to separate polymerization and mixing. The nature of the other component affects the polymerization mechanism. On the other hand, the conductivity of the materials is quite low (<0.0023 S/cm). The authors claim the reason is that FeCl₃ (Lewis acid) is the sole dopant of the polymer. Such a hypothesis disregards the fact that protons are produced during polymerization (Scheme 2) and chloride ions are produced during FeCl₃ reduction. The HCl will protonate the EB form of the polymer creating protonic acid doping. Moreover, the ratio of oxidant/aniline is 2.5, which is just enough to polymerize aniline and oxidize the polymer to emeraldine. Therefore, no FeCl₃ will be left

to act as the Lewis acid dopant, and the reduction product (FeCl_2) is a weaker Lewis acid. Abdiryim and coworkers produce nanocomposites containing PANI and MWNT [136,137], or SWNT [137]. The morphological studies (TEM) revealed that PANI/MWNT show rod-like and granular-like aggregates, while PANI/SWNTs did not display any features. A composite containing 16 wt% MWNTs show a specific capacitance (SC) of 522 F/g (measured by galvanostatic charge/discharge) [136]. When the nanocomposite (NC) with highest SC (16% MWNT, SC = 515 F/g) was compared with the best NC made using SWNT (8% SWNT, SC = 423 F/g), it is found that the NC with SWNT has a SC ca. 18% lower than the one with MWNT [137]. On the other hand, PANI/SWNTs exhibited higher cycling stability in neutral and alkaline electrolytes [137].

- Nanocomposites with photoactive materials

Yarmohamadi-Vasel et al. synthesize PANI nanofibers by oxidation with Cl_3Fe in the presence of TiO_2 NPs [117]. The nanocomposite show a conductivity of 0.79 S/cm which is higher than pure PANI NFs (0.09 S/cm) and TiO_2 (1.5×10^{-6} S/cm). It seems that MC produce more ordered chains of PANI, which decorate the low conductivity TiO_2 NPs. Since TiO_2 is photoactive, the nanocomposite is used to build hybrid (TiO_2 /PANI NF) solar cells. Rajappa et al., uses MCP to produce a NC including Fe_2O_3 nanoparticles (FeOxNP) and a photoactive dye (tetraaminophthalocyanine (Zn), TAPcZn) [134]. The PANI covered the FeOxNPs and holds the photoactive dye. The NC shows excellent activity for the photodegradation of MB in water. Valadbeigi et al. uses MCP (with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as an oxidant) to produce a nanocomposite of poly(o-toluidine) and WO_3 nanoparticles [135]. As in other MCP with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [28], they observe that the heat produced by the reaction melts the hydrated iron chloride (m.p. = 37 °C), and most of the polymerization occurs in solution (with fused salt as a solvent). The NC shows a core of WO_3 NPs surrounded by a shell of POT. The NC shows photovoltaic activity, and solar cells were built.

- Nanocomposites with metallic particles

Farrage et al. use MCP to produce PANI by oxidation of aniline with Ag^+ ions, which became reduced to Ag nanoparticles [87]. TEM images show PANI nanoparticles (200–250 nm dia) with much smaller (<10 nm) Ag NPs uniformly distributed in the PANI NP. Paulraj et al. polymerize oPD using Ag^+ (AgNO_3) as an oxidant ($E^\circ = \text{Ag}^+/\text{Ag} = 0.7996 \text{ V}_{\text{NHE}}$) [138]. oPD oxidizes ($E^\circ = 0.46 \text{ V}_{\text{NHE}}$ [143]) and polymerizes, while Ag^+ is reduced to Ag^0 , forming nanoparticles. The FESEM shows poly(oPD) particles of ca. 400 nm dia with small (<15 nm) Ag NPs evenly distributed in the polymer mass. The NCs were used as electrochemical sensors for the oxidation of hydrazine and reduction of hydrogen peroxide.

- Nanocomposites with other substances

Ding et al., produce a nanocomposite of β -CD and PANI [119]. Depending on the proportions between components, the shape of nanostructures changed. For 80/20 (aniline/ β -CD) rod-like structures are observed, Moreover, the conductivity of the 80/20 nanocomposite has higher conductivity (6.3 S/cm) than PANI without β -CD (5.1 S/cm).

3. Conclusions

Mechanochemical synthesis of polyaniline and substituted polyanilines is an ecofriendly tool to produce conducting polymers without producing large amounts of contaminated solvent (water) and/or using large reactors to hold diluted (<0.2 M) solutions. While PANIs can be formed using FeCl_3 as an oxidant, the most widely used oxidant is ammonium peroxydisulfate (APS). The stoichiometry of the polymerization reaction requires 1.25 moles of APS per aniline ring in PANI (2.5 moles of e^-). In mechanochemical polymerization (MCP) of anilines, it seems that a lower oxidant/aniline ratio produces material with higher conductivity and molecular weight. The polymerizations of substituted anilines, which produce linear polymers, are quite similar to that of aniline. On the other hand, anilines substituted with $-\text{NH}_2$ or $-\text{OH}$ groups (in *ortho* and *meta* positions on the amino group in aniline) lead to ladder polymers containing phenazine or phenoxazine rings. In that

case, the amount of oxidant should be larger, since the intramolecular attack requires more electrons. All the polymerizations produce protons (two per attack) in the formation of bonds with the aromatic rings. In all cases, salt oxidants (APS or FeCl_3) produce anions that form acid with the protons released during the electrophilic substitution. In a polymerization solution, the acids dissolve in the solvent (albeit lowering the pH), but in a solid state reaction remain in the mixture and could be used to dope the conductive form of the polymer. Moreover, volatile acids (e.g., HCl) could be released from the mixture. Experimental data are presented, suggesting that HCl is indeed released when aniline hydrochloride is used as a monomer. The known hazard of HCl gas [144] should be taken into account in the operation of the technique in open vessels (e.g., mortar). In the case of closed reactors (e.g., ball mill jars), consideration for buildup pressure and management of the gas has to be taken into account. The amount of water present during the grinding/milling of reaction mixtures is unknown, taking into account that APS or anilinium salts are very hygroscopic. Some of the published experimental procedures leave the reactant mixture for days in air to complete the reaction. It is likely that water absorption plays a role in the completion of the reaction. It should be advisable to maintain a high and constant humidity during such resting period to improve the reproducibility. Others wash the product of MCP with water (or aqueous solutions). Finally, some researchers add water directly, or use a solution such as 37% HCl, to the reactant mixture. This addition increases the polymerization rate but, in fact, converts the solid state reaction into a solution reaction at high concentration. The drawback is that the oxidative polymerization of aniline is highly exothermic. A simulation using the kinetic model predicts fast reactions (<60 s) and high temperatures (>300 °C). A quick experiment, using a nearly saturated solution of APS and AniHCl, shows a fast reaction (<2 min) with a large liberation of heat. The temperature increases until water boiling point is reached, showing the danger of working with concentrated solutions. Most of the work has been performed in open mortar and pestle devices. The grinding is usually made until a noticeable color change is observed, but then a rest period (in air without humidity control) of 1–14 days allows the reaction to continue, even with the action of oxygen from air. On the other hand, it is found that toxic fumes (aniline) are released, and protective gear should be worn. The MCP method could be applied to substituted anilines, producing material similar to PANI. A special case is the homopolymerization of 3-aminobenzenesulfonic acid, which produces a polymer by MCP while only producing oligomers in solution. The polymerization is made using a fused salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) as both oxidant and solvent. MCP below the melting point of the salt produces low yield, while the fused salt gives a good yield (46%). To the best of our knowledge, this is the only case of mechano-exclusive polymerization of a CP (i.e., a synthesis that can only be performed by MCP).

Polymerization of *o*-aminophenol and *o*-phenylenediamine seems to produce ladder polymers by a cyclization step of the linear polymer. Diphenylamine has been polymerized by MC by tail-to-tail dimerization and chain formation.

A large body of work has been devoted to the preparation of nanocomposites by MCP of aniline in the presence of other materials. Several works deal with different kinds of clays where PANI grow inside the galleries of the natural material. The clay protects intercalated PANI, improving the thermal stability. The conductivity of the nanocomposite is lower than PANI but large enough for different applications. Nanocomposites of carbon materials (nanofibers, single and multiwall nanotubes, and graphene) have been made by MCP of anilines where the milling also disperse the phases and/or exfoliate the carbon material. The carbon gives surface area and conductivity, and the nanocomposites show large capacities of electrochemical charge storage. The materials are promising for supercapacitor applications. Nanocomposites made of metal nanoparticles dispersed in polyanilines were made by MCP of silver salts mixed with anilines. The monomer is oxidized by Ag^+ , and Ag nucleates and grows to form nanoparticles. In that way, solid dispersions of small Ag NPs in larger polymer nanoparticles are produced. MCP of aniline in the presence of oxides (Fe_2O_3 , TiO_2 , or WO_3) and other photoactive species allow one to build photovoltaic electrodes.

