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Thiocyanation of aromatic and heteroaromatic compounds using polymer-supported thiocyanate ion as the versatile reagent and ceric ammonium nitrate as the versatile single-electron oxidant

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Thiocyanation of aromatic and heteroaromatic compounds using polymer-supported thiocyanate ion as the versatile reagent and ceric ammonium nitrate as the versatile single-electron oxidant

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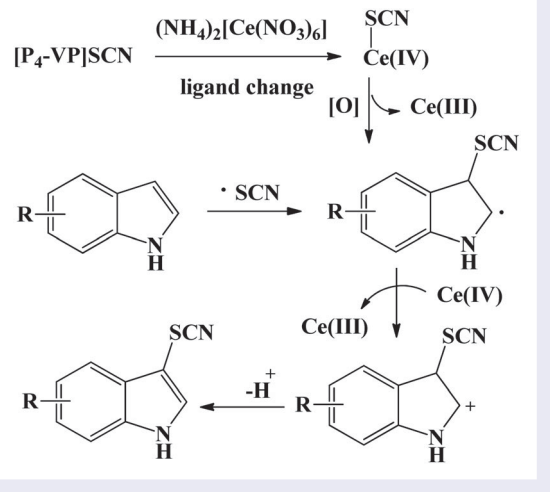
ABSTRACT

Indoles, pyrrole aniline derivatives and aromatic amino compounds undergo smooth thiocyanation with cross-linked poly (4-vinylpyridine) supported thiocyanate ion, [P_4-VP]SCN in the presence of ceric ammonium nitrate (CAN) as a versatile single-electron oxidant in ethanol at room temperature to afford the corresponding 3-indolyl 2-pyroyl and 4-aryl thiocyanates, respectively, in high to excellent yields with excellent selectivity in a short reaction time. The use of [P_4-VP]SCN/CAN makes it quite simple, more convenient, and practical. The present 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.



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KEYWORDS
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1. Introduction

The most extensively used cerium (IV) reagent in organic chemistry is ceric ammonium nitrate (CAN). The reasons for its general acceptance as a one-electron oxidant may be attributed to its large reduction potential value of + 1.61 V (vs. normal hydrogen electrode), low toxicity, and ease of handling, experimental simplicity, and solubility in a number of organic solvents. The enormous growth in the use of this reagent is evidenced by the publication of a large number of research papers and several reviews concerning CAN-mediated reactions.[1–8]

Sulfur-containing compounds have become increasingly useful and important in organic synthesis. Thiocyanates are well known in organosulfur chemistry.[9] Arylthiocyanates are well known in the area of organosulfur chemistry [10] and have found widespread applications such as insecticides, biocidal, antiasthmatic, vulcanization accelerators, and starting materials for the preparation of heterocycles.[11–14] The thiocyanation of aromatics and heteroaromatics is an important carbon-heteroatom bond formation in organic synthesis and constitutes an interesting group, which could be readily transformed into other sulfur-bearing functionalities,[15,16] especially for producing drugs and pharmaceuticals.[17,18] Also, thiocyanate is a versatile synthon which can be readily transferred to other functional groups such as sulfide,[19–22] nitrile,[23] thiocarbamate, [24,25] thionitrile,[26] and aryl thioesters.[27] Therefore, it is important to find new methods for the thiocyanation systems.

Several methods for the thiocyanation of aromatic systems using a variety of reagents such as bromine/potassium thiocyanate (only for indoles),[28] *N*-thiocyanatosuccinimide (only for 5-methoxy-2-methylindole and accompanied by two bisthiocyanates),[29] trichloroisocyanuric acid/NH_4SCN/wet SiO_2,[30] CAN/NH_4SCN,[5] acidic montmorillonite K10 clay/NH_4SCN,[31] iodine/methanol/NH_4SCN,[32] silica boron sulfonic acid/H_2O_2/NH_4SCN,[33] sodium pertborate/NH_4SCN,[34] oxone/NH_4SCN,[35] diethyl azodicarboxylate,[36] diphenylphosphinite ionic liquid,[37] potassium peroxydisulfate-copper(II),[38] ferric(III) chloride/NH_4SCN,[39] acidic alumina/NH_4SCN, [40] $Mn(OAc)_3$/NH_4SCN,[41] DDQ/NH_4SCN,[42] I_2O_5/NH_4SCN,[43] and para-toluene sulfuric acid/NH_4SCN [44] extensively studied. However, these methodologies suffer from one or more drawbacks such as the less availability or hard preparation of starting materials, [28,29] the low yields for some compounds,[5,35] and performances under certain special conditions.[31]

