An efficient and regioselective thiocyanation of aromatic and heteroaromatic compounds using cross-linked poly (4-vinylpyridine)-supported thiocyanate as a versatile reagent and potassium peroxydisulfate as a strong oxidizing agent

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(Received 2 December 2013; accepted 18 April 2014)

A green and regioselective thiocyanation of aromatic and heteroaromatic compounds has been achieved via a simple protocol using cross-linked poly (4-vinylpyridine)-supported thiocyanate ion, [P4-VP]SCN, as a versatile polymeric reagent and potassium persulfate as a strong oxidizing agent, under heterogeneous conditions.

Various indoles, phenol and aniline derivatives, and pyrroles were transformed into their corresponding aryl thiocyanates in high to excellent yields. This procedure offers advantages such as short reaction time, simple reaction work-up, and the polymeric reagents can be regenerated and reused for several times without significant loss of their activity.

Keywords: thiocyanation; potassium persulfate; regioselectivity; polymeric reagent; aryl thiocyanate

1. Introduction

Sulfur-containing compounds have become increasingly useful and important in organic synthesis. Thiocyanates are well known in organosulfur chemistry.[1] Arylthiocyanates are of interest as

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compounds with high biological activity and convenient sources of ArS\(^-\).[2–4] Thiocyanate functional group is an interesting part of a molecule, which will be readily transformed into the other sulfur-bearing functionalities,[5–7] especially for producing compounds with pharmaceutical properties.[8,9]

The general procedure for thiocyanation of organic compounds is dissolving a thiocyanic acid salt (MSCN, M=K, Na, NH\(_4\)) in an appropriate solvent, mixing with a substrate and adding an oxidant dropwise. Several methods for the thiocyanation of aromatic systems using a variety of reagents such as bromine/potassium thiocyanate (only for indoles),[10] N-thiocyanatosuccinimide (only for 5-methoxy-2-methylindole and accompanied by two bisthiocyanates),[11] trichloroisocyanuric acid/N\(_4\)SCN/wet SiO\(_2\),[12] ceric ammonium nitrate/N\(_4\)SCN[13] and acidic montmorillonite K10 clay/N\(_4\)SCN[14] have been explored.

In 2004, Yadav et al.[15] recommended I\(_2\)/NH\(_4\)SCN for thiocyanation of indoles, anilines, N-alkyloxindoles and pyrroles. Under this system, mono-2-thiocyanato and bis-2,5-dithiocyanatopyrrole were generated.

Silica boron sulfonic acid/H\(_2\)O\(_2\)/NH\(_4\)SCN,[16] sodium perborate/N\(_4\)SCN,[17] oxone/N\(_4\)SCN,[18] diethyl azodicarboxylate,[19] diphenylphosphinite ionic liquid,[20] potassium peroxysulfate-copper(II),[21] ferric(III) chloride/N\(_4\)SCN,[22] acidic alumina/N\(_4\)SCN,[23] Mn(OAc)\(_3\)/NH\(_4\)SCN and[24] DDQ/N\(_4\)SCN,[25] were also used for thiocyanation of indoles, pyrroles, anilines and also indolines.

Thiocyanated indoles, anilines and pyrroles have been accomplished in the presence of the I\(_2\)O\(_5\)/NH\(_4\)SCN system. The reaction media achieved mono-thiocyanated correspondence of pyrrole and diphenylamine.[26]

A facile method for direct thiocyanation of activated arenes using iodic acid in combination with ammonium thiocyanate is described in 2009 by Mahajan and Akamanchi.[27] Anodic thiocyanation of mono- and disubstituted aromatic compounds is reported by Gitkis, and Becke.[28] o-Iodoxybenzoic acid (IBX)/NH\(_4\)SCN was suggested by Yadav for thiocyanation of indoles, arylamines and pyrroles.[29] In 2010, para-toluene sulfuric acid/N\(_4\)SCN was used by Das and Kumar[30] for thiocyanation of indoles.

