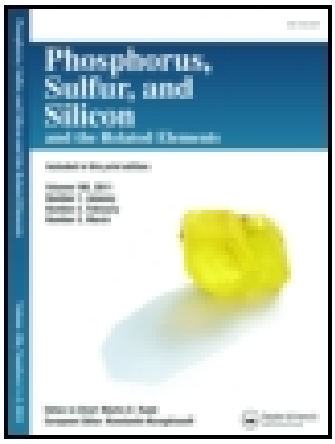

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Ring opening of epoxides by using cross-linked poly (4-vinylpyridine) supported thiocyanate in the presence of polymer-supported sulfuric acid under solvent-free conditions

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RING OPENING OF EPOXIDES BY USING CROSS-LINKED POLY (4-VINYLPYRIDINE) SUPPORTED THIOCYANATE IN THE PRESENCE OF POLYMER-SUPPORTED SULFURIC ACID UNDER SOLVENT-FREE CONDITIONS

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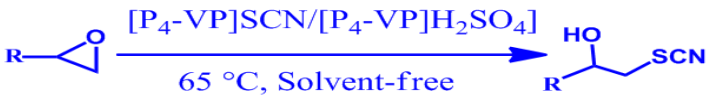
Abstract

Cross-linked poly (4-vinylpyridine) supported thiocyanate ion, [P_4-VP]SCN is introduced as recyclable polymeric reagent for the efficient and regioselective conversion of epoxides to thiocyanohydrins in the presence of cross-linked poly (4-vinylpyridine) supported sulfuric acid, [P_4-VP]H_2SO_4, as a solid proton source and as catalyst under solvent-free conditions. The ring opening reaction of epoxides take place very fast under solvent-free conditions and the regioselective thiocyanohydrins are prepared in high yields at 65 °C. The present method offers advantages such as short reaction time, simple reaction work-up, and the polymeric reagents can be regenerated and reused several times without significant loss of their activity.



Keywords: Ring opening of epoxide, Thiocyanohydrin, Polymer-supported reagent, Solvent-free conditions, Regioselectivity.

INTRODUCTION

The ring opening reaction of epoxides with nucleophiles is a very useful approach in organic synthesis for preparation of functionalized oxygenated compounds.[1-3]

Nucleophilic addition to epoxides is an easy step for preparation of several 1, 2-disubstituted products such as *β*-hydroxythiocyanates. The thiocyanate functional group will be readily transformed into the other sulfur-bearing functionalities.[4-12]

The ring opening of epoxides with thiocyanates is a widely used method for the preparation of thiiranes. The formation of thiiranes from oxiranes and thiocyanates has been explained by the intermediacy of the corresponding *β*-hydroxythiocyanate that have not been isolated due to rapid conversion into the corresponding thiiranes. [13-23] However, several methods are reported for the preparation of thiocyanohydrins. [24-41] They are limited to specific epoxides and are not applicable as versatile reagents for the preparation of *β*-hydroxythiocyanates and some of these methods suffer from disadvantages such as long reaction times.[32,33], low regioselectivity. [37,38,40-45], using of organic solvents [27,29,32,33,39], using phase-transfer catalysts [32,35], using of expensive catalysts[29],[33,34,37,39], low yields [27], or involve high temperature reaction conditions.[27, 35] Therefore, it seems that there is still a need for development of novel methods that proceed under mild and eco-friendly conditions.

Solid acids have many advantages such as simplicity in handling, decreased reactor and plant corrosion problems, and more environmentally safe disposal in different chemical processes. On the other hand, any reduction in the amount of strong inorganic acids needed and any

simplification in handling procedures are required for risk reduction and economic advantage.[41] In addition there is current research and general interest in heterogeneous systems because such systems have importance in industry and in developing technologies.[42] Recently Borah *et al*. reported the synthesis, characterization and application of poly(4-vinylpyridine)-supported Brønsted acid as reusable catalyst for acetylation reaction.[43] In this study, the use of this solid acidic resin as a new proton source for ring opening of epoxides using cross-linked poly (4-vinylpyridine supported thiocyanate ion, [P_4-VP]SCN, was studied.

