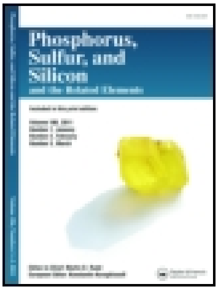

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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# Perchloric Acid-Doped Polyaniline as an Efficient and Reusable Catalyst for the Synthesis of 2-Substituted Benzothiazoles

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Version of record first published: 18 Nov 2009

To cite this article: Mohammad Abdollahi-Alibeik & Safoora Poorirani (2009): Perchloric Acid-Doped Polyaniline as an Efficient and Reusable Catalyst for the Synthesis of 2-Substituted Benzothiazoles, Phosphorus, Sulfur, and Silicon and the Related Elements, 184:12, 3182-3190

To link to this article: http://dx.doi.org/10.1080/10426500802705453

*Phosphorus, Sulfur, and Silicon*, 184:3182–3190, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500802705453

# Perchloric Acid–Doped Polyaniline as an Efficient and Reusable Catalyst for the Synthesis of 2-Substituted Benzothiazoles

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*2-Substituted benzothiazoles have been efficiently synthesized in good yields by the condensation reaction of o-aminothiophenol with aldehydes in the presence of a catalytic amount of perchloric acid–doped polyaniline ($HClO_4$/PANI). The low cost, simple recovery, and efficient reusability are remarkable characteristics of this catalyst.*

**Keywords** Benzothiazole; perchloric acid; polyaniline; polymer supported; reusability

## INTRODUCTION

Compounds with a benzothiazole moiety have received considerable attention because of their widespread occurrence in biologically active molecules such as antitumor, antimalaria, fungicide, anti-HIV, antiviral, and analgesic agents.[1] Recently, radiolabeling of benzothiazole derivatives has been developed for PET imaging in the detection of Alzheimer diseases.[2] These compounds also have many industrial applications; for example some 2-substituted benzothiazoles are utilized as fluorescence agents in textile dyeing, antioxidants, and vulcanization accelerators of rubber.[3]

Several synthetic methodologies have been developed for the synthesis of 2-substituted benzothiazoles. The most common direct methods are the condensation reaction of *o*-aminothiophenol with some functional groups to provide a substituent at the 2-position of the benzothiazole scaffold. Many acid catalysts have been used for these condensation reactions, such as the condensation of *o*-aminothiphenol with aldehydes in the presence of iodine,[4] $SiO_2$ or

Received 7 September 2008; accepted 10 December 2008.

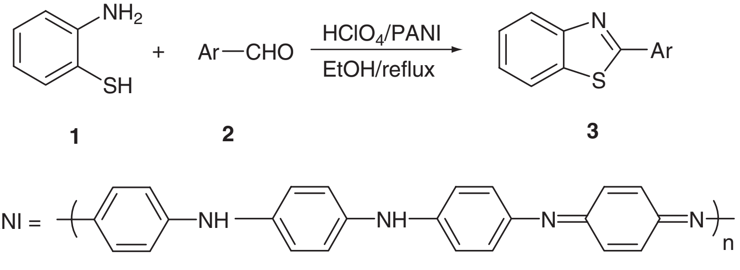
We are thankful to the Yazd University Research Council for partial support of this work.

Address correspondence to Mohammad Abdollahi-Alibeik, Department of Chemistry, Yazd University, Yazd 89195-741, Iran. E-mail: abdollahi@yazduni.ac.ir montmorillonite/graphite,[5] zirconyl chloride,[6] and $SiO_2$ under microwave irradiation,[7] and also condensation with carboxylic acids or its derivatives in the presence of iodine,[8] polyphosphoric acid,[9] polyphosphate,[10] and ionic liquid.[11] Some other methods include potassium ferricyanide–mediated cyclization of thiobenzanilides (Jacobson's method),[12] 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)–mediated cyclization of thiobenzanilides,[13] condensation of polymer-bonded esters with *o*-aminothiophenol in the presence of alkyl aluminum Lewis acids,[14] and palladium-catalyzed cyclization of *o*-bromophenylthioureas and *o*-bromothioamides.[15]

However, many of these methodologies suffer from one or more disadvantages, such as low yields of products, expensive catalysts, prolonged reaction times, high temperature, need for excess amounts of the catalysts, multistep synthesis, and non-reusability of the catalysts. Thus, there is a need for designing a simple and efficient method for the synthesis of benzothiazole derivatives.