4. Future Outlook

The parameters of aniline MCP, such as the role of water/liquids and temperature, should be studied in detail. Using mechanized milling devices (e.g., ball mill), it would be possible to study the effect of milling parameters (material of ball and jars, number and size of the balls, frequency of rotation, etc.) on the MCP of anilines, as already suggested by Krisenbaum et al. [23]. Such a study has been performed for the Gilch synthesis of poly(phenylene vinylene) [145]. Moreover, using a closed MC reactor, the atmosphere of the reaction (humidity and oxygen content) could also be controlled, and exposure to toxic volatiles could be avoided. There are other conditions where MCP could be at an advantage compared with polymerization in solution. Beadle et al. polymerize aniline at low temperatures (down to $-40\text{ }^{\circ}\text{C}$) and show that PANI with high conductivity (up to two orders of magnitude) can be produced [146]. It seems that the oxidation reaction of aniline (or the growing chain) by persulfate is little affected by temperature. However, to maintain the aqueous/alcoholic solution liquid, they have to add up to 2 M LiCl, and it has been shown that the presence of a high Cl^- concentration induces chlorine incorporation in the chain [23]. On the other hand, MCP of dry aniline salts could be made at any temperature without additives. Moreover, Konyushenko et al. show that aniline can be polymerized with frozen solutions [46]. Therefore, MCP of frozen aniline at low enough temperatures ($<-40\text{ }^{\circ}\text{C}$) could produce PANI with improved properties. In 2019 IUPAC identified reactive extrusion, a form of MC, as one of the 10 chemical innovations to change our world [147]. The technique uses a solid powder (or paste) flow reactor, which can produce industrially-relevant quantities by continuous production. The short polymerization time of PANI by MCP ($<5\text{ min}$) should allow short residence times and fast production. Moreover, since the dry mixture of anilinium salt and oxidant are stable before grinding, a single screw extruder (common in polymer processing) can be used. While great pains have been taken to use solid reactants, pure aniline could be used with solid oxidants, forming a paste. A small amount of dry solid acid (e.g., toluenesulfonic acid) will maintain the reaction acid until the protons produced in the reaction give an acid medium.

4.1. Synthesis of PANI Doped with Polyelectrolytes

Polyelectrolytes, which are soluble in water (e.g., PSS), have been used to disperse/solubilize PANI by polymerizing aniline in the presence of the anionic form at a neutral pH. To do that, the polymerization has to be carried out by enzymatic polymerization [148]. Using MCP, it is possible to make PANI in the presence of the acid form (e.g., PSSH) either by previous formation of the PSS-ANI salt in solution or using AniHCl. Then, the PSS-PANI is dissolved in basic/neutral pH where the parts of the PSS chain that do not interact with PANI dissolve in water (ion-dipole interactions) and solubilize/disperse the PSS-PANI. The Donnan effect of $-\text{SO}_3^-$ precludes the protons to leave [149]. Therefore, the PSS-PANI remains in its doped (conductive) state. While sulfonic acid groups could clearly protonate PANI, it has been shown that carboxylic groups, aided by Donnan effects, are also able to maintain PANI in the protonated state [150]. Therefore, biobased polymers (CMC, CMS, CHI, or CHSu) or biomolecules (HA, proteins) can also form complexes or nanocomposites with PANI.

4.2. Doping with Acids/Anions Insoluble in Water

Since polyaniline is not soluble but is wetted by water it is easily doped/dedoped by small ions/acids immersion the solid on aqueous solutions. On the other hand, doping with acids insoluble in water (e.g., stearic) is difficult. Moreover, the incorporation of a hydrophobic counterion is required to produce more hydrophobic doped polyaniline. Mechanical grinding of the solid acid with PANI (EB) could be used to produce doped PANI (ES) with hydrophobic counterions.

4.3. Synthesis of Oxidized/Reduced Forms

PANI is stable in air in the half-oxidized (emeraldine) form. To produce the other forms (leucoemeraldine and pernigraniline), the polymer has to be reacted with a reductant/oxidant. Usually, such reactions are performed by immersing the solid in solutions. However, the reaction occurs heterogeneously. Using solid reductants (e.g., ascorbic acid) would possibly reduce PANI in a dry state, where reoxidation by air is slower than in solution. In fact, a mechanochemical procedure for the reduction of PANI was described by Epstein and coworkers to produce highly sulfonated PAN [151], and used by Barbero et al. to introduce amide groups in the nitrogen of PANI (LEB) [152]. Mechanochemical oxidation to the fully oxidized form (PNB or PN) could be produced using solid dry persulfate salts. The absence of water avoids degradation by nucleophilic attack.

4.4. Synthesis of Functionalized Polyanilines

Polyanilines with functional groups attached to the main chain have been synthesized in solution and show better processability (solubility) and new properties, which lead to different technological applications [153]. The materials can be produced by homo/copolymerization of substituted monomers or PANI post-functionalization.

- Homopolymerization. Anilines monosubstituted in nitrogen (e.g., N-methylaniline) or bearing small electron donating groups in the ring (e.g., 2-ethylaniline) can be homopolymerized. On the other hand, anilines with electron withdrawing groups (e.g., $-\text{SO}_3^-$) only produce oligomers. Remarkably, 2-aminobenzenesulfonic acid was polymerized in a fused salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), which acts as solvent and oxidant [28]. The method could be applied to other aniline monomers bearing electron withdrawing groups (e.g., 2-nitroaniline).
- Copolymerization. Copolymerization of an unreactive aniline (e.g., 2-aminobenzoic acid) with aniline renders copolymers in solution [154]. However, the lower reactivity of the substituted aniline compared to aniline makes the polymerization slower and creates compositional shift. The data on MCP of aniline suggest that stoichiometric control is more important than kinetics. Therefore, it could be possible to produce copolymers with more a defined composition ratio using MCP of the monomer mixture.
- Post-functionalization. Direct reaction of PANI chains allows for attaching functional groups to the polymer. The most used reaction (sulfonation) is an electrophilic aromatic substitution reaction and is usually made in homogeneous solution by reacting PANI with SO_3 with the polymer dissolved in concentrated H_2SO_4 . However, Epstein and coworkers used a thermal reaction of PANI with $\text{SO}_4(\text{NH}_4)_2$ to sulfonate PANI [155]. The same reactant, or stronger solid sulfonating agents (e.g., $\text{SO}_3 \cdot \text{Pyridine}$ complex), could be used for MC functionalization of PANI. On the other hand, nucleophilic addition to PANI is usually performed heterogeneously [156]. Sulfonated polyaniline can be produced by nucleophilic addition of sulfite ions [157]. Using solid reactants, it is possible to achieve MC functionalization of PANI.

4.5. Fabrication of PANI Nano-Objects

There is evidence that PANI produced by MCP is produced as solid aggregation of nanospheres (Figure 4) or nanofibers [74–76]. Using MC and/or other deaggregation methods (e.g., ultrasound), together with stabilizers of colloids (DBSA, PVP, PSS), will be a possible way to produce stable dispersions of PANIs nanoparticles.

4.6. Synthesis of PANI Containing Nanocomposites

As shown above, the synthesis of NC by MCP of anilines in the presence of solid materials (e.g., clay) is a flourishing field of study. However, several venues for future work exist. MCP polymerization with graphene oxide (GO) or reduced graphene oxide (rGO) could produce materials comparable with the NC made from graphite, albeit with covalent linking of the reactive oxides with PANI. 2D layered materials different from graphene (e.g., MoS_2 layers) can also be used to produce NCs by MCP of anilines [158].

Large surfaces such as porous carbon materials can be either produced from lignocellulosic biomass [159], by pyrolysis and activation, or by the pyrolysis of synthetic gels [160]. Porous materials such as metal organic frameworks (MOF), covalent organic frameworks (COF), polymer organic frameworks (POF), porous disordered (e.g., silica gel), and mesoporous ordered (e.g., SBA 15) oxides can be made into nanocomposites with PANis using in situ MCP. The polymer chains could grow inside the cavities/channels in the porous structures. In that way, the dispersion will be complete and the matrix could protect the polymer against degradation. Moreover, growing PANI inside the interpenetrated porous structure will generate a porous PANI solid intertwined with the porous matrix. If the matrix could be dissolved (e.g., HF) or disassembled (e.g., changing pH), the porous PANi solid could remain in place. Such a high surface area conductive framework could have plenty of applications including supercapacitors/batteries, water remediation, catalysis, etc.