Solid phase synthesis, in particular, polymer supported nucleophiles, has been widely used in organic synthesis.[23, 43-61]

A literature search shows that there are a few reports based on polymer-supported thiocyanate ion .[23, 51,52,62,63] Very recently Cainelli et al. reported a polymeric reagent for synthesis of alkyl thiocyanates.[62] Also Hodge et al. reported that Amberlite A-26 converted a few alkyl halides to the corresponding alkyl thiocyanates (seven examples) under the same conditions of the last report.[63] Tamami and Kiasat reported that epoxides were converted to their corresponding episulfides using Amberlite IRA-400 supported thiocyanate.[23] 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,[51] synthesis of aryl thiocyanates via diazotization-thiocyanation of arylamines.[52] To the best of our knowledge, there are no reports on polymer-supported thiocyanate ion for thiocyanation of epoxide rings. In continuation of our studies on the development of application of [P_4-VP]SCN in organic synthesis[51,52], in this report, we wish to disclose a simple, convenient and efficient method for

synthesis of thiocyanohydrins by using [P_4-VP]SCN/[P_4-VP]H_2SO_4 under solvent-free conditions.

RESULTS AND DISCUSION

In connection with our organic program to develop environmentally friendly methods using polymer-supported reagents (50-61), herein we wish to report an extremely convenient and efficient method for preparation of different β-hydroxythiocyanates from regioselective ring opening of epoxides by using cross-linked poly (4-vinylpyridine) supported thiocyanate ion [P_4-VP]SCN, in the presence of cross-linked poly (4-vinylpyridinie) supported sulfuric acid, [P_4-VP]H_2SO_4, as solid proton source and as new polymeric phase transfer catalyst under solvent-free conditions at 65 °C. [P_4-VP]H_2SO_4 is easily prepared by the reaction of poly (4-vinylpyridine) cross-linked with 2% divinyl benzene, [P_4-VP] 2% DVB with mixture of diethyl ether and H_2SO_4 and [P_4-VP]SCN is easily prepared by ion exchange reaction between cross-linked poly (N-methyl-4-vinylpyridinium) iodide with an excess amount of potassium thiocyanate in water (Scheme 1).

The polymeric reagent is used in a single step reaction; its main advantage over non-polymeric reagents is its insolubility in the reaction medium and consequently its easier work-up by a simple filtration. The reactions can be driven to completion using excess amounts of reagent without the fear of excess of reagent separating from the products. One of the most disadvantage

of the polymeric reagents is their high costly but, in the present method, polymeric reagents can be regenerated and reused several times without significant loss of their activity as given in Scheme 1.

[P_4-VP]SCN can be used as a mild and efficient polymeric reagent for regioselective ring opening of epoxides in the presence of a solid polymeric acid, [P_4-VP]H_2SO_4 and consequently the corresponding β-hydroxythiocyanates are prepared (Scheme 2).

In order to increase the yields of β-thiocyanohydrins optimization of the reaction conditions was accomplished. Phenylglycidyl ether (1mmol) in the presence of [P_4-VP]H_2SO_4 was chosen as a model substrate and was converted to the corresponding β-hydroxythiocyanates in different solvents such as carbon tetrachloride, chloroform, acetonitrile, dichloromethane, ethanol, and H_2O at different temperature and under solvent-free conditions. Also, we have investigated a number of different reaction conditions for synthesis of β-hydroxythiocyanates and the results are summarized in Table 1. It was observed that, a molar ratio of 1/2.8/3.4 of phenylglycidyl ether/[P_4-VP]H2SO4/[P_4-VP]SCN under solvent-free conditions at 65 °C were the best to achieve the highest yield of the product as indicated in Table 1 (entry 16).