In recent years, there has been an ongoing effort to replace conventional acid catalysts with solid acid catalysts. This is mainly due to some advantages of solid acid catalysts such as ease of handling, nontoxicity, ease of recovery, and reusability.[16] Among the various types of solid acids, polymer-supported acid catalysts have attracted considerable attention because of their desirable characteristics. Polyaniline has a wide range of applications in organic synthesis as a support for its easy preparative protocol, from inexpensive starting material, high environmental and thermal stability, and easy doping/undoping.[17]

In continuation of our study on the application of solid supported reagents in organic transformations,[18] herein we report the application of perchloric acid–doped polyaniline ($HClO_4$/PANI) as a reusable solid acid catalyst for the synthesis of 2-substituted benzothiazoles by the condensation reaction of *o*-aminothiophenol with aldehydes (Scheme 1).



**SCHEME 1** Synthesis of 2-substituted benzothiazoles by the reaction of 2-aminothiophenol and aldehydes in the presence of $HClO_4$/PANI under reflux condition.

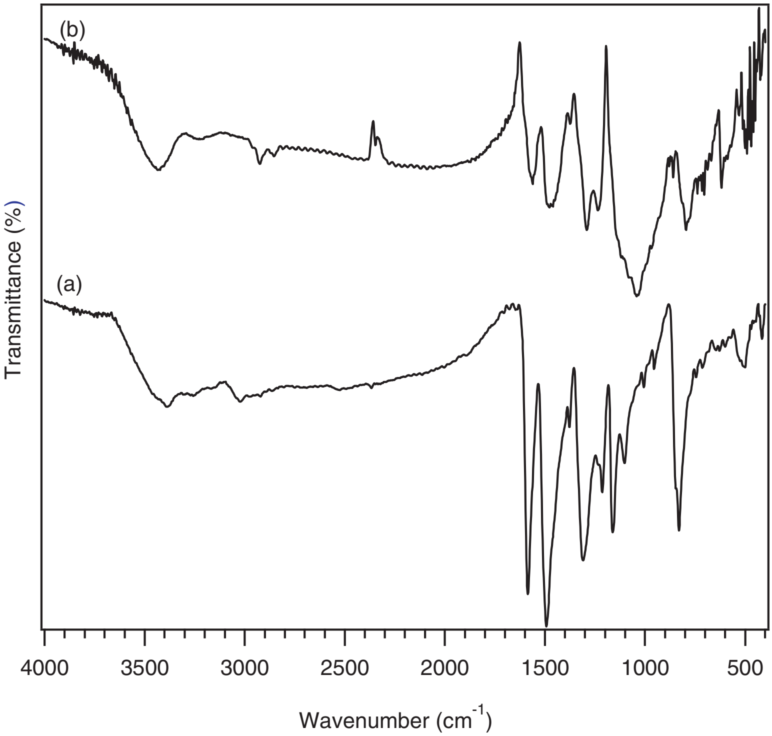


**FIGURE 1** FT-IR Spectra of (a) PANI, (b) $HClO_4$/PANI.

## RESULTS AND DISCUSSION

Initially, the polyaniline was prepared by polymerization of freshly distilled aniline as reported elsewhere.[19] Polyaniline was doped in 1.0 M $HClO_4$ solution, and $HClO_4$/PANI was obtained with 26 wt.% of perchloric acid. The doped polymer was characterized by XRD and FT-IR, and the results confirm the existence of perchlorate on the support.