4.7. Using MCP for 2D Printing of PANI Thick Films on Fabrics

As discussed above, an early example of MC is the formation of “aniline blacks” [64]. While so called “ungreenable aniline blacks” likely contain phenazine units (linear emeraldine is green) and are poor conductors, the synthesis from the linear PANI, which is then converted to aniline black [31]. An analysis of Lightfoot’s recipe [161] shows that AniHCl oxidizes with chlorate as an oxidant and copper sulfate as the catalyst. Additionally, using 95 % in weight of starch produces a thick paste. The amount of copper salts is ca. 20% of the chlorate suggesting a contribution as an oxidant. Assuming reduction of chlorate (ClO_3^-) to chloride (Cl^-) and of Cu^{+2} to Cu^0 , the amount of oxidants are twice that necessary for PANI (ES) formation. Therefore, the polymer is likely to be overoxidized to form aniline black [162]. Using a stoichiometry amount of oxidant (likely APS) would be possible for precipitating PANI (ES) on cellulosic fibers (e.g., cotton). While other procedures are known to produce PANI films on solids [82], they made thin (<300 nm) films, while thick deposits (>10 μm) can be made by this method. The PANI could be patterned by pressuring a stamp on certain regions of the pasted fabric, effectively 2D printing by MCP. Other options, like “drawing” with a rolling ball pressing the fabric at defined positions would allow for customized patterning. Those thick conductive patterns can be used directly for flexible electronics or used to deposit metals (e.g., Cu) to produce printed circuits. Moreover, thick macroporous films, made of fibers covered with thick films of PANI, could be used in applications like supercapacitors, batteries, or disposable electrodes. In those cases, the fabric should be also conductive, such as a fabric made of carbon fibers.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym15010133/s1>, Supplementary Information: Experimental data (Figures S1–S3) and experimental details.

Author Contributions: Conceptualization, C.A.B.; methodology, C.A.B. and D.F.A.; software, D.F.A.; validation, C.A.B. and D.F.A.; formal analysis, C.A.B.; investigation, C.A.B.; resources, C.A.B. and D.F.A.; data curation, C.A.B.; writing—original draft preparation, C.A.B.; writing—review and editing, D.F.A.; visualization, D.F.A.; supervision, C.A.B.; project administration, C.A.B.; funding acquisition, C.A.B. and D.F.A. All authors have read and agreed to the published version of the manuscript.

Funding: The new research described in the text was funded by SECY-UNRC (SSPR), FONCYT (PICT 240/2019), and CONICET (PUE IITEMA).

Acknowledgments: The measurement of SEM micrographs by L. Tamborini is acknowledged. The authors dedicate this review to the memory of the late Hans Desilvestro, a superb scientist who introduced us to the wonders of polyaniline.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

2,5-DMOA	2,5-dimethoxyaniline
3ASA	3-aminobenzenesulfonic acid
4ADA	4-aminodiphenylamine

ACN	acetonitrile
Ani	Aniline
AniH ₂ Sul	Aniline sulfate
AniHCl	Aniline hydrochloride
AniHSul	Aniline hydrogen sulfate
APS	ammonium peroxydisulfate.
APS	Ammonium peroxydisulfate
CA	Citric Acid
COF	covalent organic frameworks
CSA	Camphorsulfonic acid
DEE	Diethyl ether
DES	Deep Eutectic Solvent
DMSO	dimethylsulfoxide
DPA	diphenylamine
EB	Emeraldine base
EPR	Electron Paramagnetic Resonance
ES	Emeraldine salt
EtOH	Ethanol
FeOxNP	Fe ₂ O ₃ nanoparticles
FESEM	Field Emission Scanning Electron Microscope
G	Graphite
GP	Graphene
IL	Ionic liquid
IP	interfacial polymerization.
KAO	kaolinite (clay)
KPS	Potassium peroxydisulfate
LE	Leucoemeraldine
MB	methylene blue
MC	Mechanochemistry
MCP	Mechanochemical polymerization
MOF	metal organic frameworks
MS	Mechanochemical synthesis
MSA	Methanesulfonic acid
MT	Montmorillonite (clay)
MWNT	multiwall (carbon) nanotube
N-(2-HEA)	N-(2-hydroxyethyl)aniline)
NC	nanocomposite
NF	Nanofiber
NP	Nanoparticle
oAP	o-aminophenol
oAS	o-anisidine
OBM	Orbital Ball Mill
oPD	o-Phenylenediamine
oTOL	o-Toluidine
PA	H ₃ PO ₄
PAMPSA	poly(2-acrylamido-2-methyl-1-propanesulfonic acid)
PANI	Polyaniline
PBM	Planetary ball mill
PN	Pernigraniline
POF	polymer organic frameworks
POT	poly(o-toluidine)
p-TSA	p-Toluenesulfonic acid
pTSO ⁻	ion p-Toluensulfonato
SWNT	single wall (carbon) nanotube
TAPcZn	Tetraaminophthalocyanine (Zn)
W	water
XRD	X-ray diffraction
β-CD	β-cyclodextrin