We then applied these conditions in ring opening of different epoxides to prepare the corresponding thiocyanohydrins and the results are given in Table 2. This new, simple method can be successfully applied for the synthesis of a wide range of β-hydroxythiocyanates starting

from the corresponding epoxides. A variety of epoxides such as styrene oxide, allylglycidylether, cyclohexene epoxide, 1,2-epoxy-3-(4-nitrophenoxy) propane, glycidyl tosylate, N-(2,3-epoxypropyl) phthalimide, and epichlorohydrin have been converted to corresponding *β*-hydroxythiocyanates using $[P_4\text{-VP}]SCN/[P_4\text{-VP}]H_2SO_4$ under solvent-free conditions at 65 °C (Table 2).It is important to note that these polymeric reagents were stable and could be stored for a long time (months) without losing their activity and could be readily used for conversion of epoxides to the corresponding thiocyanohydrins. Also, these polymeric reagents could be regenerated and reused for several times (Scheme 1, entries 3-6 in Table 2).

The role of $[P_4\text{-VP}]H_2SO_4$ is not only to activate the epoxide but to promote ring opening reaction as phase-transfer catalyst. Generally under basic condition the nucleophile slowly attacks the less substituted *β*-carbon through an expected S_N2 mechanism and under acidic condition the reaction is much faster likely due to the protonation of the oxygen of the epoxide ring. In the present study, the cleavage of epoxides took place with high regioselectivity. Epoxides afforded the products of opening at the benzylic position or partially stable carbocation intermediates (more substituted carbon) through an S_N1-like mechanism. Although recently, we observed that, 2-arylepoxides afforded the products of opening at the benzylic position through an S_N1-like mechanism, while 2-alkylepoxides gave the products formed by cleavage at the less substituted carbon through an S_N2 borderline mechanism when $[P_4\text{-VP}]HCl$ and $[P_4\text{-VP}]HBr$ were used for synthesis of *β*-halohydrin products.[61]

The β-hydroxythiocyanate products were characterized by FT-IR; and ^{1}H- and ^{13}C-NMR spectroscopy and physical properties were compared with literature values of known compounds. In this respect, the appearance a strong band in the region 2150–2156 cm^{-1} for stretching vibration of the –SCN and another strong band in the region 3340-3477 cm^{-1} for stretching vibration of the O-H group indicate the formation of corresponding β-hydroxythiocyanate products.

Also in Figure 1, the FT-IR spectra of [P_4-VP] 2% DVB, [P_4-VP]I and [P_4-VP]SCN (a, b and c respectively) and in Figure 2, the FT-IR spectra of [P_4-VP] 2% DVB, and [P_4-VP]H_2SO_4 (a and b respectively) are compared. The pyridine pendant groups exhibit a strong C=C stretching band at 1597 cm^{-1} and C=N stretching absorption at 1412 cm^{-1}. When the pyridine ring is quaternized with methyl iodide, these peaks shift towards higher wave numbers (1636 cm^{-1} for C=C and 1445 cm^{-1} for C=N). Also, in the spectrum of [P_4-VP] 2% DVB, there is no absorption in the region N-H stretching (spectrum (a) in Figures 1 and 2), but in the spectrum of [P_4-VP]H_2SO_4 (b in Figure 2) the corresponding N-H stretching vibration is observed at 3398$cm^{-1}$and the C=C and C=N stretching peaks shift towards higher wave numbers (1634 cm^{-1} for C=C and 1501 cm^{-1} for C=N) .

In Table 3, other reported methods for nucleophilic ring opening of phenylglycidyl ether for preparation of thiocyanated product are compared with the present method. As Table 3 reveals, the reaction time of the present method is shorter than all of the previously reported methods.

This can probably be attributed to the high local concentration of thiocyanate ion species inside the pores of the polymer. Although some of the previously reported methods such as entries 3 and 9-11, have high yields and short reaction times, the present method offers advantages such as mild reaction conditions, simple reaction work-up, and the polymeric reagents can be regenerated and reused several times. On the other hand, all of the above methods have needed refluxing in acetonitrile especially entries 10 and 11, and reactions must be performed under nitrogen gas. This is not in agreement with green chemistry while, in the present method, the reactions were performed under solvent-free conditions.