The 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.[45] An interesting and fast growing branch of this area is polymer-supported reagents.[46] Although polymeric reagents and scavengers have been used in organic synthesis for decades, development of combinatorial and parallel high-throughput synthesis techniques brought this class of reagents to a wider attention. The first compound collections were based on peptides and oligonucleotides, which were stepwise assembled on a solid support,[47] following the concept developed by Merrifield.[48] In recent years, the polymeric reagents, especially anion exchange resins, have been widely applied in organic transformations.[49–66] 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, usually the spent polymeric reagents can be regenerated and reused for 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.

As far as we know there are a few reports in the literature on the application of polymer-supported thiocyanate ion [49–54] but, to the best of our knowledge, there is no report on polymer-supported thiocyanate ion for thiocyanation of aromatic or heteroaromatic rings by using CAN as the oxidant. We have recently reported an efficient method for the preparation of cross-linked poly (4-vinylpyridine) supported thiocyanate ion, [P_4-VP]SCN, and applied for the synthesis of alkyl thiocyanates [51] and aryl thiocyanates.[51–54]

2. Results and discussion

Cross-linked poly (4-vinylpyridinium) thiocyanate ion, [P_4-VP]SCN, was easily prepared according to our previously reported method [51] via the reaction of quaternized cross-linked poly (*N*-methyl-4-vinylpyridinium) iodide, [P_4-VP]I, with an aqueous solution of KSCN.

In this paper, we report the first procedure for facile and rapid thiocyanation of indoles, pyrrole, carbazole, aniline derivatives, and aromatic amino compounds using [P_4-VP]SCN as the versatile polymeric reagent and CAN as the versatile single-electron oxidant.

In order to be able to carry out such a reaction in a more efficient way, indole was chosen as the model substrate and some experimentation regarding reaction time, reaction temperature, and possible solvents were run and the results are summarized in Table 1. According to the data presented in Table 1, ethanol and methanol have been the same and the best solvents (Entries 3 and 6). Based on green chemistry and environmental-friendly nature, ethanol was chosen as the solvent for thiocyanation of different aromatic and heteroaromatic compounds. During our optimization studies, it was found that a 1.0/2.5/2.2 mole ratio of indole/[P_4-VP]SCN/CAN in ethanol at room temperature was the best, for complete conversion in a short reaction time, to achieve the highest yield of 3-indolyl thiocyanate product (Entry 3).

Under optimized reaction conditions, the thiocyanation of different aromatic and heteroaromatic compounds such as indoles, pyrrole, carbazole, aromatic amino compounds, and aniline derivatives was investigated and the results are summarized in Table 2.

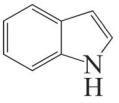
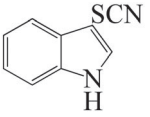
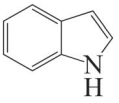
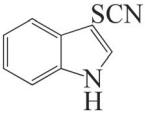
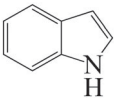
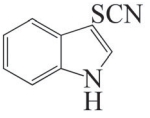
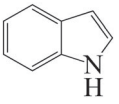
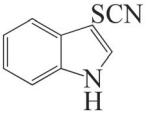
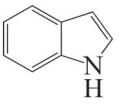
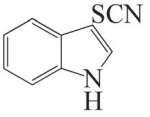
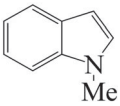
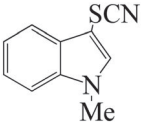
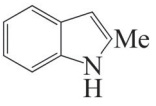
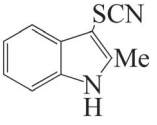
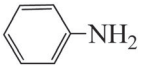
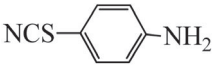
Table 1. Optimization of the reaction conditions for thiocyanation of indole (1mmol) in different solvents and different molar ratio of [P_4-VP] SCN/CAN at room temperature.