References

1. Reynolds, J.R.; Thompson, B.C.; Skotheim, T.A. *Handbook of Conducting Polymers*, 4th ed.; CRC Press: Boca Raton, FL, USA, 2019.
2. Shahapurkar, K.; Gelaw, M.; Tirth, V.; Soudagar, M.E.M.; Shahapurkar, P.; Mujtaba, M.A.; Kiran, M.C.; Ahmed, G.M.S. Comprehensive review on polymer composites as electromagnetic interference shielding materials. *Polym. Polym. Compos.* **2022**, *30*, 09673911221102127. [[CrossRef](#)]
3. Fungo, F.; Jenekhe, S.A.; Bard, A.J. Plastic electrochromic devices: Electrochemical characterization and device properties of a phenothiazine-phenylquinoline donor-acceptor polymer. *Chem. Mater.* **2003**, *15*, 1264–1272. [[CrossRef](#)]
4. Zhang, S.; Sun, G.; He, Y.; Fu, R.; Gu, Y.; Chen, S. Preparation, Characterization, and Electrochromic Properties of Nanocellulose-Based Polyaniline Nanocomposite Films. *ACS Appl. Mater. Interfaces* **2017**, *9*, 16426–16434. [[CrossRef](#)]
5. Bongiovanni Abel, S.; Gallarato, L.A.; Dardanelli, M.S.; Barbero, C.A.; Rivarola, C.R.; Yslas, E.I. Photothermal lysis of *Pseudomonas aeruginosa* by polyaniline nanoparticles under near infrared irradiation. *Biomed. Phys. Eng. Express* **2018**, *4*, 045037. [[CrossRef](#)]
6. Molina, M.A.; Rivarola, C.R.; Miras, M.C.; Lescano, D.; Barbero, C.A. Nanocomposite synthesis by absorption of nanoparticles into macroporous hydrogels. Building a chemomechanical actuator driven by electromagnetic radiation. *Nanotechnology* **2011**, *22*, 245504. [[CrossRef](#)]
7. Singh, N.; Kumar, A.; Riaz, U. Conducting Polymer-Based Micro- and Nano-batteries for Biomedical Applications: A Short Review. *ChemistrySelect* **2022**, *7*, e202201302. [[CrossRef](#)]
8. Abdelhamid, M.E.; O'Mullane, A.P.; Snook, G.A. Storing energy in plastics: A review on conducting polymers & their role in electrochemical energy storage. *RSC Adv.* **2015**, *5*, 11611–11626. [[CrossRef](#)]
9. Dhandapani, E.; Thangarasu, S.; Ramesh, S.; Ramesh, K.; Vasudevan, R.; Duraisamy, N. Recent development and prospective of carbonaceous material, conducting polymer and their composite electrode materials for supercapacitor—A review. *J. Energy Storage* **2022**, *52*, 104937. [[CrossRef](#)]
10. Li, Y.; Gong, Q.; Han, L.; Liu, X.; Yang, Y.; Chen, C.; Qian, C.; Han, Q. Carboxymethyl cellulose assisted polyaniline in conductive hydrogels for high-performance self-powered strain sensors. *Carbohydr. Polym.* **2022**, *298*, 120060. [[CrossRef](#)]
11. Molina, M.A.; Rivarola, C.R.; Barbero, C.A. Effect of copolymerization and semi-interpenetration with conducting polyanilines on the physicochemical properties of poly(N-isopropylacrylamide) based thermosensitive hydrogels. *Eur. Polym. J.* **2011**, *47*, 1977–1984. [[CrossRef](#)]
12. Schmidt, V.M.; Barbero, C.; Kötz, R. The ion exchange in polypyrrole in aqueous electrolytes. A probe beam deflection study of the effect of fixed negative charges. *J. Electroanal. Chem.* **1993**, *352*, 301–307. [[CrossRef](#)]
13. Abel, S.B.; Yslas, E.I.; Rivarola, C.R.; Barbero, C.A. Synthesis of polyaniline (PANI) and functionalized polyaniline (F-PANI) nanoparticles with controlled size by solvent displacement method. Application in fluorescence detection and bacteria killing by photothermal effect. *Nanotechnology* **2018**, *29*, 125604. [[CrossRef](#)] [[PubMed](#)]
14. Kushwaha, C.S.; Singh, P.; Shukla, S.K.; Chehimi, M.M. Advances in conducting polymer nanocomposite based chemical sensors: An overview. *Mater. Sci. Eng. B Solid State Mater. Adv. Technol.* **2022**, *284*, 115856. [[CrossRef](#)]
15. Okhay, O.; Tkach, A. Synergetic Effect of Polyaniline and Graphene in Their Composite Supercapacitor Electrodes: Impact of Components and Parameters of Chemical Oxidative Polymerization. *Nanomaterials* **2022**, *12*, 2531. [[CrossRef](#)]
16. Batista, A.F.; Rodrigues-Siqueli, A.C.; de Oliveira, A.P.S.; Petraconi, G.; Baldan, M.R. Facile synthesis of polyaniline catalyzed by carbon fiber for supercapacitor applications. *Synth. Met.* **2022**, *289*, 117116. [[CrossRef](#)]
17. Stejskal, J.; Gilbert, R.G. Polyaniline. Preparation of a conducting polymer (IUPAC Technical Report). *Pure Appl. Chem.* **2002**, *74*, 857–867. [[CrossRef](#)]
18. Takacs, L. The historical development of mechanochemistry. *Chem. Soc. Rev.* **2013**, *42*, 7649–7659. [[CrossRef](#)]
19. Krusenbaum, A.; Grätz, S.; Tigineh, G.T.; Borchardt, L.; Kim, J.G. The mechanochemical synthesis of polymers. *Chem. Soc. Rev.* **2022**, *51*, 2873–2905. [[CrossRef](#)] [[PubMed](#)]
20. Qiu, Y.-Y.; Ding, W.-H. Mechanochemically synthesized zeolitic imidazolate framework-8 as sorbent for dispersive solid-phase extraction of benzophenone-type ultraviolet filters in aqueous samples. *J. Chromatogr. A* **2022**, *1681*, 463443. [[CrossRef](#)] [[PubMed](#)]
21. Talari, M.K.; Deni, M.S.M.; Zor, N.M.; Thota, V.; Zakaria, A. Effect of diluents on crystallite size and electronic band gap of ZnO nanoparticles synthesized by mechanochemical processing. *Adv. Mater. Res.* **2013**, *626*, 786–790. [[CrossRef](#)]
22. Terban, M.W.; Madhau, L.; Cruz-Cabeza, A.J.; Okeyo, P.O.; Etter, M.; Schulz, A.; Rantanen, J.; Dinnebier, R.E.; Billinge, S.J.L.; Moneghini, M.; et al. Controlling desolvation through polymer-assisted grinding. *CrystEngComm* **2022**, *24*, 2306–2313. [[CrossRef](#)]
23. Lee, G.S.; Lee, H.W.; Lee, H.S.; Do, T.; Do, J.-L.; Lim, J.; Peterson, G.I.; Frišćić, T.; Kim, J.G. Mechanochemical ring-opening metathesis polymerization: Development, scope, and mechano-exclusive polymer synthesis. *Chem. Sci.* **2022**, *13*, 11496–11505. [[CrossRef](#)] [[PubMed](#)]
24. Modarresi-Alam, A.R.; Zeraatkar, V.; Tabatabaei, F.A.; Bazrafkan, M.; Dastgerdi, A.S.; Malekmakan, R. A solid-state synthesis, mechanism, and characterization of high molecular weight poly (3-aminobenzenesulfonic acid) with FeCl₃·6H₂O as a binary oxidant and dopant. *J. Polym. Res.* **2019**, *26*, 22. [[CrossRef](#)]
25. Wang, G.-W. Mechanochemical organic synthesis. *Chem. Soc. Rev.* **2013**, *42*, 7668–7700. [[CrossRef](#)] [[PubMed](#)]
26. Horie, K.; Barón, M.; Fox, R.B.; He, J.; Hess, M.; Kahovec, J.; Kitayama, T.; Kubisa, P.; Maréchal, E.; Mormann, W.; et al. Definitions of terms relating to reactions of polymers and to functional polymeric materials: (IUPAC Recommendations 2003). *Pure Appl. Chem.* **2004**, *76*, 889–906. [[CrossRef](#)]