The FT-IR spectra of PANI and $HClO_4$/PANI are shown in Figure 1. The spectrum of $HClO_4$/PANI is similar to that of PANI base, except a bond around 2930 $cm^{-1}$ that is assigned to $NH_2^+$ group and indicates the formation of polyaniline salt.[17e]

When compared with polyaniline base, the bond at 1580 $cm^{-1}$ (arising from both $C = N$ and $C = C$ stretching of the quinoid diimine unit) and the bond at 1470 $cm^{-1}$ (arising from C=C aromatic ring stretching of the benzenoid diimine unit) in $HClO_4$/PANI are shifted to lower wave numbers. The bond at 1040 $cm^{-1}$, appeared in the spectrum of $HClO_4$/PANI, is also assigned to Cl-O stretching of $ClO_4^-$

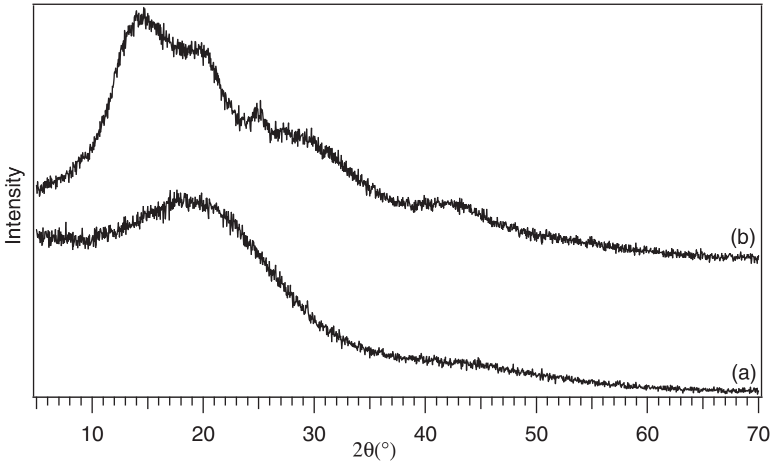


**FIGURE 2** XRD pattern of (a) PANI (b) $HClO_4$/PANI.

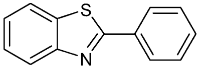
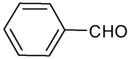
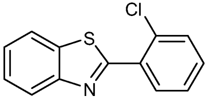
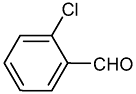
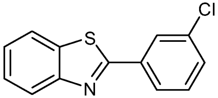
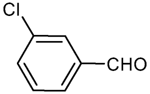
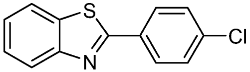
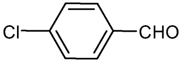
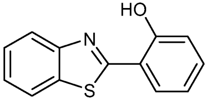
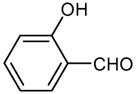
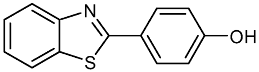
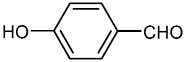
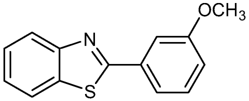
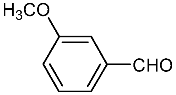
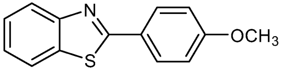
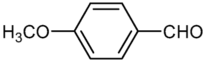
anion. Although there is not any report about exact characterization of $HClO_4$/PANI, these results however confirm good doping of PANI with $HClO_4$ with regard to literature reports for doping of polyaniline with other Brønsted acids.[17e,20]