Aqueous H\(_5\)IO\(_6\)/KSCN and aqueous HCl/H\(_2\)O\(_2\)/KSCN were prosperous reagents for thiocyanation of indoles, pyrroles, anilines and also indolines that was reported by Khazaei et al.[31] Reaction of (dichloroiodo) benzene/N\(_4\)SCN or Zn(SCN)\(_2\) was used for thiocyanation of anilines.[32] Poly (4-diacetoxyiodo) styrene (PDAIS)/NH\(_4\)SCN[33] was also used for thiocyanation of indoles and anilines. However, these methodologies suffer from one or more drawbacks such as the less availability or hard preparation of starting materials,[10,11] the requirement for a large excess of strong oxidizing reagents, low yields for some compounds[13,18] and performances under certain special conditions.[14] Therefore, it is important to find new and fast methods for synthesis of the thiocyanate group containing aromatic systems.

Persulfates are the most chemically active of the peroxygens, with great utility in a variety of chemical processes. Persulfates are key components in many industrial processes and commercial products. Potassium peroxysulfate (PPDS) has been explored by Bhatt and Perumal for the conversion of electron rich benzylic hydrocarbons to the corresponding carbonyl compounds.[34] Also, there are several reported investigations in the literature based on oxidizing properties of PPDS due to its strong redox potential such as Baeyer–Villiger oxidation.[35,36] The peroxydisulfate ion is a versatile oxidizing agent in aqueous solution[37] and is used in many organic reactions in the presence of metals acetates such as cobalt(III),[38] copper and iron.[39] The reactions involving these ions are generally slow at room temperature and the rate of peroxydisulfate decomposition increases greatly at a higher temperature.[38]

Recent developments in polymer-supported reactions have led to the propagation of combinatorial chemistry as a method for the rapid and efficient preparation of novel functionalized molecules.[40] An interesting and fast growing branch of this area is polymer-supported
reagents.[41] In recent years, the polymeric reagents, especially anion exchange resins, have been widely applied in organic transformations.[42–57] A literature search shows that there are a few reports in preparation of alkyl or aryl thiocyanates by using a polymer-supported thiocyanate ion.[42–45,58] Previously, Cainelli et al. reported a polymeric reagent for synthesis of alkyl thiocyanates. This polymeric reagent was prepared by treating the chloride form of Amberlyst A-26 (a macroporous resin containing quaternary ammonium groups) with aqueous potassium thiocyanate. This polymeric reagent converts a few alkyl halides to the corresponding alkyl thiocyanates in benzene under reflux conditions.[58] Also Hodge et al. reported that Amberlyst A-26 converted a few alkyl halides to the corresponding alkyl thiocyanates (seven examples) under the same conditions of the last report.[42] Tamami and Kiasat reported that epoxides were converted to their corresponding episulfides using Amberlit IRA-400 supported thiocyanate.[43] We have recently reported an efficient method for preparation of cross-linked poly (4-vinylpyridine)-supported thiocyanate ion, \([P_4-VP]SCN\), and used for synthesis of alkyl thiocyanates from alkyl halides [44] and for synthesis of aryl thiocyanates via diazotization-thiocyanation of arylamines.[45]

As far as we know, there are no reports on polymer-supported thiocyanate ion for electrophilic thiocyanation of aromatic or heteroaromatic rings hence, in this report, we wish to disclose a simple, convenient and efficient protocol for the thiocyanation of indoles, phenol and aniline derivatives, and pyrroles using \([P_4-VP]SCN\) as a versatile polymeric reagent and PPDS as a strong oxidant.

2. Results and discussion

In this paper, we report the first procedure for facile and rapid thiocyanation of indoles, phenol and aniline derivatives, and pyrroles using \([P_4-VP]SCN\) as a versatile polymeric reagent and PPDS as a strong and cheap oxidizing agent.

\([P_4-VP]SCN\) was prepared as our previously reported method [44] via the reaction of quaternized cross-linked poly (N-methyl-4-vinylpyridinium) iodide, \([P_4-VP]I\), with an aqueous solution of KSCN. A variety of activated aromatics such as anilines, and heterocyclic aromatics such as indoles and pyrroles were also subjected to thiocyanation reaction.