27. Johnston, J.; Adams, L.H. On the effect of high pressures on the physical and chemical behavior of solids. *Am. J. Sci.* **1913**, XXXV, 206–251. [[CrossRef](#)]
28. Huang, J.; Virji, S.; Weiller, B.H.; Kaner, R.B. Polyaniline nanofibers: Facile synthesis and chemical sensors. *J. Am. Chem. Soc.* **2003**, 125, 314–315. [[CrossRef](#)]
29. Takacs, L. Metal-metal oxide systems for nanocomposite formation by reaction milling. *Nanostructured Mater.* **1993**, 2, 241–249. [[CrossRef](#)]
30. Michaelson, J.C. Aniline in history and technology. *Endeavour* **1993**, 17, 121–126. [[CrossRef](#)]
31. Willstätter, R.; Dorogi, S. Über Anilinschwarz. III. *Ber. Dtsch. Chem. Ges.* **1909**, 42, 4118–4135. [[CrossRef](#)]
32. Green, A.G.; Woodhead, A.E. CCXLIII.—Aniline-black and allied compounds. Part I. *J. Chem. Soc. Trans.* **1910**, 97, 2388–2403. [[CrossRef](#)]
33. De Surville, R.; Jozefowicz, M.; Yu, L.T.; Pepichon, J.; Buvet, R. Electrochemical chains using protolytic organic semiconductors. *Electrochim. Acta* **1968**, 13, 1451–1458. [[CrossRef](#)]
34. Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heeger, A.J. Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)_x. *J. Chem. Soc. Chem. Commun.* **1977**, 578–580. [[CrossRef](#)]
35. Gospodinova, N.; Terlemezyan, L. Conducting polymers prepared by oxidative polymerization: Polyaniline. *Prog. Polym. Sci.* **1998**, 23, 1443–1484. [[CrossRef](#)]
36. Yang, H.; Bard, A.J. The application of fast scan cyclic voltammetry. Mechanistic study of the initial stage of electropolymerization of aniline in aqueous solutions. *J. Electroanal. Chem.* **1992**, 339, 423–449. [[CrossRef](#)]
37. Miras, M.C.; Barbero, C.; Haas, O. Preparation of polyaniline by electrochemical polymerization of aniline in acetonitrile solution. *Synth. Met.* **1991**, 43, 3081–3084. [[CrossRef](#)]
38. Planes, G.A.; Rodríguez, J.L.; Miras, M.C.; García, G.; Pastor, E.; Barbero, C.A. Spectroscopic evidence for intermediate species formed during aniline polymerization and polyaniline degradation. *Phys. Chem. Chem. Phys.* **2010**, 12, 10584–10593. [[CrossRef](#)]
39. Konaka, R.; Kuruma, K.; Terabe, S. Mechanisms of Oxidation of Aniline and Related Compounds in Basic Solution. *J. Am. Chem. Soc.* **1968**, 90, 1801–1806. [[CrossRef](#)]
40. Barbero, C.; Salavagione, H.J.; Acevedo, D.F.; Grumelli, D.E.; Garay, F.; Planes, G.A.; Morales, G.M.; Miras, M.C. Novel synthetic methods to produce functionalized conducting polymers I. Polyanilines. *Electrochim. Acta* **2004**, 49, 3671–3686. [[CrossRef](#)]
41. Šeděnková, I.; Trchová, M.; Stejskal, J.; Bok, J. Polymerization of aniline in the solutions of strong and weak acids: The evolution of infrared spectra and their interpretation using factor analysis. *Appl. Spectrosc.* **2007**, 61, 1153–1162. [[CrossRef](#)]
42. Plater, M.J.; Harrison, W.T.A. Synthetic derivatives of mauveine. *J. Chem. Res.* **2013**, 37, 427–434. [[CrossRef](#)]
43. Plater, M.J.; Raab, A. Synthesis and analysis by liquid chromatography-mass spectrometry of a mauveine composition similar to museum-stored mauveine. *J. Chem. Res.* **2018**, 42, 589–594. [[CrossRef](#)]
44. Campbell, D.K.; Baeriswyl, D.; Mazumdar, S. Electron-electron interaction effects in quasi-one-dimensional conducting polymers and related systems. *Synth. Met.* **1987**, 17, 197–202. [[CrossRef](#)]
45. Liang, S.-D.; Bai, Y.-H.; Beng, B. Peierls instability and persistent current in mesoscopic conducting polymer rings. *Phys. Rev. B Condens. Matter Mater. Phys.* **2006**, 74, 113304. [[CrossRef](#)]
46. Yáñez-Heras, J.; Planes, G.A.; Williams, F.; Barbero, C.A.; Battaglini, F. Sequential electrochemical polymerization of aniline and their derivatives showing electrochemical activity at neutral pH. *Electroanalysis* **2010**, 22, 2801–2808. [[CrossRef](#)]
47. Morales, G.M.; Salavagione, H.J.; Grumelli, D.E.; Miras, M.C.; Barbero, C.A. Soluble polyanilines obtained by nucleophilic addition of arenosulphonic acids. *Polymer* **2006**, 47, 8272–8280. [[CrossRef](#)]
48. Jaworski, J.S.; Kalinowski, M.K. Electrochemistry of anilines. In *The Chemistry of Anilines, Part 1*; Rappoport, Z., Ed.; Wiley: Chichester, UK, 2007.
49. Konyushenko, E.N.; Stejskal, J.; Trchová, M.; Blinova, N.V.; Holler, P. Polymerization of aniline in ice. *Synth. Met.* **2008**, 158, 927–933. [[CrossRef](#)]
50. Cavallo, P.C.; Muñoz, D.J.; Miras, M.C.; Barbero, C.; Acevedo, D.F. Extracting kinetic parameters of aniline polymerization from thermal data of a batch reactor. Simulation of the thermal behavior of a reactor. *J. Appl. Polym. Sci.* **2014**, 131, 39409. [[CrossRef](#)]
51. Tzou, K.; Gregory, R.V. Kinetic study of the chemical polymerization of aniline in aqueous solutions. *Synth. Met.* **1992**, 47, 267–277. [[CrossRef](#)]
52. Balasubramanian, S.; Gupta, M.K.; Singh, K.K. Cryogenics and its application with reference to spice grinding: A review. *Crit. Rev. Food Sci. Nutr.* **2012**, 52, 781–794. [[CrossRef](#)]
53. Tang, H.; Ding, Y.; Zang, C.; Gu, J.; Shen, Q.; Kan, J. Effect of temperature on electrochemical degradation of polyaniline. *Int. J. Electrochem. Sci.* **2014**, 9, 7239–7252.
54. Gul, S.; Shah, A.-U.-H.A.; Bilal, S. Effect of high temperature on the electrochemical and optical properties of emeraldine salt doped with DBSA and sulfuric acid. *J. Chem.* **2015**, 2015, 826358. [[CrossRef](#)]
55. Syed, A.A.; Dinesan, M.K. Polyaniline: Reaction stoichiometry and use as an ion-exchange polymer and acid/base indicator. *Synth. Met.* **1990**, 36, 209–215. [[CrossRef](#)]
56. Morales, G.M.; Tuninetti, J.; Miras, M.C.; Barbero, C. Photolithography of polyaniline on solid substrates using photoassisted polymerization of aniline. *Mol. Cryst. Liq. Cryst.* **2010**, 522, 389–396. [[CrossRef](#)]
57. Barbero, C.A. Ion exchange at the electrode/electrolyte interface studied by probe beam deflection techniques. *Phys. Chem. Chem. Phys.* **2005**, 7, 1885–1899. [[CrossRef](#)] [[PubMed](#)]
58. Salavagione, H.; Morales, G.M.; Miras, M.C.; Barbero, C. Synthesis of a self-doped polyaniline by nucleophilic addition. *Acta Polym.* **1999**, 50, 40–44. [[CrossRef](#)]

59. Morales, G.M.; Llusa, M.; Miras, M.C.; Barbero, C. Effects of high hydrochloric acid concentration on aniline chemical polymerization. *Polymer* **1997**, *38*, 5247–5250. [[CrossRef](#)]
60. Abel, S.B.; Riberi, K.; Rivarola, C.R.; Molina, M.; Barbero, C.A. Synthesis of a smart conductive block copolymer responsive to heat and near infrared light. *Polymers* **2019**, *11*, 1744. [[CrossRef](#)]
61. Tang, S.-J.; Wang, A.-T.; Lin, S.-Y.; Huang, K.-Y.; Yang, C.-C.; Yeh, J.-M.; Chiu, K.-C. Polymerization of aniline under various concentrations of APS and HCl. *Polym. J.* **2011**, *43*, 667–675. [[CrossRef](#)]
62. Šeděnková, I.; Konyushenko, E.N.; Stejskal, J.; Trchová, M.; Prokeš, J. Solid-state oxidation of aniline hydrochloride with various oxidants. *Synth. Met.* **2011**, *161*, 1353–1360. [[CrossRef](#)]
63. Sbaite, P.; Huerta-Vilca, D.; Barbero, C.; Miras, M.C.; Motheo, A.J. Effect of electrolyte on the chemical polymerization of aniline. *Eur. Polym. J.* **2004**, *40*, 1445–1450. [[CrossRef](#)]
64. Rasmussen, S.C. The Early History of Polyaniline: Discovery and Origins. *Substantia* **2017**, *1*, 99–109. [[CrossRef](#)]
65. Gong, J.; Cui, X.-J.; Xie, Z.-W.; Wang, S.-G.; Qu, L.-Y. The solid-state synthesis of polyaniline/H₄SiW₁₂O₄₀ materials. *Synth. Met.* **2002**, *129*, 187–192. [[CrossRef](#)]
66. Huang, J.; Moore, J.A.; Acquaye, J.H.; Kaner, R.B. Mechanochemical route to the conducting polymer polyaniline. *Macromolecules* **2005**, *38*, 317–321. [[CrossRef](#)]
67. Abdiryim, T.; Jamal, R.; Nurulla, I. Doping effect of organic sulphonic acids on the solid-state synthesized polyaniline. *J. Appl. Polym. Sci.* **2007**, *105*, 576–584. [[CrossRef](#)]
68. Abdiryim, T.; Xiao-Gang, Z.; Jamal, R. Comparative studies of solid-state synthesized polyaniline doped with inorganic acids. *Mater. Chem. Phys.* **2005**, *90*, 367–372. [[CrossRef](#)]
69. Bekri-Abbes, I.; Srasra, E. Investigation of structure and conductivity properties of polyaniline synthesized by solid-solid reaction. *J. Polym. Res.* **2011**, *18*, 659–665. [[CrossRef](#)]
70. Zhou, Z.H.; Zhang, X.X.; Tian, D.; Xiong, R.; Lu, C.H. Solvent free synthesis of polyaniline with improved molecular weight through solid state mechanochemical milling at ambient temperature. *Mater. Res. Innov.* **2013**, *17*, 84–91. [[CrossRef](#)]
71. Perumal, M.; Jesuraj, D.; Konda Kannan, S.K. Selenious acid-doped polyaniline synthesis and characterization by chemical oxidative solid-state polymerization of aniline with SeO₂ as an oxidizing agent. *Polym. Int.* **2022**, *71*, 770–776. [[CrossRef](#)]
72. Bhandari, S.; Khastgir, D. Synergistic effect of simultaneous dual doping in solvent-free mechanochemical synthesis of polyaniline supercapacitor comparable to the composites with multiwalled carbon nanotube. *Polymer* **2015**, *81*, 62–69. [[CrossRef](#)]
73. Posudievsky, O.Y.; Goncharuk, O.A.; Barillé, R.; Pokhodenko, V.D. Structure-property relationship in mechanochemically prepared polyaniline. *Synth. Met.* **2010**, *160*, 462–467. [[CrossRef](#)]
74. Bhandari, S.; Khastgir, D. Template-free solid state synthesis of ultra-long hairy polyaniline nanowire supercapacitor. *Mater. Lett.* **2014**, *135*, 202–205. [[CrossRef](#)]
75. Du, X.-S.; Zhou, C.-F.; Wang, G.-T.; Mai, Y.-W. Novel solid-state and template-free synthesis of branched polyaniline nanofibers. *Chem. Mater.* **2008**, *20*, 3806–3808. [[CrossRef](#)]
76. Zhou, C.-F.; Du, X.-S.; Liu, Z.; Ringer, S.P.; Mai, Y.-W. Solid phase mechanochemical synthesis of polyaniline branched nanofibers. *Synth. Met.* **2009**, *159*, 1302–1307. [[CrossRef](#)]
77. Gribkova, O.L.; Nekrasov, A.A.; Ivanov, V.F.; Kozarenko, O.A.; Posudievsky, O.Y.; Vannikov, A.V.; Koshechko, V.G.; Pokhodenko, V.D. Mechanochemical synthesis of polyaniline in the presence of polymeric sulfonic acids of different structure. *Synth. Met.* **2013**, *180*, 64–72. [[CrossRef](#)]
78. Jensen, J.L.; Gardner, M.P. Solvent isotope effects on pK_a of anilinium ions in aqueous sulfuric acid. *J. Phys. Chem.* **1973**, *77*, 1557–1562. [[CrossRef](#)]
79. Sun, Y.; Wei, Y.; Tang, X. Molecular weight of chemically polymerized polyaniline. *Makromol. Chem.* **1988**, *9*, 829–834. [[CrossRef](#)]
80. Mapother, D.; Crooks, H.N.; Maurer, R. Self-diffusion of sodium in sodium chloride and sodium bromide. *J. Chem. Phys.* **1950**, *18*, 1231–1236. [[CrossRef](#)]
81. Zhilenko, M.P.; Muravieva, G.P.; Ehrlich, H.V.; Lisichkin, G.V. Production of highly dispersed sodium chloride: Strategy and experiment. *Russ. J. Appl. Chem.* **2016**, *89*, 857–864. [[CrossRef](#)]
82. Šeděnková, I.; Trchová, M.; Blinova, N.V.; Stejskal, J. In-situ polymerized polyaniline films. Preparation in solutions of hydrochloric, sulfuric, or phosphoric acid. *Thin Solid Films* **2006**, *515*, 1640–1646. [[CrossRef](#)]
83. Sadegh, F.; Modarresi-Alam, A.R.; Noroozifar, M.; Mansouri-Torshizi, H. Solid-state synthesis of pani-tio2 nanocomposite: Investigation of reaction conditions, nature of oxidant and electrical properties. *Express Polym. Lett.* **2021**, *15*, 2–15. [[CrossRef](#)]
84. Nestorović, G.D.; Jeremić, K.B.; Jovanović, S.M. Kinetics of aniline polymerization initiated with iron(III) chloride. *J. Serb. Chem. Soc.* **2006**, *71*, 895–904. [[CrossRef](#)]
85. Benahmed, W.N.; Bekri-Abbes, I.; Srasra, E. Spectroscopic study of polyaniline/AgCl@Ag nanocomposites prepared by a one-step method. *J. Spectrosc.* **2018**, *2018*, 7320654. [[CrossRef](#)]
86. Monzon, L.M.A.; Ackland, K.; Mosivand, S.; Venkatesan, M.; Coey, J.M.D. The role of polyaniline in the formation of iron-containing nanocomposites. *J. Nanopart. Res.* **2013**, *15*, 1533. [[CrossRef](#)]
87. Farrage, N.M.; Oraby, A.H.; Abdelrazek, E.M.M.; Atta, D. Synthesis, characterization of Ag@PANI core-shell nanostructures using solid state polymerization method. *Biointerface Res. Appl. Chem.* **2019**, *9*, 3934–3941. [[CrossRef](#)]
88. Miras, M.C.; Barbero, C.; Kötz, R.; Haas, O. Electroactive Polyaniline Film from Proton Free Nonaqueous Solution. *J. Electrochem. Soc.* **1991**, *138*, 335–336. [[CrossRef](#)]