CONCLUSIONS

In summary, we describe a novel, eco-friendly, and efficient protocol for the synthesis of thiocyanohydrins by the regioselective ring opening of epoxides with [P_4-VP]SCN in the presence of [P_4-VP]H_2SO_4 as an inexpensive and green polymeric catalyst. This method suffer several advantages including mild reaction conditions, high conversions, high regioselectivity, short reaction time, clean reaction profiles, and high isolated yields which make it a useful and attractive process for the synthesis of thiocyanohydrins.

EXPERIMENTAL

Materials and instruments

The chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), or and Merck (Germany) chemical companies. Poly (4-vinylpyridine) cross-linked with 2% divinyl benzene (DVB), [P_4-VP] 2% DVB; (white powder, 100–200 mesh) was purchased from Fluka. [P_4-VP]I and [P_4-VP]I were synthesized according to our reported procedures.[50] The progress of the reaction was monitored by thin-layer chromatography (TLC) with silica gel PolyGram SIL G/UV 254 plates. All products were characterized by comparison of their melting points, Germany, Fourier transform infrared (FT-IR) spectroscopy, and ^{1}H NMR spectral data with those of known samples, and all yields refer to the isolated pure products. The FTIR spectra were obtained with a Bruker Equinox (model 55), Germany, and the NMR spectra were recorded on a Bruker AC 400 Avance DPX spectrophotometer, Germany at 400 MHz in $CDCl_3$ solution.

Preparation of [P_4-VP]SCN

[P_4-VP]SCN, was prepared as our previously reported method[50] by ion exchange reaction between [P_4-VP]I and KSCN (aq.), the I^{-1} ion was released in the solution and SCN^{-1} ion was supported on the polymer. After filtration, the amount of the I^{-1} ion (that was exchanged with SCN^{-1} 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^{-1} ion on the polymer was obtained (3.4 mmol g^{-1} of the polymer).

Preparation of $[P_4\text{-VP}]H_2SO_4$

To a solution of 0.6 mL of concentrated sulfuric acid (16 M) in distilled water (10 mL), $[P_4\text{-VP}]$ 2% DVB (1 g) was added, and stirred for 24 h. The mixture was filtered and washed with distilled water until the filtrate gave a negative test for H_2SO_4. Then it was dried in vacuum at 50 °C for 5 h to give 2.2 g of $[P_4\text{-VP}]H_2SO_4$. The amount of acid group present in the polymeric chain was calculated based on the weight of supported polymer salt obtained and the weight of poly(4-vinylpyridine) used. The capacity of the polymer was determined by potentiometric titration of the unreacted sulfuric acid by poly(4-vinylpyridine) used, with a 0.1 M solution of sodium hydroxide. The obtained capacity of polymer was 5.56 mmol/g of the polymer.

General procedure for conversion of epoxides using $[P_4\text{-VP}]SCN$/$[P_4\text{-VP}]H_2SO_4$ under solvent-free conditions

In a mortar, a mixture of an epoxide (1mmol), $[P_4\text{-VP}]$ SCN (0.50 g, 1.7 mmol) and $[P_4\text{-VP}]H_2SO_4$ (0.50 g, 2.8 mmol) were pulverized for 3-5 min. The mixture was stirred at 65 °C in a water bath for the appropriate time as indicated in Table 2. The progress of the reaction was monitored by TLC using n-hexane/ethyl acetate (80:20) as eluent. After completion of the reaction, the mixture was poured in of $CHCl_3$ (10 mL). The suspension was filtered, and was washed with $CHCl_3$ (3×5 mL). The combined organic layer was dried over anhydrous $CaCl_2$, and was filtered. The solvent was evaporated to obtain *β*-hydroxythiocyanates in good to high isolated yields (80-95%). When further purification is needed, preparative TLC or column chromatography on silica gel provides highly pure products.