Entry	Solvent	[P_4-VP]SCN (mmol of SCN ion)	CAN (mmol)	Time (min)	Yield[a] (%)
1	CCl_4	2.50	2.20	120	0.0
2	H_2O	2.50	2.20	30	40
3	C2H5OH	2.50	2.20	5	98
4	CH_3CN	2.50	2.20	40	52
5	CH_3COCH_3	2.50	2.20	35	65
6	CH3OH	2.50	2.20	5	98
7	CH_2Cl_2	2.50	2.20	120	0.0
8	CH_2H_5OH	2.50	2.50	5	97
9	CH_2H_5OH	2.50	1.50	5	76
10	CH_2H_5OH	2.80	2.20	5	96
11	CH_2H_5OH	2.00	2.00	5	92

[a]Isolated yields.

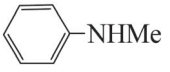
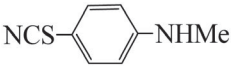
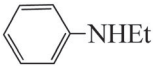
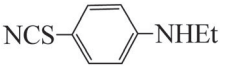
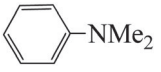
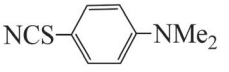
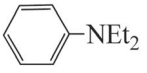
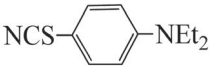
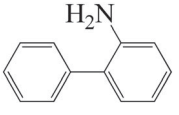
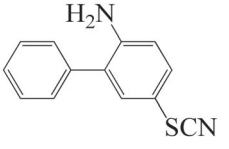
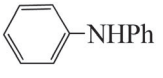
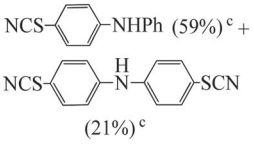
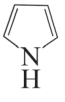
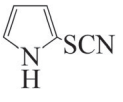
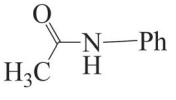
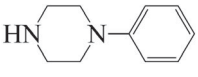
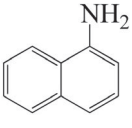
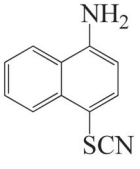
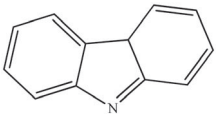
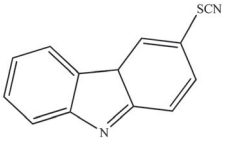
The reaction of indole at room temperature yielded the desired product 3-thiocyanato-1H-indole in 98% yield (Table 2, Entry 1). The same reaction using *N*-methyl indole as the starting material gave 3-thiocyanato-*N*-methyl indole in 96% yield (Table 2, Entry 6). The reaction was further extended to include with other substituted indoles. It was found that 2-methylindole gave 94% yield of 3-thiocyanato-2-methylindole (Table 2, Entry 7). The lower yield is probably attributed to the steric hindrance of 2-substituted indole. As Table 2 reveals, using indoles (Entries 1–7) as substrates, the reaction gave unique

Table 2. Thiocyanation of aromatic and heteroaromatic compounds with [P_4-VP]SCN/CAN in ethanol at room temperature.

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. Found	M.p. Reported
1			5	98	75–76	73–76,[41] 105–106[42]
2[b]			5	98	75–76	73–76,[41] 105–106[42]
3[b]			6	98	75–76	73–76,[41] 105–106[42]
4[b]			8	98	75–76	73–76,[41] 105–106[42]
5[b]			10	94	75–76	73–76,[41] 105–106[42]
6			10	96	82–84	83–84 [41], 76–78 [33]
7			10	94	100–102	99–101[42], 104–106[33]
8			25	86	51–52	52–53 [41], 96–98 [34]

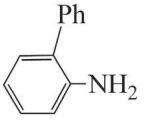
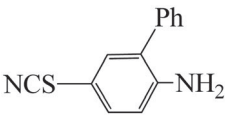
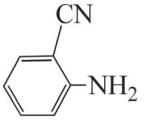
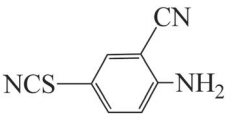
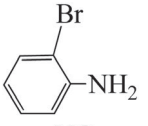
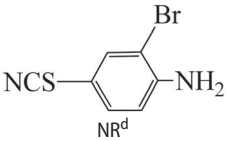
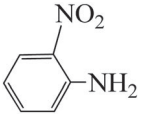
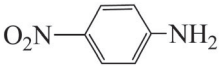
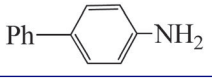
(*continued*).