89. Yslas, E.I.; Ibarra, L.E.; Peralta, D.O.; Barbero, C.A.; Rivarola, V.A.; Bertuzzi, M.L. Polyaniline nanofibers: Acute toxicity and teratogenic effect on *Rhinella arenarum* embryos. *Chemosphere* **2012**, *87*, 1374–1380. [[CrossRef](#)]
90. Shumaila; Lakshmi, G.B.V.S.; Alam, M.; Siddiqui, A.M.; Zulfequar, M.; Husain, M. Synthesis and characterization of Se doped polyaniline. *Curr. Appl. Phys.* **2011**, *11*, 217–222. [[CrossRef](#)]
91. Budavari, S. (Ed.) *The Merck Index—An Encyclopedia of Chemicals, Drugs, and Biologicals*; Merck and Co., Inc.: Whitehouse Station, NJ, USA, 1996; p. 1448.
92. Barbero, C.; Kötz, R. Electrochemical formation of a self-doped conductive polymer in the absence of a supporting electrolyte. The copolymerization of o-aminobenzenesulfonic acid and aniline. *Adv. Mater.* **1994**, *6*, 577–580. [[CrossRef](#)]
93. Barbero, C.; Miras, M.C.; Kötz, R.; Haas, O. Sulphonated polyaniline (SPAN) films as cation insertion electrodes for battery applications part II: Exchange of mobile species in aqueous and non-aqueous solutions. *J. Electroanal. Chem.* **1997**, *437*, 191–198. [[CrossRef](#)]
94. Acevedo, D.F.; Miras, M.C.; Barbero, C.A. Combinatorial synthesis and screening of photochromic dyes and modified conducting polymers. In *Combinatorial and High-Throughput Discovery and Optimization of Catalysts and Materials*; CRC: Boca Raton, FL, USA, 2006; pp. 239–256. [[CrossRef](#)]
95. Bavastrello, V.; Stura, E.; Carrara, S.; Erokhin, V.; Nicolini, C. Poly(2,5-dimethylaniline)-MWNTs nanocomposite: A new material for conductometric acid vapours sensor. *Sens. Actuators B Chem.* **2004**, *98*, 247–253. [[CrossRef](#)]
96. Salavagione, H.J.; Acevedo, D.F.; Miras, M.C.; Barbero, C. Redox Coupled Ion Exchange in Copolymers of Aniline with Aminobenzoic Acids. *Port. Electrochim. Acta* **2003**, *21*, 245–254. [[CrossRef](#)]
97. Planes, G.A.; Rodriguez, J.L.; Miras, M.C.; Pastor, E.; Barbero, C.A. Spectroelectrochemical studies of poly(N-methylaniline) formation, redox behaviour and degradation. A comparison with polyaniline. *Electrochim. Acta* **2014**, *122*, 39–49. [[CrossRef](#)]
98. Jamal, R.; Abdiryim, T.; Ding, Y.; Nurulla, I. Comparative studies of solid-state synthesized poly(o-methoxyaniline) doped with organic sulfonic acids. *J. Polym. Res.* **2008**, *15*, 75–82. [[CrossRef](#)]
99. Palaniappan, S.; Chang, Y.-T.; Liu, C.-M.; Manisankar, P. Mechanochemical synthesis and characterization of poly(2,5-dimethoxy aniline) salts. *J. Appl. Polym. Sci.* **2012**, *124*, 4281–4288. [[CrossRef](#)]
100. Khadieva, A.I.; Gorbachuk, V.V.; Latypov, R.R.; Stoikov, I.I. Synthesis and Comparison of the Electrical Properties of Polyaniline and Poly[(N-2-hydroxyethyl)aniline]. *Semiconductors* **2019**, *53*, 2090–2093. [[CrossRef](#)]
101. Abdiryim, T.; Xiao-Gang, Z.; Jamal, R. Synthesis and characterization of poly(o-toluidine) doped with organic sulfonic acid by solid-state polymerization. *J. Appl. Polym. Sci.* **2005**, *96*, 1630–1634. [[CrossRef](#)]
102. Viva, F.A.; Andrade, E.M.; Florit, M.I.; Molina, F.V. Electropolymerization of 2-methoxyaniline. Polymerization kinetics and phenazine insertion at low monomer concentration. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2293–2300. [[CrossRef](#)]
103. Barbero, C.; Silber, J.J.; Sereno, L. Formation of a novel electroactive film by electropolymerization of ortho-aminophenol. Study of its chemical structure and formation mechanism. Electropolymerization of analogous compounds. *J. Electroanal. Chem.* **1989**, *263*, 333–352. [[CrossRef](#)]
104. Iseminger, P.W.; Gregory, M.; Weakley, T.J.R.; Caple, G.; Sykes, A.G. Characterization of 3-Aminophenazin-2-ol Isolated from the Chemical Oxidation of o-Phenylenediamine. *J. Org. Chem.* **1997**, *62*, 2643–2645. [[CrossRef](#)]
105. Tucceri, R.; Arnal, P.M.; Scian, A.N. poly(o-aminophenol) film electrodes: Synthesis and characterization and formation mechanisms—A review article. *Can. J. Chem.* **2013**, *91*, 91–112. [[CrossRef](#)]
106. Mazeikiene, R.; Malinauskas, A. The stability of poly(o-phenylenediamine) as an electrode material. *Synth. Met.* **2002**, *128*, 121–125. [[CrossRef](#)]
107. Salavagione, H.J.; Arias-Pardilla, J.; Pérez, J.M.; Vázquez, J.L.; Morallón, E.; Miras, M.C.; Barbero, C. Study of redox mechanism of poly(o-aminophenol) using in situ techniques: Evidence of two redox processes. *J. Electroanal. Chem.* **2005**, *576*, 139–145. [[CrossRef](#)]
108. Iwan, A.; Sek, D. Polymers with triphenylamine units: Photonic and electroactive materials. *Prog. Polym. Sci.* **2011**, *36*, 1277–1325. [[CrossRef](#)]
109. Eswaran, M.; Dhanusuraman, R.; Chokkiah, B.; Tsai, P.-C.; Wabaidur, S.M.; Alothman, Z.A.; Ponnusamy, V.K. Poly(diphenylamine) and its Nanohybrids for Chemicals and Biomolecules Analysis: A Review. *Curr. Anal. Chem.* **2022**, *18*, 546–562. [[CrossRef](#)]
110. Pankratov, A.N. Structure of the products of the oxidation of diphenylamine, the first member in a family of analytical redox reagents. *J. Anal. Chem.* **2001**, *56*, 140–142. [[CrossRef](#)]
111. Zoromba, M.S.; Abdel-Aziz, M.H. Ecofriendly method to synthesize poly(o-aminophenol) based on solid state polymerization and fabrication of nanostructured semiconductor thin film. *Polymer* **2017**, *120*, 20–29. [[CrossRef](#)]
112. Palaniappan, S.; Chang, Y.-T.; Liu, C.-M.; Manisankar, P. Template-free mechanochemical route to prepare crystalline and electroactive polydiphenylamine nanostructures. *Mater. Chem. Phys.* **2011**, *129*, 948–954. [[CrossRef](#)]
113. Zoromba, M.S.; Abdel-Aziz, M.H.; Bassyouni, M.; El-Ashtouky, E.-S.Z.; Abdel-Hamid, S.M.S. Synthesis of o-aminophenol-m-phenylenediamine copolymer: An eco-friendly approach. *J. Polym. Res.* **2019**, *26*, 34. [[CrossRef](#)]
114. Ghanem, M.A. Development of Conducting Poly(o-Aminophenol) Film and its Capacitance Behavior. *Int. J. Electrochem. Sci.* **2016**, *11*, 9987–9997. [[CrossRef](#)]
115. Baláž, P.; Achimovicová, M.; Baláž, M.; Billik, P.; Zara, C.-Z.; Criado, J.M.; Delogu, F.; Dutková, E.; Gaffet, E.; Gotor, F.J.; et al. Hallmarks of mechanochemistry: From nanoparticles to technology. *Chem. Soc. Rev.* **2013**, *42*, 7571–7637. [[CrossRef](#)] [[PubMed](#)]
116. Senna, M. The promising aspects of processing nanomaterials under mechanical stressing for physicochemical viewpoints. *Adv. Powder Technol.* **2010**, *21*, 586–591. [[CrossRef](#)]