Preparation of 2-thiocyanato-3-phenoxypropanol from phenylglycidyl ether by using [P_4-VP]SCN/[P_4-VP]H_2SO_4 under solvent-free conditions as a typical procedure

In a mortar, a mixture of phenylglycidyl ether (1mmol) [P_4-VP] SCN (1.00 g, 3.4 mmol) and [P_4-VP]H_2SO_4 (0.5 g, 2.8 mmol) were pulverized for 3-5 min. The mixture was stirred at 65 °C in a water bath for 15 min. The progress of the reaction was monitored by TLC using n-hexane/ethyl acetate (80:20) as eluent. After completion of the reaction, the mixture was poured into $CHCl_3$ (10 mL). Then, the suspension was filtered, and was washed with $CHCl_3$ (3×5 mL). The combined organic layer was dried over anhydrous $CaCl_2$, and was filtered. The solvent was evaporated to obtain 2-hydroxy-3-phenoxypropylthiocyanate in high isolated yield (198 mg, 95%).

Regeneration of [P_4-VP]SCN

The spent cream-colored polymer (1.00 g) was added to a solution of methyl iodide (20 mmol) in acetonitrile (10 mL), and the mixture was slowly stirred for 24 h at room temperature. The polymer was filtered and added to a 3 M aqueous solution of potassium thiocyanate (40 mL), and was slowly stirred for 24 h. The mixture was filtered and washed with distilled water (3 × 8 mL), and dried under vacuum in the presence of P_2O_5 at 40 °C overnight. The activity of the regenerated polymer was the same as the original form. The regenerated polymer reused several times, without significant loss of their activity(Table 2, entries 3–6).

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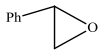
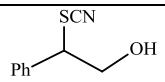
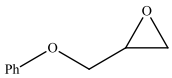
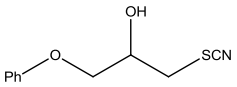
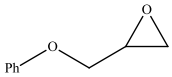
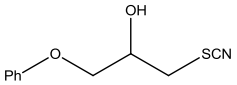
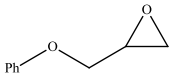
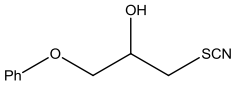
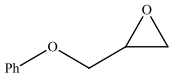
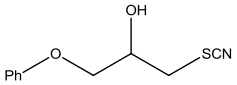
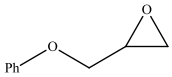
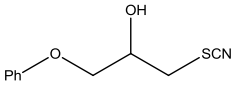
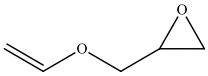
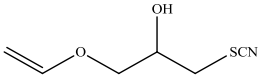
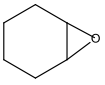
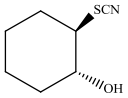
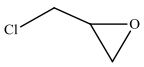
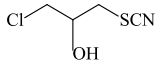
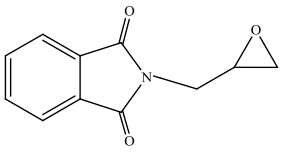
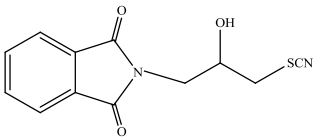
Table 1: Optimization of the reaction conditions for ring opening of model substrate (phenylglycidyl ether, 1mmol)