Since the nature of the solvent influences the rate of the reaction, the thiocyanation of indole (1 mmol) as a model substrate was performed in various solvents such as H2O, ethanol (EtOH), methanol, acetone, acetonitrile, CCl4, CH2Cl2 and mixture of EtOH and H2O at 55°C. According to the data presented in Table 1, EtOH/H2O = 1/1 (v/v) has been selected as a solvent (Entry 7). One reason for the observed different reaction times perhaps could be the swelling of the reagent in the proper solvent, or the solubility of the starting materials in the solvents used in this study. In the next step, the optimization of the \([P_4-VP]SCN/PPDS\) molar ratio in EtOH/H2O=1/1 (v/v) was tested. The results presented in Table 1 showed that the optimized molar ratio of \([P_4-VP]SCN/PPDS\) was 1.5/1 (Entry 7). The model reaction is generally slow at room temperature and the rate of peroxydisulfate decomposition increases greatly at a higher temperature, hence, 55°C was chosen for thiocyanation reaction of aromatic and heteroaromatic compounds.

Under the optimized reaction conditions, the thiocyanation of different aromatic and heteroaromatic compounds such as phenol and aniline derivatives, and pyrroles were investigated and the results are summarized in Table 2. The reaction of indole at 55°C yielded the desired product, 3-thiocyanato-1\(H\)-indole in 97% yield (Table 2, Entry 1).

Indole was chosen as a model substrate and reusability of the polymer was tested by using \([P_4-VP]SCN\) that is recycled for first, second, third, and fourth time, respectively, under identical conditions and the results are summarized in Table 2 (Entries 2–5).
This remarkable catalytic activity of PPDS in the thiocyanation of indole prompted us to study it in reactions with other indoles such as N-methylindole and 2-methylindole, pyrrole, carbazole and aniline and its derivatives and a few phenol derivatives such as 2-methyl, 2,5-dimethyl and 3,5-dimethyl phenols. Similarly, N-methylindole and 2-methylindole also afforded the corresponding 3-thiocyanatoindoles in excellent yields. The reaction of [P₄-VP]SCN/PPDS with aniline and phenol derivatives performed under the same condition described above afforded desired products (4-thiocyanatoderivatives) (Table 2, Entries 8–18). Different mono and N,N-disubstituted anilines were also examined with [P₄-VP]SCN/PPDS, all gave high yields (87–90%) of the corresponding products (Table 2, Entries 9–13). As Table 2 reveals, aromatic amino compounds and phenol derivatives were readily converted to the mono-thiocyanated products with high para-selectivity (Scheme 1 and Table 2, Entries 8–12 and 14–18) and the thiocyanato group is selectively added to the para position of the amino or hydroxyl groups. These observations are also supported by other reported methods.[14,19–21,34–37] One exception was observed when diphenylamine was subjected to this approach (Table 3, Entry 13), thiocyanation occurred on 4-position of phenyl (57%) and over thiocyanation was followed on 4-position of the second phenyl ring (30%). The same result has been reported by Nair et al. when using cerium(IV) ammonium nitrate for thiocyanation of diphenylamine by ammonium thiocyanate (32% mono and 6% bis-thiocyanated products were separated).[13] As Table 2 reveals, using indoles (Entries 1–7) as substrates, the reaction gave unique 3-thiocyanato substituted indoles in high yields (94–97%) but, unique 2-thiocyanato substituted pyrrole was obtained in 81% isolated yield when, thiocyanation of pyrrole was treated (Entry 19).

The regiochemistry of substitution was achieved by the interpretation of ¹H NMR spectra and their comparison with the spectral and physical data of authentic samples.

On the other hand, one of the disadvantages of polymeric reagents is their expense, but in this case, the spent polymeric reagents can in principle be recycled (Scheme 1, step 7) and reused many times (Table 2, Entries 2–5). In Scheme 1, the preparation of [P₄-VP]SCN (steps 1 and 2), regioselective thiocyanation of aromatic and heteroaromatic compounds (steps 3–6) and regeneration of the polymer (step 7) are presented.