Table 2. continued.

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. Found	M.p. Reported
9			15	84	45–47	46–47 [43], Liquid [42]
10			15	88	51–53	53–54 [67], 52–53 [68]
11			15	87	72–74	71–72[42], 72–73 [33]
12			20	89	Oil	Liquid [33]
13			15	88	Oil	–
14		 (59%)[c] + (21%)[c]	15	80	60–62 109–111	58–60 [43], 62–64 [42] 110–111 [42]
15			8	82	Oil	Oil [42, 43]
16		NR[d]	120	–	–	–
17		NR[d]	120	–	––	–
18			20	75	–	–
19			90	72	Oil	–

(*continued*).

Table 2. continued

Entry	Substrate	Product	Time (min)	Yield (%)[a]	M.p. Found	M.p. Reported
20			12	86	Oil	–
21			50	45	98–99	–
22			40	70	44–45	–
23		NR[d]	120	–	–	–
24		NR[d]	120	–	–	–
25		NR[d]	120	–	–	–

[a]Isolated yields.
[b]The Entries 2–5, refer to the use of the [P_4-VP]SCN that is recycled first, second, third, and fourth time, respectively, under identical conditions.
[c]Dithiocyanated product was also observed, when thiocyanation reaction of diphenylamine was performed.
[d]NR: No reaction.

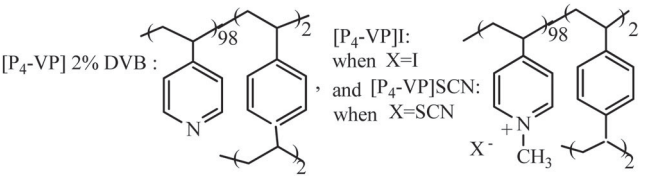
3-thiocyano-substituted indoles in high yields (94–96%), but unique 2-thiocyano substituted pyrrole was obtained in 82% isolated yield, when thiocyanation of pyrrole was treated (Entry 15).

We then explored the reactions of aniline and its derivatives. Thiocyanation of aniline performed under described above conditions afforded the desired product (4-thiocyanatoanilline) in 86% yield (Table 2, Entry 8). Different mono and di-*N*-substituted anilines were also used, and they all gave high yields (84–89%) of the corresponding products (Table 2, Entries 9–12) except when 1-phenyl piperazine, 4-aminobiphenyl and aniline derivatives with electron-withdrawing groups such as *N*-phenylacetamide, 2-bromoaniline, 2-nitroaniline and 4-nitroaniline (Table 2, Entries 17,25,16,22–24, respectively) were used for the thiocyanation reaction, no product was observed. As Table 2 reveals, aromatic amino compounds were readily converted to the mono thiocyanated products with high para-selectivity (Table 2, Entries 8–13 and 20–22) and the thiocyanato group is selectively substituted to the para position of the amino group. These observations are also supported by other reported methods.[37,41–43,48–51,53,54] One exception was observed when diphenylamine was subjected to this approach because

