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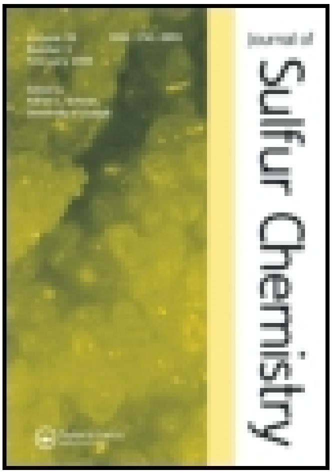

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Synthesis of alkyl thiocyanates from alcohols using a polymer-supported thiocyanate ion promoted by cyanuric chloride/dimethylformamide

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A convenient procedure for one-pot conversion of alcohols into the corresponding alkyl thiocyanates in the presence of cross-linked poly (N-propyl-4-vinylpyridinium) thiocyanate ion [P4-VP]Pr-SCN, promoted by cyanuric chloride/dimethylformamide, is described. Various alcohols were converted to their corresponding alkyl thiocyanates and it was observed that substituted benzyl alcohol with electron-withdrawing or electron-donating groups were transformed into the corresponding benzyl thiocyanate derivatives in high to excellent yields in a short reaction time but, sterically hindered alcohols produced the corresponding thiocyanates in very low yields.

$$\mathrm{ROH}\ \xrightarrow[\mathrm{CC/DMF,\ 50\ ^{\circ}C}]{[\mathrm{P_4\text{-}VP}]\mathrm{Pr\text{-}SCN}}\ \mathrm{RSCN}$$

Keywords: alcohol; benzyl thiocyanate; polymeric reagent; cyanuric chloride; selectivity

1. Introduction

Sulfur-containing compounds have become increasingly useful and important in organic synthesis. Thiocyanates are well known in organosulfur chemistry.[1] Thiocyanate is a versatile synthon which has been used extensively in synthetic organic chemistry,[2] with a wide range of applications particularly in biological and heterocyclic chemistry.[3] For example, properties such as high biological activity,[4] insecticide,[5] biocide,[6] and vulcanization accelerators, and starting materials for the preparation of heterocycles[7] have been reported for organic thiocyanates. A literature search shows that there are a few reports in the preparation of alkyl or aryl thiocyanates,[8–13] and the most general one involves conversion of alkyl halides to alkyl thiocyanates with metal thiocyanates such as sodium or potassium thiocyanate.[7] Thiocyanates can also be obtained from alcohols, silylethers, or amines with electrophilic phosphorane $Ph_3P(SCN)_2$.[8] However, the results are not reproducible because of the low thermal stability of the required intermediate $(SCN)_2$. The toxicity of the starting material, $Ph_3P(SCN)_2$, is also a major drawback of this thiocyanation method. Recently a number of different methods for conversion of alcohols to the corresponding alkyl thiocyanates have been reported.[10–16] However, these methods have certain limitations arising from the use

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*Corresponding author. Email: makarimi@yazd.ac.ir of expensive and explosive reagents, prolonged reaction times, tedious work-up, and the formation of the corresponding isothiocyanates as by-products.[9–11,14] Therefore, new methods that use environmental-friendly, cheap, and easily available reactants to efficiently perform these reactions would be of considerable interest.

In recent years, the polymeric reagents, especially anion exchange resins, have been widely applied in organic transformations.[17–22]