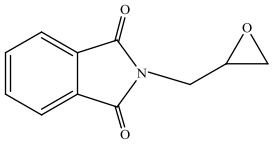
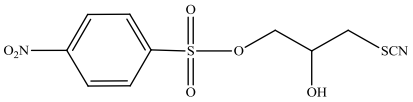
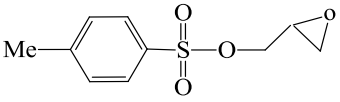
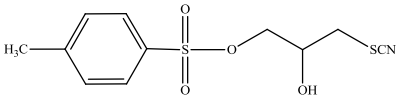
entry	Solvent	Catalyst (mmol of H_2SO_4)	Temp (°C)	$[P_4$-VP]SCN (mmol of SCN- ion)	Time (h)	Yield [a] (%)
1	CCl_4	-	65	3.4	8	-
2	$CHCl_3$	-	65	3.4	8	-
3	CH_3CN	-	65	3.4	8	-
4	CH_2Cl_2	-		3.4	8	-
5	C_2H_5OH	-	65	3.4	8	-
6	H_2O [b]	-	65	3.4	8	-
7	C_2H_5OH	$[P_4$-VP]H_2SO_4 (2.8)	rt	3.4	8	35
8	H_2O [b]	$[P_4$-VP]H_2SO_4 (2.8)	rt	3.4	8	50
9	CH_2Cl_2	$[P_4$-VP]H_2SO_4 (2.8)	45	3.4	12	78
10	C_2H_5OH	$[P_4$-VP]H_2SO_4 (2.8)	45	3.4	2.5	87
11	H_2O [b]	$[P_4$-VP]H_2SO_4 (2.8)	45	3.4	1	85
12	Solvent-Free	-	45	3.4	5	-
13	Solvent-Free	$[P_4$-VP]H_2SO_4 (2.8)	rt	3.4	2	40
14	Solvent-Free	$[P_4$-VP]H_2SO_4 (2.8)	65	1.7	30 min	80
15	Solvent-Free	$[P_4$-VP]H_2SO_4 (1.4)	65	3.4	30 min	85
16	Solvent-Free	$[P_4$-VP]H_2SO_4 (2.8)	65	3.4	15 min	95

[a] Isolated yields;

[b] In water as solvent, H_2O was reacted as nucleophile and 1,2-diol product was obtained

Table 2: Ring opening of epoxides using $[P_4\text{-VP}]SCN/[P_4\text{-VP}]H_2SO_4$ under solvent-free conditions at 65 °C

Entry	Epoxide	Product	Time (min)	Yield (%)[a]
1			15	95
2			15	95
3[a]			15	92
4[a]			15	88
5[a]			20	82
6[a]			20	80
7			15	90
8			15	92
9			15	92
10			25	85

11			25	80
12			25	80

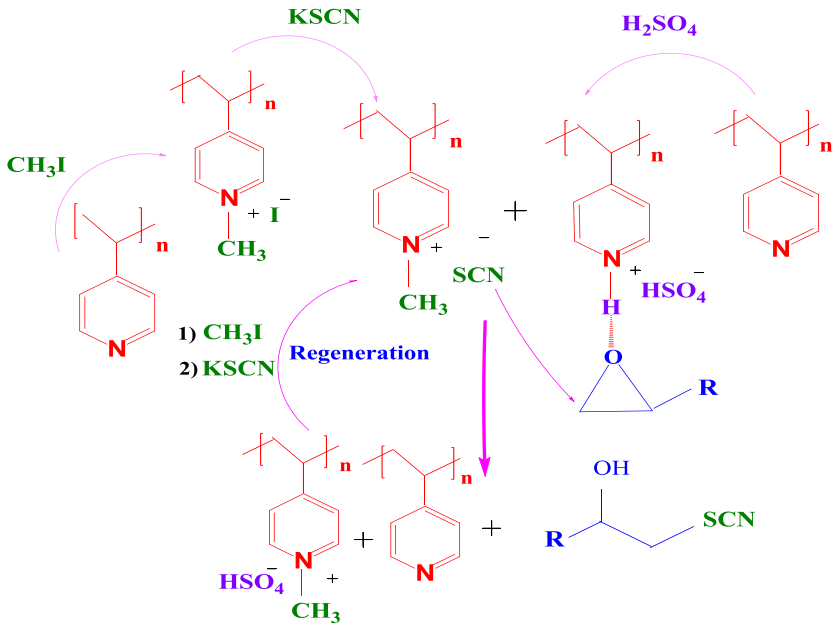
[a] Isolated yields; [b] The entries 3-6, refer to the use of the [P_4-VP]SCN that is recycled first, second, third and fourth time, respectively, under identical conditions.