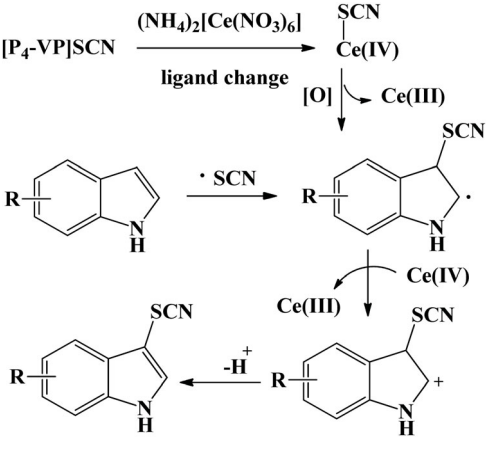
mono and dithiocyanated products could be produced. Thiocyanation occurred on 4-position of phenyl (59%) and over thiocyanation was followed on 4-position of the second phenyl ring (21%), (Table 2, Entry 14). The same results has been reported by Nair et al. when CAN was used for thiocyanation of diphenylamine by ammonium thiocyanate (32% mono and 6% di thiocyanated products) [5] and by our recent studies when using [P_4-VP]SCN/potassium peroxydisulfate (57% mono and 30% di thiocyanated products) [53] and by using [[P_4-VP]SCN/oxone (60% mono and 25% di thiocyanated products).[54] The regiochemistry of substitution was achieved by the interpretation of ^{1}H NMR spectra and their comparison with the spectra and physical data of authentic samples.

The recycling of the polymer was examined. For this purpose, the polymer was recovered from the reaction of indole (in model reaction) and reloaded with KSCN (aq.) (Scheme 1, step 4) and reused for the conversion of indole to its corresponding thiocyanated product without considerable loss of reactivity. Entries 2–5 in Table 2 refer to the use of the [P_4-VP]SCN that is recycled first, second, third, and fourth time, respectively, under identical conditions. Preparation of the [P_4-VP]SCN (steps 1 and 2), regioselective thiocyanation of aromatic and heteroaromatic compounds (steps 3), and regeneration of the polymer (step 4) are shown in Scheme 1.

The proposed thiocyanation mechanism of indole with [P_4-VP]SCN/CAN is shown in Scheme 2.



Scheme 1. Preparation of [P_4-VP]SCN, thiocyanation of aromatic and heteroaromatic compounds and regeneration of the polymer.



Scheme 2. The plausible mechanism of thiocyanation of indole.

Table 3. Comparison of the reaction times and yields of thiocyanation of model reaction from the present method with other reported classical methods.

Entry	Time (min)	Yield (%)	M.p.	Ref.
1	120	83	73–76	[41]
2	20	97	105–106	[42]
3	15	95	78	[34]
4	45	88	–	[44]
5	50	85	–	[32]
6	43	98	72–73	[35]
7	20	93	70–72	[43]
8	5	97	75–76	[53]
9	10	96	73–74	[54]
10	5	98	74–76	A[a]

[a]A: Present method Table 2 (Entry 1).

In Table 3, the model reaction of the present method is compared with other reported classical methods.[32,34,35,41–44,53,54] As Table 3 reveals, in this method, the reaction times are always shorter than the other methods but the yields are compatible. This can probably be attributed to the local concentration of thiocyanate ion species inside the pores of the polymer.

The advantages of the present method over conventional classical methods are mild reaction conditions, safe handling, rapid, and very simple work-up. In addition, there is current research and general interest in heterogeneous systems because such systems are important in industry and developing technologies.[69]

3. Conclusions

We have developed an efficient, rapid, experimentally simple method for regioselective thiocyanation of indoles, pyrrole, carbazole, aniline derivatives, and aromatic amino compounds via a green and simple protocol using cross-linked poly (4-vinylpyridine) supported thiocyanate ion as the versatile polymeric reagent and CAN as the versatile single-electron oxidant. The spent polymeric reagent can be easily separated by filtration and can be easily regenerated by treating with aqueous solution of KSCN and reused for several cycles without significant loss of their activity.

4. Experimental

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, [P_4-VP]I, and cross-linked Poly (N-methyl-4-vinylpyridine) thiocyanate, [P_4-VP]SCN, were synthesized according to our reported procedures.[50] Progress of the reaction was monitored by thin layer chromatography using silica gel Poly Gram SIL G/UV 254 plates (Fluka). Melting points were determined with a Buchi melting point B-540 B.V. CHI apparatus. The arylthiocyanate products were

characterized by fourier transform-infrared (FT-IR); and ^{1}H- and ^{13}C-NMR spectroscopy. IR spectra showed the characteristic peak of –SCN between 2144 and 2160 cm^{-1} and the –C–S stretching at 642–749 cm^{-1}. The characteristic spectral data of some arylthiocyanate products are given below.