A literature search showed that there are a few reports in the literature on application of polymer-supported thiocyanate ion [19–25] but, to the best of our knowledge, there are no reports in the literature for conversion of alcohols into aryl thiocyanates based on polymer-supported thiocyanate ion. Previously, Cainelli and Manescalchi [23] have described the reactions of polymer-supported thiocyanate with few alkyl halides. 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. Also, Harrison and Hodge [24] reported that Amberlyst A-26 converted a few alkyl halides to the corresponding alkyl thiocyanates (seven examples) under analogous reaction conditions of the last report. They observed that in some reactions the thiocyanates are the only products and in a few reactions isothiocyanates are also formed as by-products. Tamami and Kiasat reported synthesis of thiiranes from oxiranes using polymer-supported thiocyanate.[25] Recently we have prepared cross-linked poly (N-methyl-4-vinylpyridinium) thiocyanate ion and used for the synthesis of alkyl thiocyanates from alkyl halides,[20] aryl thiocyanates via diazotization–thiocyanation of aromatic amines,[21] thiocyanation of aromatic and heteroaromatic compounds in the presence of oxone [19] and for the synthesis of thiocyanohydrins via ring opening of epoxides using cross-linked poly (N-methyl-4-vinylpyridinium) thiocyanate ion and cross-linked poly (4-vinylpyridine)-supported sulfuric acid, $[P_4\text{-VP}]H_2SO_4$.[22]

A search of the literature revealed that the treatment of cyanuric chloride (CC), a very cheap reagent, with alcohols produced the corresponding chlorides.[26–29] CC/dimethyl formamide (DMF) was also used for the synthesis of alkyl thiocyanates from alcohols by using potassium thiocyanate (KSCN).[12] This method has certain limitations arising from the use of solvent (CH_2Cl_2) that is not in agreement with green chemistry, excess KSCN is required (5 equivalents), long reaction times (4–14 h), heating is needed during the reaction (70°C) and in some reactions the alkyl halides are the only products. Hence, in continuation of our studies on organic transformations using polymer-supported thiocyanate reagent,[19–22] we wish to report a simple, one-pot procedure for the synthesis of alkyl thiocyanates from alcohols using cross-linked poly (N-propyl-4-vinylpyridinium) thiocyanate ion, $[P_4\text{-VP}]$Pr-SCN promoted by CC/DMF.

2. Results and discussion

$[P_4\text{-VP}]$Pr-SCN was prepared similar to our previously reported method [20] via the reaction of quaternized cross-linked poly (N-propyl-4-vinylpyridinium) bromide, $[P_4\text{-VP}]$Pr-Br, with an aqueous solution of KSCN. We then tested the presence of Br^- ion in the filtrates that was exchanged with SCN^- ion in the reaction of $[P_4\text{-VP}]$Pr-Br with KSCN (aq.) and used for the synthesis of alkyl thiocyanates from alcohols promoted by CC/DMF. The amount of Br^- ion was determined by potentiometric titration of the filtrates with a 0.1 mol L^{-1} aqueous solution of silver nitrate and consequently, the capacity of SCN^- ion on the polymer was obtained (6.4 mmol g^{-1} of the polymer). Direct evidence of the formation of $[P_4\text{-VP}]$Pr-Br and $[P_4\text{-VP}]$Pr-SCN can be obtained from their FT-IR spectra. It is known that the C=N and C=C stretching frequencies of vinyl pyridine polymers shift to higher frequencies upon protonation.[30] In our case, the

$$\mathrm{ROH}\xrightarrow[\mathrm{CC/DMF,\ 50\ ^{o}C}]{[\mathrm{P_4\text{-}VP}]\mathrm{Pr\text{-}SCN}}\mathrm{RSCN}$$

Scheme 1. Synthesis of alkyl thiocyanates from alcohols.

bands found at 1594 and 1412 cm^{-1} are attributed to C=N and C=C bond stretching of pyridine pendent groups in the polymer chain of [P$_4$-VP] 2% divinyl benzene (DVB) (a, in Figure 1). When [P$_4$-VP] 2% DVB was treated with propyl bromide and the pyridine rings of the polymer were quaternized, these peaks were shifted to 1634 and 1460 cm^{-1}, respectively (b, in Figure 1). Also when [P$_4$-VP]Pr-Br was treated with KSCN (aq) and converted to [P$_4$-VP]Pr-SCN by ion exchange reaction, these peaks were also shifted to 1640 and 1468 cm^{-1}, respectively, and the appearance of a sharp new peak at 2049 cm^{-1}for stretching of SCN$^-$ indicates that the SCN$^-$ was supported on the polymer (c, in Figure 1). Figure 1 also reveals that the FT-IR spectra of [P$_4$-VP]Pr-SCN (c) and regenerated polymer (d) are similar. This interaction increases the stiffness of the associated ring and consequently more energy is required to deform the aromatic cycle, reflected in higher frequencies (Figure 1 is given as supplementary data.).