The arylthiocyanate products were characterized by FT-IR; and ¹H and ¹³C NMR spectroscopy and physical properties were compared with known compounds. IR spectrum showed the characteristic peak of –SCN between 2145 and 2160 cm⁻¹ and the –C–S stretching around 642–755 cm⁻¹. Characteristic spectral data of some arylthiocyanate products are given in

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Table 1. Optimization of the reaction conditions for thiocyanation of indole (1 mmol) in different solvents and different molar ratios of [P₄-VP]SCN/PPDS at 55°C.

| Entry | Solvent     | [P₄-VP]SCN (mmol of SCN ion) | Persulfate (mmol of K₂S₂O₈) | Time (min) | Yield (%) |
|-------|-------------|-----------------------------|-----------------------------|------------|-----------|
| 1     | H₂O         | 1.50                        | 1.00                        | 15         | 82        |
| 2     | C₂H₅OH      | 1.50                        | 1.00                        | 120        | 15        |
| 3     | CH₃CN       | 1.50                        | 1.00                        | 60         | 96        |
| 4     | CH₃COCH₃b   | 1.50                        | 1.00                        | 120        | 0.0       |
| 5     | CH₃OH       | 1.50                        | 1.00                        | 120        | 10        |
| 6     | CH₂Clb      | 1.50                        | 1.00                        | 120        | 0.0       |
| 7     | (H₂O/EtOH: 1/1) | 1.50                  | 1.00                        | 5          | 97        |
| 8     | (H₂O/EtOH: 1/2) | 1.50                  | 1.00                        | 20         | 90        |
| 9     | (H₂O/EtOH: 2/1) | 1.50                  | 1.00                        | 10         | 92        |
| 10    | (H₂O/EtOH: 1/1) | 3.00                  | 0.50                        | 5          | 71        |
| 11    | (H₂O/EtOH: 1/1) | 1.00                  | 1.00                        | 5          | 86        |
| 12    | (H₂O/EtOH: 1/1) | 2.00                  | 1.00                        | 5          | 97        |

aIsolated yields.
bReflux.
Table 2. Thiocyanation of aromatic and heteroaromatic compounds with \([\text{P}_4\text{-VP}]\text{SCN}/\text{PPDS}\) in \(\text{H}_2\text{O}/\text{EtOH}\) at 55°C.

| Entry | Substrate | Product | Time (min) | Yield (%)<sup>a</sup> | Mp. | Found | Reported [Lit.] |
|-------|-----------|---------|------------|----------------------|-----|--------|-----------------|
| 1     |           |         | 5          | 97                   | 75–76 | 73–76[24], 105–106[25], 76[13] |
| 2<sup>b</sup> |           |         | 5          | 97                   | 75–76 | 73–76[24], 105–106[25], 76[13] |
| 3<sup>b</sup> |           |         | 6          | 96                   | 75–76 | 73–76[24], 105–106[25], 76[13] |
| 4<sup>b</sup> |           |         | 6          | 96                   | 75–76 | 73–76[24], 105–106[25], 76[13] |
| 5<sup>b</sup> |           |         | 8          | 94                   | 75–76 | 73–76[24], 105–106[25], 76[13] |
| 6     | Me        |         | 5          | 96                   | 82–84 | 83–84[25], 76–78[16] |
| 7     |           |         | 5          | 97                   | 100–102 | 99–101[25], 104–106[16] |
| 8     | NH<sub>2</sub> | NCS-NH<sub>2</sub> | 10 | 87 | 51–52 | 52–53[24], 51–52[26] 96–98[17] |
| 9     | NMe      | NCS-NMe | 10 | 89 | 45–47 | 46–47[26], Liquid[25] |
| 10    | NH<sub>Et</sub> | NCS-NH<sub>Et</sub> | 10 | 90 | 51–53 | 53–54[27], 52–53[28] |
| 11    | NMe<sub>2</sub> | NCS-NMe<sub>2</sub> | 10 | 88 | 72–74 | 71–72[25,28], 72–73[16], 72–74[15], 75[23] |
| 12    | NEt<sub>2</sub> | NCS-NEt<sub>2</sub> | 10 | 90 | Brown red oil | Liquid[15,16], 82–84[31] |
| 13    | NHPPh    | NCS-NHPPh | 15 | 87 | 60–62 | 58–60[26], 62–64[25] |
| 14    | H<sub>2</sub>N-Ph | H<sub>2</sub>N-Ph-SCN | 5 | 95 | 44–45 | – |