4.1.1. 3-Thiocyanatoindole

FT-IR (neat), ν_{max} (cm^{-1}) = 3395 (NH), 2156 (SCN), 1504, 1455, 1410, 1339, 1239, 1097, 744 (C–S); ^{1}H NMR (400 MHz), δ (ppm) = 8.71 (1H, s), 7.68 (1H, t, J = 4.0 Hz), 7.23 (4H, m); ^{13}C NMR (100 MHz), δ (ppm) = 136.1, 131.2, 127.6, 123.8, 121.8, 118.6, 112.4, 112.2, 91.6.

4.1.2. 1-Methyl-3-thiocyanatoIndole

FT-IR (neat), ν_{max} (cm^{-1}) = 2153 (SCN), 1513, 1459, 1422, 1336, 1244, 1157, 1012, 742 (C–S), 544;^{1}H NMR (400 MHz), δ (ppm) = 3.81 (3H, s, CH_3), 7.37 (4H, m), 7.64 (1H, d, J = 6.8 Hz), 3.81 (3H, s, CH_3); ^{13}C NMR (100 MHz), δ (ppm) = 37.2, 135.1, 128.5, 123.4, 121.6, 118.9, 111.9, 110.2, 89.8, 33.4.

4.1.3. 2-Methyl-3-thiocyanatoIndole

FT-IR (neat), ν_{max} (cm^{-1}) = 3395 (NH), 2149 (SCN), 1406, 1228, 739 (C–S), 644, 595; ^{1}H NMR (400 MHz), δ (ppm) = 2.47 (3H, s, CH_3), 7.28 (2H, m), 7.71 (1H, d, J = 7.6 Hz), 7.73 (1H, d, J = 7.6 Hz), 8.71 (1H, s, NH);^{13}C NMR (100 MHz), δ (ppm) = 142.3, 135.2, 128.7, 122.9, 121.5, 117.9, 112.5, 111.6, 111.4, 11.9.

4-Thiocyanatoaniline

FT-IR (neat), ν_{max} (cm^{-1}) = 3375 (NH_2), 2152 (SCN), 1625, 1595, 1496, 824, 739 (C–S);^{1}H NMR (400 MHz), δ (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), δ (ppm) = 148.8, 134.5, 116.0, 112.4, 109.5.

4-Thiocyanato-N-methylaniline

FT-IR (neat), ν_{max} (cm^{-1}): 3409 (NH), 2898, 2151 (SCN), 1595, 1513, 1330, 1184, 819, 675 (C–S);^{1}H NMR (400 MHz), δ (ppm) = 2.86 (3H, s, CH_3), 4.13(s,1H,NH), 6.58 (2H, d, J = 8.80 Hz), 7.39 (2H, d, J = 8.80 Hz); ^{13}C NMR (100 MHz), δ (ppm) = 151.1, 134.7, 113.3, 112.7, 107.3, 30.2.

4-Thiocyanato-N-ethylaniline

FT-IR (neat), ν_{max} (cm^{-1}) = 3382 (NH), 2974, 2152 (SCN), 1598, 1514, 1335, 1150, 815, 748 (C–S);^{1}H NMR (400 MHz), δ (ppm) = 1.24 (3H, t, J = 7.20 Hz), 3.12 (2H, q, J = 7.20 Hz), 4.09 (1H, s, NH), 6.56 (2H, d, J = 8.80 Hz), 7.35 (2H, d, J = 8.80 Hz);^{13}C NMR (100 MHz), δ (ppm) = 150.3, 134.8, 113.6, 112.9, 106.8, 38.0, 14.5.

4-Thiocyanato-N,N-dimethylaniline

FT-IR (neat), ν_{max} (cm^{-1}) = 2144 (SCN), 1595, 1510, 1444, 1321, 1266, 1231, 1198, 1074,990, 947, 809, 737 (C–S) 519.