This is also in agreement with our previously reported methods for the synthesis of β-halohydrins via regioselective ring opening reaction of epoxides using cross-linked poly (4-vinylpyridine)-supported HCl and HBr under solvent-free conditions,[31] conversion of epoxides to azidohydrins in the presence of cross-linked poly (4-vinylpyridine)-supported azide ion [32] and synthesis of thiocyanohydrins via ring opening of epoxides using cross-linked poly (N-methyl-4-vinylpyridinium) thiocyanate ion/[P$_4$-VP]H$_2$SO$_4$.[22]

The polymeric reagent was very stable at room temperature and could be recycled and reused for several times and also this polymeric reagent could be stored as a bench top catalyst for months without significant change in their reactivity and can be readily used for conversion of alcohols into alkyl thiocyanates (Scheme 1).

Since the nature of the solvent influences the rate of reaction, benzyl alcohol (1 mmol) was selected as a model substrate and was converted to benzyl thiocyanate in different solvents and under solvent-free conditions at different temperatures, using 1 mmol of CC, 0.5 mL of DMF, and 1.0 g of [P$_4$-VP]Pr-SCN. The model reaction was performed in various solvents such as acetonitrile, H$_2$O, DMF, tetrahydrofuran, acetone, dichloromethane, ethyl acetate, and under solvent-free conditions and the results are given in Table 1.

As Table 1 reveals, when the reaction was performed under solvent-free conditions at 50°C, the highest yield of the product was obtained in a short reaction time (Entry 11). The next step was the optimization of the molar ratio of CC/[P$_4$-VP]Pr-SCN in different amounts of DMF for the model reaction. The model reaction was performed in different molar ratios under solvent-free conditions at 50°C and the results are summarized in Table 2.

The results presented in Table 2 showed that the optimized molar ratio of CC/[P$_4$-VP]Pr-SCN was 1/3 in 0.50 mL of DMF (Entry 12).

We then applied these conditions for the synthesis of various alkyl thiocyanates from alcohols and the results are summarized in Table 3.

This new, simple method can be successfully applied for the synthesis of a wide range of alkyl thiocyanates starting from the corresponding alcohols. Under optimized reaction conditions, several structurally diverse alcohols were examined for the thiocyanation reaction. Representative results are summarized in Table 3. As is clear from Table 3, primary benzylic alcohols (Entries 1–13) were easily converted into corresponding thiocyanates in high to excellent yields while, allyl alcohol (Entry 14) and primary alkyl alcohol such as n-penthyl alcohol (Entry 15) or secondary alcohols such as diphenylmethanol (Entry 17) and cyclohexanol (Entry 20) produced desired products in very low and negligible yields. Previously, Cainelli and Manescalchi [23] have described the reactions of a polymer-supported thiocyanate (Amberlyst A-26 SCN$^-$ form)

Table 1. Optimization of the reaction conditions for conversion of benzyl alcohol to benzyl thiocyanate using [P_4-VP]Pr-SCN/CC/DMF (1.0 g/1 mmol/0.5 mL).

Entry	Temperature (°C)	Solvent	Time (min)	Isolated yield (%)
1	R.t.	Acetonitrile	120	20
2	R.t.	H_2O	120	0.0
3	R.t.	DMF	120	0.0
4	R.t.	Tetrahydrofurane	120	0.0
5	R.t.	Acetone	120	0.0
6	R.t.	Dichloromethane	120	10
7	R.t.	Ethyl acetate	120	0.0
8	R.t.	*n*-Hexane	120	75
9	R.t.	Solvent free	120	90
10	50°C	Solvent free	10	95
11	70°C	Solvent free	30	50

Table 2. Optimization of the molar ratio of CC/[P_4-VP]Pr-SCN in different amounts of DMF for the model reaction under solvent-free conditions at 50°C.