Table 3: Comparison of different methods for synthesis of 3-phenoxy-1-hydroxypropylthiocyanates

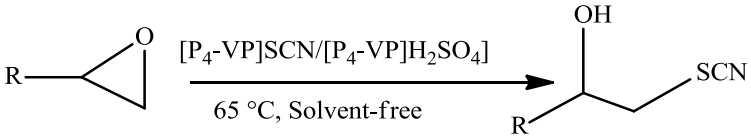
Entry	Reaction conditions	Time (min)	Isolated yield (%)	Ref.
1	$[P_4\text{-VP}]SCN/[P_4\text{-VP}]H_2SO_4$, solvent-free, 65 °C	15	95	A
2	PEG[a]-$SO_3H/NH_4SCN/CH_2Cl_2$/rt.	60	96	28
3	T(4-OHP)P[b]/NH_4SCN/CH_3CN/reflux	20	96	29
4	MPTC[c]/NH_4SCN/H_2O	15	88	30
5	PTC[d]/NH_4SCN/CH_3CN/rt	90	90	32
6	Selectfluor [c]/NH_4 SCN/CH_3CN/rt.	150	80	33
7	PEG[a]-$SO_3H/NH_4SCN/H_2O$/rt.	60	83	34
8	DDQ[f]/NH_4SCN/CH_3CN/reflux	50	80	37
9	BABMB[g]/NH_4SCN/CH_3CN/reflux	10	91	40
10	CO^{II}T(4-OHP)P[h]/NH_4SCN/CH_3CN/reflux/N_2	25	96	64
11	$[P(TPP)Cl_2]Cl$[i]/NH_4SCN/CH_3CN/reflux/N_2	22	96	65
12	PPI[j]/NH_4SCN/CH_3CN/reflux	45	95	66

A: Present method (Table 2, entry 2); [a] PEG: Poly (ethylene glycol)-bound sulphonic acid; [b] T(4-OHP)P: 5,10,15,20-Tetrakis (4-nitrophenyl) porphyrin; [c] MPTC: Multi-site phase-transfer catalyst;

[d] PTC: poly [N-(2-aminoethylacrylamido] trimethyl ammonium chloride; [e] Selectfluor: 1-Chloromethyl-4-fluoro-1, 4-diazoniabicyclo [2.2.2] octane bis(tetrafluoroborate); [f] DDQ: 2,3-Dichloro-5, 6-dicyano-1, 4-benzoquinone; [g] BABMB: bis [2-(o-aminophenoxy) methyl]-4-bromo-1-methoxybenzene; [h] CO^{II} T (4-OHP) P: Metalloporphyrins; [i] [P(TPP)Cl2]Cl: Dichloro (5,10,15,20) tetraphenylporphyrine) phosphorus (V) chloride; [j] PPI: 2-Phenyl-2-(2-pyridyl) imidazolidine.



Scheme 1: Preparation stages of $[P_4\text{-VP}]SCN$, and $[P_4\text{-VP}]H_2SO_4$, the plausible reaction pathway of ring opening of epoxides and regeneration of the polymeric reagent.



Scheme 2: Synthesis of thiocyanohydrins using $[P_4\text{-VP}]SCN/[P_4\text{-VP}]H_2SO_4$ under solvent-free conditions at 65 °C.