(Continued)
Table 2. Continued

| Entry | Substrate | Product | Time (min) | Yield (%) | Mp.       |
|-------|-----------|---------|------------|-----------|-----------|
| 15    | NC       | NC-SCN  | 10         | 83        | 97–98     | 58–60 [31] |
| 16    | HO       | HO-SCN  | 5          | 96        | 80–81     | –          |
| 17    | HO       | HO-SCN  | 15         | 64        | 70–72     | 71–72 [27] |
| 18    | HO       | HO-SCN  | 5          | 94        | 124–126   | 128–129 [c] |

Table 3. Comparison of the model reaction with the previous reported methods in the literature.

| Entry | Time (min) | Yield (%) | Mp. | Ref. |
|-------|------------|-----------|-----|------|
| 1     | 120        | 85        | 76.5–78 | 14  |
| 2     | 120        | 83        | 73–76  | 24  |
| 3     | 15         | 95        | 78    | 17  |
| 4     | 45         | 88        | –     | 30  |
| 5     | 50         | 85        | –     | 15  |
| 6     | 43         | 98        | 72–73  | 18  |
| 7     | 20         | 93        | 70–72  | 26  |
| 8     | 45         | 85        | 70–71  | 20  |
| 9     | 120        | 83        | 73–74  | 19  |
| 10    | 5          | 97        | 75–76  | A   |

Note: A: Present method Table 2 (Entry 1).

The proposed thiocyanation mechanism of indole by PPDS is shown in Scheme 2. The radical mechanism has been reported by Wu et al. for the first time. The reduction potential of oxone and the oxidation potential of indole and ammonium thiocyanate in anhydrous methanol were determined by Wu et al.[22] The reduction and oxidation potentials of oxone and indole were estimated to be +0.325 V and −1.050 V, respectively. Yet, the thiocyanate ion exhibited no oxidation potential. The standard oxidation–reduction potential of PPDS in oxidation reactions is estimated to be -2.01 V.[39] So, it might be assumed that PPDS oxidized indole rather than the thiocyanate ion. The oxidation occurs at the C–C double bond on the hetero-, five-membered ring.

The Entries 2–5, refer to the use of [P4-VP]SCN that is recycled for first, second, third and fourth time, respectively, under identical conditions.

Behrenz, W. US Patent 3,437,684, 1969.
of indole, giving a cation radical of indole which was stabilized by a resonance effect (I in Scheme 2). It was followed by nucleophilic attack of SCN at the 3-position and the radical intermediate so formed (II in Scheme 2) then undergoes a 3-H-abstraction by KSO\textsuperscript{4+}, that generated from PPDS during its decomposition (when solutions of the persulfates are heated, free radicals are formed), affording the end product, as depicted in pathway (a) in Scheme 2. In another pathway (Path b) probably, electron transfer occurs between KSO\textsuperscript{4−} and (II), and giving a cation intermediate (III) and KSO\textsuperscript{4−}. It was followed by 3-proton-abstraction by KSO\textsuperscript{4−}, affording the end product, as depicted in pathway (b) in Scheme 2.

In Table 3, the result of the present work for the model reaction was compared with the previous reported methods in the literature.[14,15,17–20,24,26,30] As Table 3 reveals, this method is
superior to other methods. The reaction time in the present method is shorter than the previously reported methods (Table 3, Entry 9). This can probably be attributed to the local concentration of thiocyanate ion species inside the pores of the polymer.