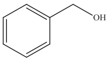
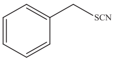
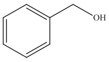
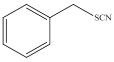
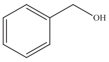
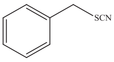
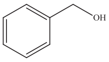
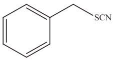
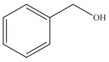
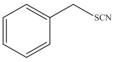
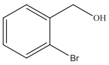
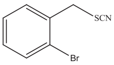
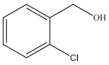
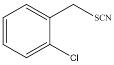
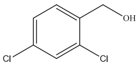
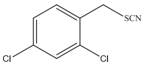
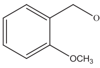
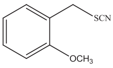
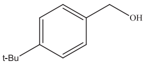
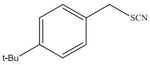
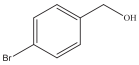
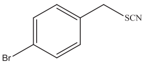
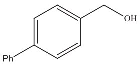
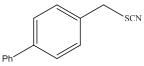
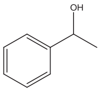
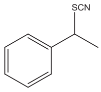
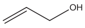
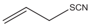
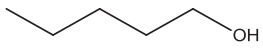
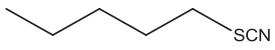
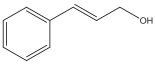
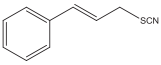
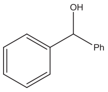
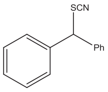
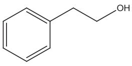
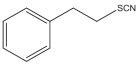
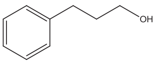
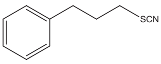
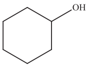
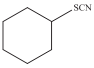
Entry	CC (mmol)	DMF (mL)	[P_4-VP]Pr-SCN (mmol of SCN^-)	Time (min)	Isolated yield (%)
1	0.33	0.10	6.4	30	20
2	0.66	0.10	6.4	30	30
3	1.0	0.10	6.4	30	45
4	1.0	0.15	6.4	30	61
5	1.0	0.25	6.4	30	80
6	1.0	0.50	6.4	10	95
7	1.0	0.75	6.4	10	95
8	1.0	0.50	1.0	10	26
9	1.0	0.50	1.5	10	41
10	1.0	0.50	2.0	10	60
11	1.0	0.50	2.5	10	81
12	1.0	0.50	3.0	10	95
13	1.0	0.50	3.5	10	95

with few alkyl halides. They reported that larger substrates generally required harsher reaction conditions than the smaller substrates in order to obtain good yields of product. Recently, we also observed similar results for the conversion of alkyl halides into alkyl thiocyanates using cross-linked poly (N-methyl-4-vinylpyridinium) thiocyanate.[20] Our results in the present method for the synthesis of alkyl thiocyanates also support this observation (Table 3, Entries 15–20). It may be that the larger molecules have more difficulty gaining access to the active sites of the polymer. This result is in agreement with the previously reported method for conversion of alcohols to the corresponding alkyl thiocyanates by using trichloroisocyanuric acid with triphenylphosphine.[16]