117. Yarmohamadi-Vasel, M.; Modarresi-Alam, A.R.; Noroozifar, M.; Hadavi, M.S. An investigation into the photovoltaic activity of a new nanocomposite of (polyaniline nanofibers)/(titanium dioxide nanoparticles) with different architectures. *Synth. Met.* **2019**, *252*, 50–61. [[CrossRef](#)]
118. Bekri-Abbes, I.; Srasra, E. Characterization and AC conductivity of polyaniline-montmorillonite nanocomposites synthesized by mechanical/chemical reaction. *React. Funct. Polym.* **2010**, *70*, 11–18. [[CrossRef](#)]
119. Ding, Y.; Abdiryim, T.; An, S.; Nurulla, I. Effect of β -cyclodextrin on the solid-state synthesized polyaniline doped with hydrochloric acid. *J. Appl. Polym. Sci.* **2008**, *107*, 3864–3870. [[CrossRef](#)]
120. García-Gallegos, J.C.; Vega-Cantú, Y.I.; Rodríguez-Macías, F.J. Fast mechanochemical synthesis of carbon nanotube-polyaniline hybrid materials. *J. Mater. Res.* **2018**, *33*, 1486–1495. [[CrossRef](#)]
121. Jamal, R.; Shao, W.; Xu, F.; Abdiryim, T. Comparison of structure and electrochemical properties for PANI/TiO₂/G and PANI/G composites synthesized by mechanochemical route. *J. Mater. Res.* **2013**, *28*, 832–839. [[CrossRef](#)]
122. Du, X.; Liu, H.-Y.; Cai, G.; Mai, Y.-W.; Baji, A. Use of facile mechanochemical method to functionalize carbon nanofibers with nanostructured polyaniline and their electrochemical capacitance. *Nanoscale Res. Lett.* **2012**, *7*, 111. [[CrossRef](#)] [[PubMed](#)]
123. Bekri-Abbes, I.; Srasra, E. Solid-state synthesis and electrical properties of polyaniline/Cu- montmorillonite nanocomposite. *Mater. Res. Bull.* **2010**, *45*, 1941–1947. [[CrossRef](#)]
124. Bekri-Abbes, I.; Srasra, E. Green synthesis of polyaniline/clay/iron ternary nanocomposite by the one step solid state intercalation method. *Mater. Sci. Semicond. Process.* **2015**, *40*, 543–549. [[CrossRef](#)]
125. Yoshimoto, S.; Ohashi, F.; Ohnishi, Y.; Nonami, T. Synthesis of polyaniline-montmorillonite nanocomposites by the mechanochemical intercalation method. *Synth. Met.* **2004**, *145*, 265–270. [[CrossRef](#)]
126. Yoshimoto, S.; Ohashi, F.; Kameyama, T. Simple preparation of sulfate anion-doped polyaniline-clay nanocomposites by an environmentally friendly mechanochemical synthesis route. *Macromol. Rapid Commun.* **2004**, *25*, 1687–1691. [[CrossRef](#)]
127. Yoshimoto, S.; Ohashi, F.; Kameyama, T. Characterization and thermal degradation studies on polyaniline- intercalated montmorillonite nanocomposites prepared by a solvent-free mechanochemical route. *J. Polym. Sci. B Polym. Phys.* **2005**, *43*, 2705–2714. [[CrossRef](#)]
128. Zheng, H.; Feng, X.; Zhou, L.; Ye, Y.; Chen, J. Intercalated polyaniline-kaolinite nanocomposite prepared via in situ mechanochemical synthesis. *J. Appl. Polym. Sci.* **2016**, *133*, 43551. [[CrossRef](#)]
129. Kalaivasan, N.; Syed Shafi, S. Synthesis of various polyaniline/clay nanocomposites derived from aniline and substituted aniline derivatives by mechanochemical intercalation method. *E-J. Chem.* **2010**, *7*, 1477–1483. [[CrossRef](#)]
130. Shakoor, A.; Rizvi, T.Z.; Sangra, A.N. Polyaniline-montmorillonite (PANI-MMT) nanocomposites: Mechanochemical synthesis, structure, thermostability and electrical properties. *Polym. Sci. Ser. A* **2010**, *52*, 1034–1043. [[CrossRef](#)]
131. Bekri-Abbes, I.; Srasra, E. Solid phase mechanochemical synthesis of polyaniline-montmorillonite nanocomposite using grinded montmorillonite as oxidant. *Mater. Sci. Semicond. Process.* **2016**, *56*, 76–82. [[CrossRef](#)]
132. Koosheh, H.B.; Modarresi-Alam, A.R. Solid-state synthesis of a new core-shell nanocomposite of polyaniline and silica via oxidation of aniline hydrochloride by FeCl₃.6H₂O. *Polym. Adv. Technol.* **2016**, *27*, 1038–1049. [[CrossRef](#)]
133. Jiang, Y.; Ji, J.; Huang, L.; He, C.; Zhang, J.; Wang, X.; Yang, Y. One-pot mechanochemical exfoliation of graphite and: In situ polymerization of aniline for the production of graphene/polyaniline composites for high-performance supercapacitors. *RSC Adv.* **2020**, *10*, 44688–44698. [[CrossRef](#)]
134. Rajappa, S.; Shivarathri, P.G.; Aruna Kumari, M.L.; Swamygowda, D.K.; Devendrachari, M.C.; Kotresh, H.M.N. Mechanochemical route for tetra amino zinc phthalocyanine embedded PANI sensitized Fe₂O₃ heteroarchitecture for photodegradation of dyes under the influence of low power LED light source. *Surf. Interfaces* **2022**, *29*, 101720. [[CrossRef](#)]
135. Valadbeigi, E.; Modarresi-Alam, A.R.; Noroozifar, M.; Rezvani, A.R. Synthesis and characterization of new nanocomposites of [poly(o-toluidine)]/(WO₃ nanoparticles) and their application in novel hybrid solar cells. *Express Polym. Lett.* **2022**, *16*, 939–959. [[CrossRef](#)]
136. Ubul, A.; Jamal, R.; Rahman, A.; Awut, T.; Nurulla, I.; Abdiryim, T. Solid-state synthesis and characterization of polyaniline/multi-walled carbon nanotubes composite. *Synth. Met.* **2011**, *161*, 2097–2102. [[CrossRef](#)]
137. Abdiryim, T.; Ubul, A.; Jamal, R.; Rahman, A. Solid-state synthesis of polyaniline/single-walled carbon nanotubes: A comparative study with polyaniline/multi-walled carbon nanotubes. *Materials* **2012**, *5*, 1219–1231. [[CrossRef](#)]
138. Paulraj, P.; Manikandan, A.; Manikandan, E.; Pandian, K.; Moodley, M.K.; Roro, K.; Murugan, K. Solid-State Synthesis of POPD@AgNPs Nanocomposites for Electrochemical Sensors. *J. Nanosci. Nanotechnol.* **2018**, *18*, 3991–3999. [[CrossRef](#)] [[PubMed](#)]
139. Pandian, P.; Kalimuthu, R.; Arumugam, S.; Kannaiyan, P. Solid phase mechanochemical synthesis of Poly(o-anisidine) protected Silver nanoparticles for electrochemical dopamine sensor. *Mater. Today Commun.* **2021**, *26*, 102191. [[CrossRef](#)]
140. Grumelli, D.E.; Forzani, E.S.; Morales, G.M.; Miras, M.C.; Barbero, C.A.; Calvo, E.J. Microgravimetric Study of Electrochemically Controlled Nucleophilic Addition of Sulfite to Polyaniline. *Langmuir* **2004**, *20*, 2349–2355. [[CrossRef](#)]
141. Bicak, N.; Karagoz, B. Polymerization of aniline by copper-catalyzed air oxidation. *J. Polym. Sci. A Polym. Chem.* **2006**, *44*, 6025–6031. [[CrossRef](#)]
142. Kumru, B.; Bicak, N. Polymerization of aniline in microemulsion by catalytic air oxidation. *Macromol. Symp.* **2015**, *352*, 42–45. [[CrossRef](#)]
143. Zivari-Moshfegh, F.; Nematollahi, D.; Khoram, M.M.; Rahimi, A. Electrochemical oxidation of o-phenylenediamine and 1,3 dihydrospiro[benzo[d]imidazole-2,1'-cyclohexane]. A comprehensive study and introducing a novel case of CE mechanism. *Electrochim. Acta* **2020**, *354*, 136700. [[CrossRef](#)]
144. Available online: <https://www.epa.gov/toxics-release-inventory-tri-program/hydrochloric-acid> (accessed on 3 October 2022).
145. Ravnsbæk, J.B.; Swager, T.M. Mechanochemical synthesis of poly(phenylene vinylenes). *ACS Macro Lett.* **2014**, *3*, 305–309. [[CrossRef](#)]