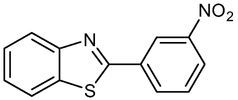
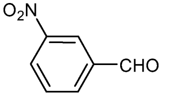
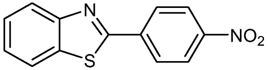
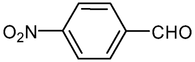
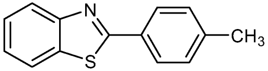
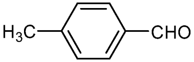
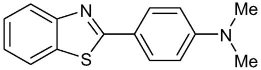
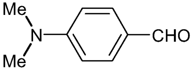
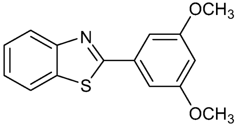
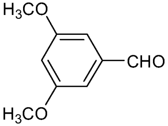
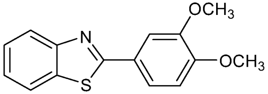
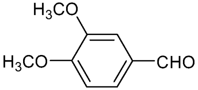
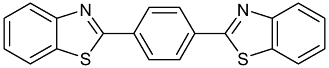
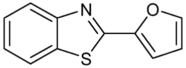
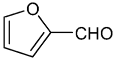
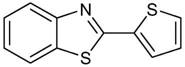
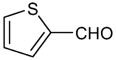
The XRD pattern of the PANI base and $HClO_4$/PANI are shown in Figure 2. As shown in the pattern (a), the XRD of the PANI base indicates the amorphous nature with peak at $2\theta = 19.5^\circ$. In the XRD pattern of $HClO_4$/PANI, broad peaks around $2\theta = 15^\circ$, $2\theta = 19.5^\circ$, and $2\theta = 25^\circ$ were observed. The peaks at $2\theta = 15^\circ$ and $2\theta = 25^\circ$ are stronger than that of $2\theta = 19.5^\circ$, which it similar to that of highly doped PANI salt as reported elsewhere.[20]

The condensation reaction of the benzaldehyde as a model substrate with *o*-aminothiophenol was investigated by using a catalytic amount of $HClO_4$/PANI in EtOH under reflux conditions. In a typical experiment, *o*-aminothiophenol (1 mmol) and benzaldehyde (1 mmol) were reacted together in the presence of $HClO_4$/PANI (100 mg) in EtOH at reflux. The condensation was complete after 2 h. The crude product with high purity was achieved by filtration of the catalyst, addition of water, and filtration of the obtained precipitate. Further purification was achieved by recrystallization of the crude product in ethanol/water, and 2-substituted benzothiazole was obtained in 85% yield (Table I, **3a**).

To explore the generality of this reaction, various types of aromatic aldehydes with both electron-donating and electron-withdrawing substituents were reacted with *o*-aminothiophenol under the same reaction

**TABLE I Synthesis of 2-Substituted Benzothiazoles by the Reaction of *o*-Aminothiophenol with Aldehydes in the Presence of a Catalytic Amount of $HClO_4$/PANI**

| Ref. | Mp (°C) [Lit.] | Time (h) | Yield[a] (%) | Benzothiazole (**3**) | Aldehyde (**2**) | Entry |
|---|---|---|---|---|---|---|
| 5 | 111–112 [113] | 2 | 85 |  |  | a |
| 7 | 78–79 [81–82] | 3 | 78 |  |  | b |
| 5 | 94–95 [96.5] | 2.5 | 75 |  |  | c |
| 21 | 116–117<br>[117–119] | 4 | 80 |  |  | d |
| 7 | 126–128<br>[131–132] | 5 | 80 |  |  | e |
| 5 | 219–220 [221] | 3.5 | 63 |  |  | f |
| 22 | 81–83 [81–82] | 3 | 70 |  |  | g |
| 7 | 120–121<br>[121–122] | 1.5 | 86 |  |  | h |

| | | | | | | |
|---|---|---|---|---|---|---|
| 5 | 178—179<br>[182.5] | 4.5 | 80 |  |  | i |
| 5 | 226—227 [229] | 4 | 78 |  |  | j |
| 7 | 83—84 [85] | 4 | 75 |  |  | k |
| 23 | 169—170 [173] | 7 | 68 |  |  | l |
| 24 | 85—86 [88] | 4 | 68 |  |  | m |
| 21 | 130—131<br>[132–134] | 4 | 80 |  |  | n |
| 25 | 255 [257–258] | 4 | 73 |  |  | o |
| 7 | 102—103<br>[103–104] | 4 | 68 |  |  | p |
| 7 | 97—99 [99] | 4 | 68 |  |  | q |

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[a] Isolated yields.