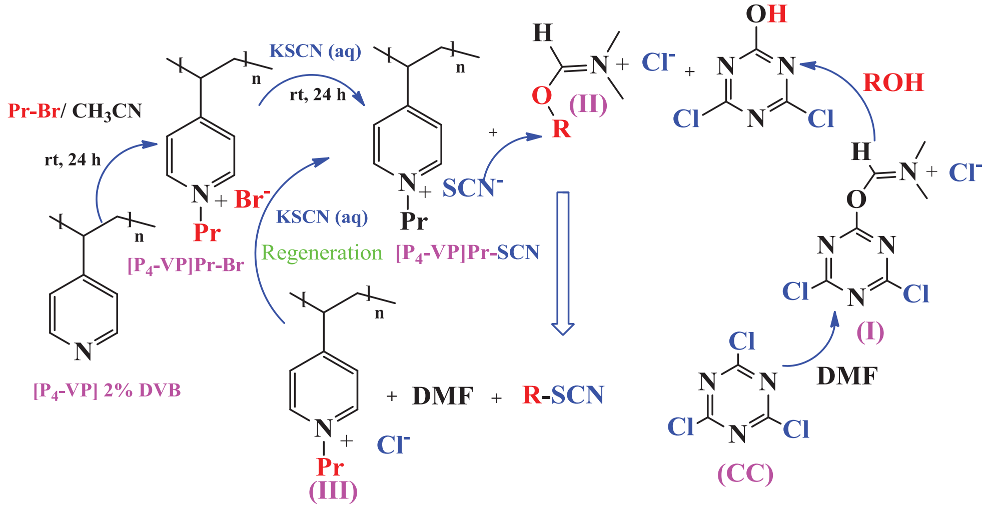
Another report in this field is described by Harrison and Hodge.[24] Their results also support this view, but they observed that in a few reactions isothiocyanates were also formed. The thiocyanate group is unstable when heated or subjected to acidic conditions, so the reaction can give mixtures of thiocyanates and isothiocyanates, or can proceed selectively to either isomer. However in our study we observed that thiocyanates are the only products, and isothiocyanates as by-products were not formed.

We have also successfully applied this new method in a larger scale, for example, up to 15 mmol of benzyl alcohol (Table 3, Entry 1) which could be converted into benzyl thiocyanate without significant loss of their activity. The spent polymeric reagent can also be regenerated and reused several times without significant loss of their activity (Table 3, Entries 2–5).

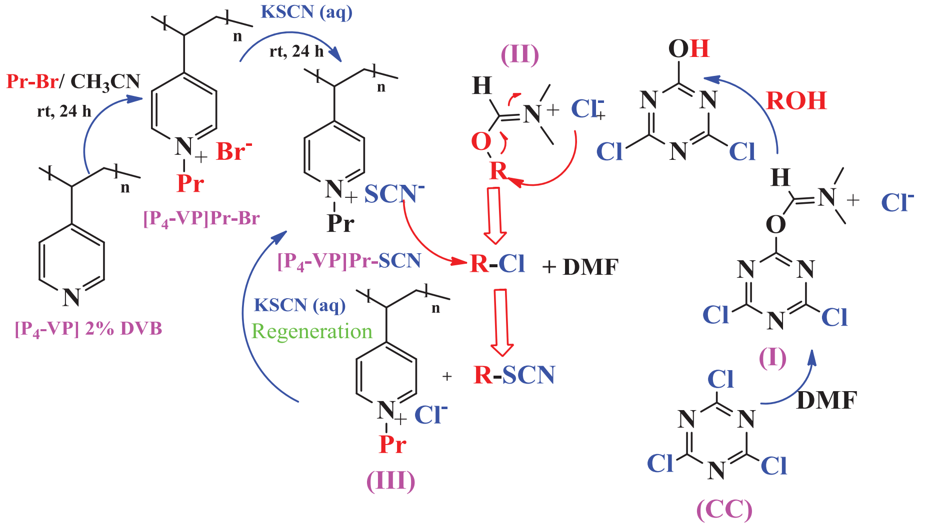
Table 3. Synthesis of alkyl thiocyanates from alcohols using [P_4-VP]Pr-SCN/CC/DMF under solvent-free conditions at 50°C.