The advantages of this technique over conventional classical methods are mild reaction conditions, safe handling, rapid and very simple work-up. On the other hand, the spent polymeric reagents can usually be regenerated and reused several times without significant loss of their activity. In addition, many ion-exchange resins, and indeed reagents supported on them, are commercially available and are relatively inexpensive and there is current research and general interest in heterogeneous systems because such systems are important in industry and developing technologies.[59]

### 3. Conclusions

We have developed an efficient, rapid, experimentally simple method for regioselective thiocyanation of indoles, pyrroles, anilines and phenol derivatives via a green and simple protocol using cross-linked poly (4-vinylpyridine)-supported thiocyanate ion as a versatile polymeric reagent and PPDS as a mild, cheap and versatile oxidizing agent. On the other hand, the spent polymeric reagents can usually be regenerated and reused several times without significant loss of their activity.

### 4. Experiment

#### 4.1. Materials and instruments

Chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), and Merck chemical companies. Poly (4-vinylpyridine) cross-linked with 2\% divinyl benzene (DVB), (white powder, and 100–200 mesh), \([P_4-VP]\)
2% DVB, was purchased from Fluka (Buchs, Switzerland). Cross-linked poly (N-methyl-4-vinylpyridinium) iodide, [P4-VP], and cross-linked Poly (N-methyl-4-vinylpyridine) thiocyanate [P4-VP]SCN, were synthesized according to our reported procedures.[44] Progress of the reaction was monitored by thin layer chromatography (TLC) using silica gel Poly Gram SIL G/UV 254 plates (Fluka). All products were characterized by comparison of their melting point, FT-IR, and in some cases $^1\text{H}$-NMR spectral data, with known samples and all yields refer to the isolated pure products. Melting points were determined with a Buchi melting point B-540 B.V. CHI apparatus.

### 3-ThiocyanatoIndole

FT-IR (neat), $v_{\text{max}}$ (cm$^{-1}$): 3395 (NH), 2155 (SCN), 1455, 1410, 1338, 1239, 1097, 743 (C=S); $^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 8.71 (1H, s), 7.67–7.69 (1H, t, $J$= 4.0 Hz), 7.17–7.29 (4H, m); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 136.1, 131.2, 127.6, 123.8, 121.8, 118.6, 112.4, 112.2, 91.6.

#### 1-Methyl-3-thiocyanatoIndole

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 2.46 (3H, s, CH$_3$), 7.33–7.40 (4H, m), 7.64 (1H, d, $J$= 6.8 Hz); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 137.2, 135.1, 128.5, 123.4, 116.8, 111.9, 110.2, 89.8, 33.4.

#### 1-H-Methyl-3-thiocyanatoIndole

FT-IR (neat), $v_{\text{max}}$ (cm$^{-1}$): 2145 (SCN), 1512, 1244, 742 (C=S); $^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 4.00 (2H, s, NH$_2$), 6.68 (2H, d, $J$= 8.80 Hz), 7.36 (2H, d, $J$= 8.80 Hz); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 148.8, 134.5, 116.0, 112.4, 109.5.

### 2-Thiocyanatopyrrole

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 6.15 (1H, s, NH), 6.92 (2H, d, $J$= 9.20 Hz), 7.39 (2H, d, $J$= 9.20 Hz); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 151.3, 134.8, 113.6, 112.9, 106.8, 38.0, 14.5.

### 4-Thiocyanatopyridine

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 7.67–7.72 (1H, m), 7.73–7.80 (2H, m), 7.90 (1H, t, $J$= 8.80 Hz), 8.71 (1H, s, NH); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 149.3, 135.0, 112.8, 112.6, 104.8, 44.5, 12.3.

### 4-Thiocyanatopyridine

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 7.67–7.72 (1H, m), 7.73–7.80 (2H, m), 7.90 (1H, t, $J$= 8.80 Hz), 8.71 (1H, s, NH); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 149.3, 135.0, 112.8, 112.6, 104.8, 44.5, 12.3.