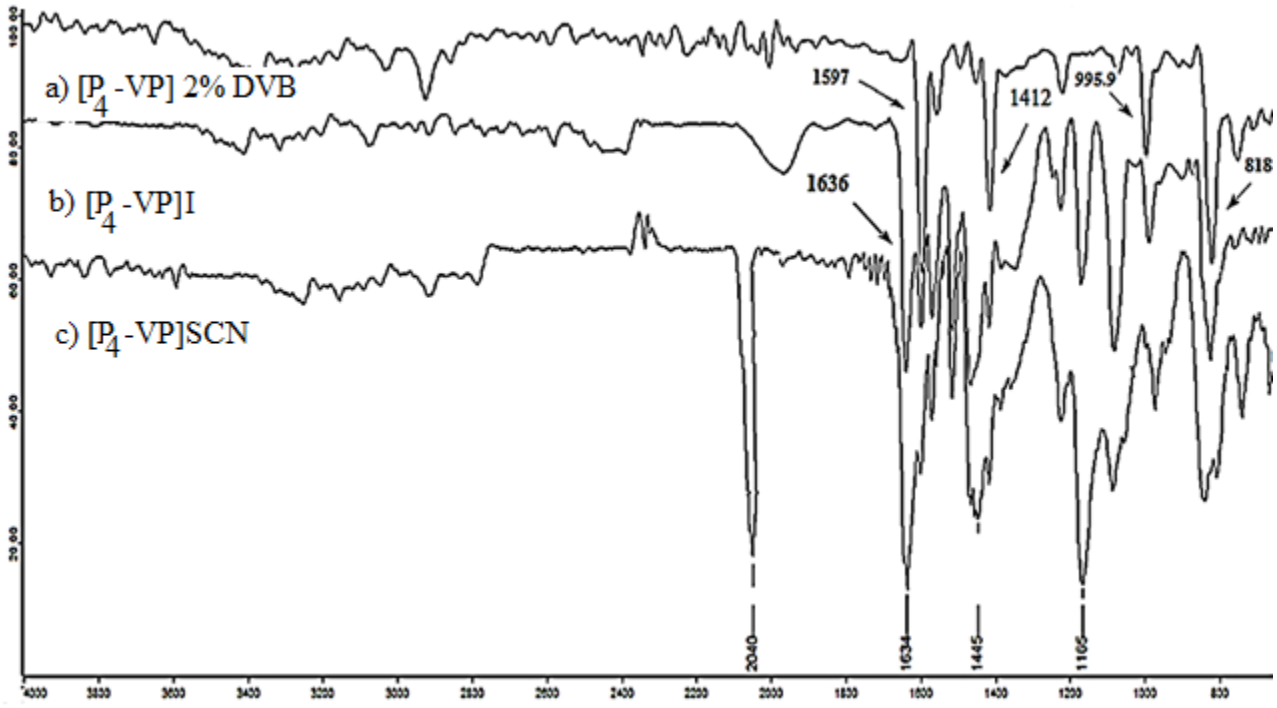


Figure 1: The FT-IR spectra of [P_4-VP] 2% DVB, [P_4-VP]I and [P_4-VP]SCN (a, b and c respectively)

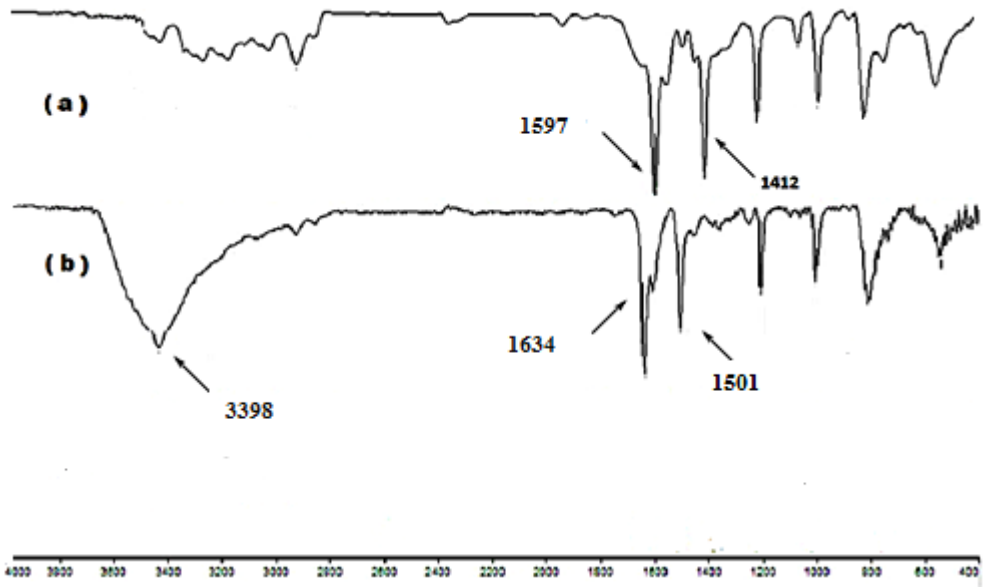


Figure 2: The FT-IR spectra of [P_4-VP] 2% DVB, and [P_4-VP]H_2SO_4 (a and b respectively)