Entry	Alcohol	Product	Time (min)	Yields (%)[a]	Ref.
1			10	95	[8,10,12]
2[b]			10	95	[8,10,12]
3[b]			11	95	[8,10,12]
4[b]			12	93	[8,10,12]
5[b]			15	93	[8,10,12]
6			40	94	
7			35	95	[11]
8			35	94	
9			45	90	[13]
10			60	85	
11			15	95	
12			60	85	[14]
13			120	90	[11,14]
14			720	Trace	[8]
15			720	Trace	
16			150	50	[8,14]
17			720	30	[8,10,11,14]
18			120	54	[8,10–12,14]
19			180	40	[8,10,12]
20			720	20	[8,10–12,14]

[a] Yields refer to the Isolated pure products.
[b] The Entries 2–5, refer to the use of the [P_4-VP]Pr-SCN that is recycled first, second, third, and fourth time, respectively, under identical conditions.



Path a



Path b

Scheme 2. Preparation of $[P_4\text{-VP}]$Pr-SCN, the reaction pathway of benzyl thiocyanate preparation and regeneration of the polymer.

Adduct (1), is isolated by Gold [27] in the reaction of CC with DMF but, when excess of DMF is used, Gold's salt [29] is also observed. Based on the previous reports,[12,27–29] and our observation, the following mechanism is suggested for this conversion (Scheme 2). In the first step, positively charged adduct (I) is produced by CC and DMF. Then alcohol attacked adduct (I), and intermediate (II) is produced. Finally, alkyl thiocyanate is obtained by thiocyanate ion attachment to intermediate (II), as shown in Scheme 2 (path a). Also, if the chloride ion attachment on the intermediate (II) occurred, alkyl chloride is obtained by thiocyanate ion substitution on the obtained alkyl chloride, the corresponding alkyl thiocyanate is produced (path b). By using larger substrates and secondary alcohols, alkyl chlorides were formed in the reaction mixture as intermediate that cannot be easily converted into alkyl thiocyanates under this reaction condition;

Table 4. Synthesis of benzyl thiocyanate from benzyl alcohol in different methods.

Entry	Reaction conditions	Time	Yield (%)	Ref.
1	[P4-VP]SCN/CC/DMF/50°C/Solvent-free	10 min	95	[A][a]
2	NTS[b]/NH_4SCN/CH_3CN, r.t.	30 min	95	[11]
3	$NH_4SCN/CC/DMF/CH_2Cl_2$/70°C	6 h	76	[12]
4	TClCA[c]/PPh_3/CH_3CN	3 h	62	[16]
5	NH_4SCN/CMPI[d]/CH_3CN/60°C	1.5 h	76	[15]
6	Silphos[e]/$I_2/NH_4SCN/CH_3CN$, Reflux	24 h	90	[13]
7	IL-$OPPh_2$[f]/Br_2/KSCN/80°C	30 min	98	[9]

Note: [A], present method Table 2 (Entry 1); NTS, N-thiocyanatosuccinimide; TClCA, trichloroisocyanuric acid; CMPI, 2-Chloro-1-methylpyridinium iodide; silphos, [PCl_{3}-n(SiO_2)$_n$]; IL-$OPPh_2$, diphenylphosphinite ionic liquid.

hence, the isolated yields of alkyl thiocyanate products in these reactions were low. This may be because the larger molecules have more difficulty in gaining access to the active sites in the polymer.

All of the products are known compounds [8,10–14] and were identified by comparison of their physical and spectral data with those of authentic samples.

The FT-IR spectrum showed the characteristic peak of –SCN between 2145 and 2160 cm^{-1} and the –C–S stretching at 642–755 cm^{-1}. The characteristic spectral data of some alkyl thiocyanate products and the FT-IR, ^1H NMR, and ^{13}CNMR spectra of 4-*t*-butylbenzyl thiocyanate products are given as supplemental data.

In Table 4, the reaction time and isolated yields of the model reaction are compared with other reported methods. As it is demonstrated, in this procedure, the yield of the reaction was higher and the reaction time was shorter than previously reported methods.[9,11–13,15,16] This can probably be attributed to the local concentration of thiocyanate ion species inside the pores.