### 4-Thiocyanatopyridine

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 7.67–7.72 (1H, m), 7.73–7.80 (2H, m), 7.90 (1H, t, $J$= 8.80 Hz), 8.71 (1H, s, NH); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 149.3, 135.0, 112.8, 112.6, 104.8, 44.5, 12.3.

### 4-Thiocyanatopyridine

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 7.67–7.72 (1H, m), 7.73–7.80 (2H, m), 7.90 (1H, t, $J$= 8.80 Hz), 8.71 (1H, s, NH); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 149.3, 135.0, 112.8, 112.6, 104.8, 44.5, 12.3.

### 4-Thiocyanatopyridine

$^1\text{H}$ NMR (400 MHz), $\delta$ (ppm): 7.67–7.72 (1H, m), 7.73–7.80 (2H, m), 7.90 (1H, t, $J$= 8.80 Hz), 8.71 (1H, s, NH); $^{13}$C NMR (100 MHz) $\delta$ (ppm): 149.3, 135.0, 112.8, 112.6, 104.8, 44.5, 12.3.
2-Methyl-4-thiocyanatophenol: FT-IR (neat), $\nu_{\text{max}}$ (cm$^{-1}$): 3408 (OH), 2924 (C–H), 2161 (SCN), 1592, (C9C), 1494 (C9C), 1464, 1241 (C–O), 1177, 1108, 843, 753.

2-Bromo-4-thiocyanatoaniline: FT-IR (neat), $\nu_{\text{max}}$ (cm$^{-1}$): 3474 (NH$_2$), 3370 (NH$_2$), 2924 (C–H), 2154 (SCN), 1616 (C9C), 1582 (C9C), 1485, 1399, 1314, 1291, 813, 750, 592.

2-Cyano-4-thiocyanatoaniline: FT-IR (neat), $\nu_{\text{max}}$ (cm$^{-1}$): 3445 (NH$_2$), 3363 (NH$_2$), 3235, 2924 (C–H), 2583, 2219 (CN), 2156 (SCN), 1632 (C9C), 1598 (C9C), 1557 (C9C), 1493, 1458, 1315, 1265, 905, 824, 749, 500.

4.2. Preparation of [P$_4$-VP]SCN

Cross-linked poly (N-methyl-4-vinylpyridinium) thiocyanate, [P$_4$-VP]SCN, was synthesized and its capacity was determined according to our reported procedure.[44] The obtained capacity of the polymer was 3.3 mmol of thiocyanate ion per gram of polymer.

4.3. General procedure for thiocyanation of aromatic or heteroaromatic compounds using [P$_4$-VP]SCN/PPDS

An aromatic or heteroaromatic compound (1 mmol) is dissolved in EtOH (5 mL) and was slowly added dropwise to a suspension of [P$_4$-VP]SCN (455 mg, 1.5 mmol of SCN ion) and 270 mg of PPDS (1 mmol) in distilled water (5 mL) by stirring at 55°C for the appropriate time as mentioned in Table 2. The progress of the reaction was monitored by TCL [eluent: n-hexane/ethyl acetate (8/2)]. After complete conversion as indicated by TLC, the polymer was separated by filtration and the filtrate was diluted with distilled water (15 mL) and extracted with dichloromethane (4 × 8 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel (eluted with n-hexane/ethylacetate: 8/2) to afford the corresponding thiocyanated products.

4.4. Regeneration of [P$_4$-VP]SCN

The spent polymer (1.00 g) was added to an excess aqueous solution of KSCN and was stirred for 24 h at room temperature. The mixture was filtered and washed several times with distilled water and ethanol and dried overnight under vacuum in the presence of P$_2$O$_5$ at 40°C (Scheme 1, step 7). The regenerated polymer can be reused for several cycles without significant loss of their activity (Table 2, Entries 2–5).

Supplemental data

Supplemental data for this article can be accessed here 10.1080/17415993.2014.917375.

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