**TABLE II Reusability of $HClO_4$/PANI in the Reaction of *o*-Aminothiophenol with Benzaldehyde**

| Entry | Time (h) | Yield[a] (%) |
|---|---|---|
| 1 | 2 | 85 |
| 2 | 2:30 | 80 |
| 3 | 2:45 | 75 |
| 4 | 2:45 | 75 |

[a] Isolated yields.

conditions, and the corresponding 2-aryl benzothiazoles were obtained in 68–86% yields (Table I, **3b–3o**).

The reaction of heteroaryl aldehydes was also investigated in the same reaction condition, and the corresponding 2-heteroaryl benzothiazoles were obtained in 68% yields (Table I, **3p–3q**).

All of the synthesized products are known compounds and were characterized by comparing their melting points (Table I) and IR spectra. All of the FT-IR spectra show a bond around 1560–1620 $cm^{-1}$, arising from stretching frequency of $C = N$ in benzothiazole rings.

Catalyst reusability is one of the most important characteristics of solid acid catalysts. To study the reusability of $HClO_4$/PANI, the recovered catalyst from the reaction of *o*-aminothiophenol with benzaldehyde was applied in the same reaction four times. After each run, the catalyst was washed with acetone and dried at 120°C for 1 h. The results show that there is no substantial change in the catalyst reactivity (Table II), and there is only a steady decline in the yields and times of the reactions during third time of reuse, while this moderate deactivation is stopped in the forth run. These results suggest that the loss in catalytic activity is due to the blockage of the active site of the catalyst by coke deposition during the reaction.

In summary, we introduced $HClO_4$/PANI as a solid acid catalyst for efficient synthesis of 2-substituted benzothiazoles by the reaction of *o*-aminothiophenol with aldehydes. The ease of the catalyst preparation, simple workup, simple recovery, and reusability of the catalyst make this method advantageous for organic chemistry.

## EXPERIMENTAL

All of the chemicals were commercial products. Aniline from E. Merck was distilled prior to use. High purity grade perchloric acid, reagent grade solvents, and sodium persulfate (E. Merck) were used without purification. *o*-Aminothiophenol and benzaldehyde were distilled and freshly used, and other aldehydes (E. Merck and Aldrich) were used as received. Polyaniline was synthesized by oxidative polymerization of aniline in acidic solution, according to the method described in the literature.[19] All melting points were obtained by Buchi B-540 apparatus and are uncorrected. All reactions were monitored by TLC, and all yields refer to isolated products. $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ on a Bruker 500 MHz spectrometer. Infrared spectra were recorded on a Bruker FT-IR Equinax-55 spectrophotometer in KBr with absorption in $cm^{-1}$. XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer using nickel filtered Cu K$\alpha$ radiation.

## Synthesis of Perchloric Acid–Doped Polyaniline

Polyaniline (0.5 g) was added to a 1.0 M aqueous solution of $HClO_4$ (50 mL) in a 100 mL round bottom flask under vigorous stirring. The mixture was stirred for 4 h. The solid was filtered, washed with water (100 mL) followed by acetone (50 mL), and dried at 120°C for 1 h. Polyaniline salt with 26 wt.% for $HClO_4$ was obtained.

## General Experimental Procedure for the Synthesis of 2-Substituted Benzothiazoles

A mixture containing *o*-aminothiophenol (1 mmol), ethanol (5 mL), $HClO_4$/PANI (100 mg), and aldehyde (1 mmol) was taken in a 10 mL round bottom flask under reflux conditions. After completion of the reaction (monitored by TLC, EtOAc:*n*-hexane, 30:70), the reaction mixture was filtered, washed with EtOH (10 mL), and 50% of the solvent was evaporated under vacuum. To the obtained solution, water (5 mL) was added, and the precipitate was filtered and washed with water (5 mL). After drying of the solid, the corresponding 2-substituted benzothiazole was obtained with high purity. Further purification was achieved by column chromatography on silica-gel (eluent: EtOAc:*n*-hexane, 20:80). The corresponding 2-substituted benzothiazoles were obtained in 68–86% yields.

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