146. Beadle, P.M.; Nicolau, Y.F.; Banka, E.; Rannou, P.; Djurado, D. Controlled polymerization of aniline at sub-zero temperatures. *Synth. Met.* **1998**, *95*, 29–45. [[CrossRef](#)]
147. Gomollón-Bel, F. Ten Chemical Innovations That Will Change Our World: IUPAC identifies emerging technologies in Chemistry with potential to make our planet more sustainable. *Chem. Int.* **2019**, *41*, 12–17. [[CrossRef](#)]
148. Liu, W.; Kumar, J.; Tripathy, S.; Senecal, K.J.; Samuelson, L. Enzymatically synthesized conducting polyaniline. *J. Am. Chem. Soc.* **1999**, *121*, 71–78. [[CrossRef](#)]
149. Asturias, G.E.; Jang, G.-W.; MacDiarmid, A.G.; Doblhofer, K.; Zhong, C. Membrane-properties of polymer films. The acid-doping reaction of polyaniline. *Ber. Bunsenges. Phys. Chem.* **1991**, *95*, 1381–1384. [[CrossRef](#)]
150. Barbero, C.; Miras, M.C.; Haas, O.; Kötz, R. Electrochemical and ion exchange properties of polyaniline-poly(vinylsulfonate) composites in aqueous and nonaqueous media. *J. Electrochem. Soc.* **1997**, *144*, 4170–4174. [[CrossRef](#)]
151. Wei, X.-L.; Wang, Y.Z.; Long, S.M.; Bobeczko, C.; Epstein, A.J. Synthesis and physical properties of highly sulfonated polyaniline. *J. Am. Chem. Soc.* **1996**, *118*, 2545–2555. [[CrossRef](#)]
152. Barbero, C.; Morales, G.M.; Grumelli, D.; Planes, G.; Salavagione, H.; Marengo, C.R.; Miras, M.C. New methods of polyaniline functionalization. *Synth. Met.* **1999**, *101*, 694–695. [[CrossRef](#)]
153. Andriianova, A.N.; Biglova, Y.N.; Mustafin, A.G. Effect of structural factors on the physicochemical properties of functionalized polyanilines. *RSC Adv.* **2020**, *10*, 7468–7491. [[CrossRef](#)]
154. Salavagione, H.J.; Acevedo, D.F.; Miras, M.C.; Motheo, A.J.; Barbero, C.A. Comparative study of 2-amino and 3-aminobenzoic acid copolymerization with aniline synthesis and copolymer properties. *J. Polym. Sci. A Polym. Chem.* **2004**, *42*, 5587–5599. [[CrossRef](#)]
155. Yue, J.; Gordon, G.; Epstein, A.J. Comparison of different synthetic routes for sulphonation of polyaniline. *Polymer* **1992**, *33*, 4410–4418. [[CrossRef](#)]
156. Han, C.-C.; Hong, S.-P.; Yang, K.-F.; Bai, M.-Y.; Lu, C.-H.; Huang, C.-S. Highly conductive new aniline copolymers containing butylthio substituent. *Macromolecules* **2001**, *34*, 587–591. [[CrossRef](#)]
157. Acevedo, D.F.; Salavagione, H.J.; Miras, M.C.; Barbero, C.A. Synthesis, properties and applications of functionalized polyanilines. *J. Braz. Chem. Soc.* **2005**, *16*, 259–269. [[CrossRef](#)]
158. Gallardo, A.; Pereyra, Y.; Martínez-Campos, E.; García, C.; Acitores, D.; Casado-Losada, I.; Gómez-Fatou, M.A.; Reinecke, H.; Ellis, G.; Acevedo, D.; et al. Facile one-pot exfoliation and integration of 2D layered materials by dispersion in a photocurable polymer precursor. *Nanoscale* **2017**, *9*, 10590–10595. [[CrossRef](#)]
159. Tzvetkov, G.; Mihaylova, S.; Stoitchkova, K.; Tzvetkov, P.; Spassov, T. Mechanochemical and chemical activation of lignocellulosic material to prepare powdered activated carbons for adsorption applications. *Powder Technol.* **2016**, *299*, 41–50. [[CrossRef](#)]
160. Bruno, M.M.; Cotella, N.G.; Miras, M.C.; Barbero, C.A. A novel way to maintain resorcinol-formaldehyde porosity during drying: Stabilization of the sol-gel nanostructure using a cationic polyelectrolyte. *Colloids Surf. A Physicochem. Eng. Asp.* **2010**, *362*, 28–32. [[CrossRef](#)]
161. Aniline Black. *Sci. Am.* **1869**, *20*, 353–354. [[CrossRef](#)]
162. Available online: <https://pubchem.ncbi.nlm.nih.gov/compound/Aniline-Black> (accessed on 28 November 2022).

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.