The advantages of this method over conventional classical methods are: separation of the support from the reaction mixture by simple filtration, low reaction time, and excess of polymeric reagent can be readily employed without incurring complication in work-up. In addition, there is current research and general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.[33] On the other hand, we were the first to develop a method for the facile diazotization–thiocyanation of aromatic amines by using a polymer-supported thiocyanate ion.

3. Conclusions

Cross-linked poly (N-propyl-4-vinylpyridine)-supported thiocyanate ion, [P_4-VP]Pr-SCN, has been introduced as an efficient polymeric reagent for the synthesis of alkyl thiocyanates via direct conversion of alcohols into alkyl thiocyanates promoted by CC/DMF, in high to excellent yields. The present method has the advantages such as operational simplicity, mild reaction conditions, ready availability, fast reaction rates, and simple reaction work-up. The spent polymeric reagent can be regenerated and reused several times without significant loss of their activity.

4. Experimental design

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% DVB, (white powder, and 100–200 mesh), [P_4-VP] 2% DVB, was purchased from Fluka (Buchs, Switzerland). Cross-linked poly (N-propyl-4-vinylpyridinium) bromide, [P_4-VP]Pr-Br, and cross-linked Poly (N-propyl-4-vinylpyridine) thiocyanate, [P_4-VP]Pr-SCN, were prepared in our laboratory. 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}H NMR spectral data, with those of known samples and all yields refer to the isolated pure products. FT-IR spectra were obtained by using a Bruker, Equinox (model 55) (Germany) and NMR spectra were recorded on a Bruker AC 400, Avance DPX spectrometer (Germany) at 400 MHz in $CDCl_3$.

4.2. *Preparation of [P_4-VP]Pr-SCN*

[P_4-VP] 2% DVB (1.00 g) was added to a solution of excess propyl bromide (5 mL) in acetonitrile (5 mL) and the mixture was stirred slowly for 24 h at ambient temperature. The white quaternized polymer, [P_4-VP]Pr-Br, was filtered and washed with acetone successively (3 × 5 mL). It was then dried under vacuum in the presence of P_2O_5 at 40°C overnight. The obtained [P_4-VP]Pr-Br was added to 40 mL of a 3 M solution of potassium thiocyanate and slowly stirred for 24 h. The prepared resin, [P_4-VP]Pr-SCN, was filtered off and was washed with distilled water. It was then washed with diethyl ether and dried under vacuum in the presence of P_2O_5 at 40°C. The capacity of the polymer was determined by the gravimetric method and potentiometric titration with a 0.1 mol L^{-1} of silver nitrate and it was found to be 3.2 mmol of thiocyanate ion per gram of the polymer.

4.3. *General procedure for the synthesis of alkyl thiocyanates from alcohols using [P_4-VP]Pr-SCN*

CC (0.183 g, 1.0 mmol) was added to DMF (0.5 mL) and the mixture was stirred at ambient temperature until the CC disappeared. The reaction was monitored by TLC. Then, 1 mmol of an alcohol and 468 mg of [P_4-VP]Pr-SCN (3 mmol of SCN^-)were added and the mixture was stirred at 50°C in a water bath until the alcohol disappeared (TLC). After the reaction completion, the mixture was filtered and washed successively with *n*-hexane (5 × 2 mL). The solvent was evaporated and the pure product was obtained in moderate to high yields (20–95%). If further purification is needed, flash chromatography on silica gel (eluent: *n*-hexane) could be used which provides highly pure products.

4.4. *Regeneration of [P_4-VP]Pr-SCN*

The spent polymer (1.00 g) was added to an excess aqueous solution of KSCN (seven equivalents) and was stirred for 24 h at room temperature. The mixture was filtered, washed several times with distilled water, and dried overnight under vacuum in the presence of P_2O_5 at 40°C. The regenerated polymer can be reused several times without losing significantly its activity.

Disclosure statement

No potential conflict of interest was reported by the authors.

Supplemental data

Supplemental data for this article can be accessed at doi:10.1080/17415993.2015.1035273.

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