4-Thiocyanato-N,N-diethylaniline

FT-IR (neat), ν_{max} (cm^{-1}) = 2151 (SCN), 1591, 1507, 1274, 749 (C–S);^{1}H NMR (400 MHz), δ (ppm) = 1.17 (6H, t, J = 7.20 Hz), 3.35 (4H, q, J = 7.20 Hz), 6.65 (2H, d, J = 9.20 Hz), 7.39 (2H, d, J = 9.20 Hz);^{13}C NMR (100 MHz), δ (ppm): 149.3, 135.0, 112.8, 112.6, 104.8, 44.5, 12.3.

4-Thiocyanato-N-phenylaniline

FT-IR (neat), ν_{max} (cm^{-1}): 3360 (NH), 2153 (SCN), 1585, 1493,1322, 750, 697 (C–S);^{1}H NMR (400 MHz), δ (ppm) = 5.98 (1H, s, NH), 6.87 (2H, d, J = 8.80 Hz), 6.92 (1H, t, J = 7.60 Hz), 7.00 (2H, d, J = 7.60 Hz), 6.92 (2H, t, J = 7.60 Hz), 7.26 (2H, d, J = 8.80 Hz); ^{13}C NMR (100 MHz), δ (ppm) = 146.2, 141.0, 134.1, 129.6, 123.0, 120.1, 117.1.

4,4′-Dithiocyanatodiphenylamine

FT-IR (neat), ν_{max} (cm^{-1}) = 3368 (NH), 2150 (SCN), 1573,1740, 1583, 1486, 1340, 1215, 806, 642 (C–S);^{1}H NMR (400 MHz), δ (ppm) = 6.15 (1H, s, NH), 7.03 (4H, d, J = 8.80 Hz), 7.40 (4H, d, J = 8.80 Hz); ^{13}C NMR (100 MHz), δ (ppm) = 143.8, 133.6, 119.2, 114.4, 111.5.

2-Thiocyanatopyrrole

FT-IR (neat), ν_{max} (cm^{-1}) = 3267 (NH), 2160 (SCN), 1523, 1415, 1033, 796, 686 (C–S).

4-Amino-1-naphthyl thiocyanate

FT-IR (neat), ν_{max} (cm^{-1}) = 3425, 3384 (NH_2), 2151 (SCN), 1634, 1514, 1442, 1345, 1293, 817, 738 (C–S).

3-Thiocyanatocarbazole

FT-IR (neat), ν_{max} (cm^{-1}) = 3415 (N–H), 2151 (SCN), 1595, 1448, 1318, 1276, 1235, 893, 815, 734 (C–S).

2-Phenyl-4-Thiocyanato aniline

3481, 3378 (NH_2), 2153 (SCN), 1619, 1499, 1484, 1445, 1402, 1300, 1155, 895, 818, 774, 704 (C–S).

2-Cyano-4-Thiocyanato aniline

FT-IR (neat), ν_{max} (cm^{-1}) = 3445, 3362, 2923, 2219 (CN), 2156 (SCN), 1632, 1557, 1493, 1458, 1315, 1265, 1185, 1160, 905, 824, 748 (C–S).

2-Bromo-4-Thiocyanato aniline

FT-IR (neat), ν_{max} (cm^{-1}) = 3474, 3370 (NH_2), 2924, 2154 (SCN), 1616, 1582, 1485, 1398, 1260, 1156, 813, 750 (C–S), 699.

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 (Scheme 1).[51]

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/CAN

About 1.2 g of CAN (2.2 mmol) that dissolved in ethanol (10 mL) was added dropwise to a suspension of [P_4-VP]SCN (757 mg, 2.50 mmol of SCN ion) and an aromatic or heteroaromatic compound (1 mmol) in ethanol (5 mL) and the reaction mixture was stirred at room temperature for the appropriate time according to Table 2. The progress of the reaction was monitored by TCL [eluent: *n*-hexane/ethyl acetate (8/2)]. Then the polymer was separated by filtration and the filtrate was diluted with water (15 mL) and extracted with dichloromethane (4 × 8 mL). The combined organic layer was dried over anhydrous Na_2SO_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_2O_5 at 40°C (Scheme 1, step 8). The regenerated polymer can be reused several cycles without losing significantly its activity (Table 2, Entries 2–5).

Disclosure statement

No potential conflict of interest was reported by the authors.

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