

## Poly (vinylpyrrolidone)-Grafted Silica as a Polymeric Cosolvent Catalyst for Organic Transformations in Organic and Aqueous Media

S. Ghasemi\*, B. Tamami, R. Teymoori, and H. Allahyari

*Department of Chemistry, Faculty of Sciences, Shiraz University, Shiraz 7194684795, Islamic Republic of Iran*

Received: 20 April 2015 / Revised: 28 July 2015 / Accepted: 10 August 2015

### Abstract

Poly (vinylpyrrolidone)-grafted silica as an organic-inorganic hybrid material was used as an effective heterogeneous polymeric cosolvent catalyst in organic reactions. This modified silica catalyzed nucleophilic displacement of alkyl halides for easy preparation of alkyl thiocyanates, alkyl cyanides, alkyl azides and alkyl aryl ethers. Furthermore, the catalyst was applied for the conversion of epoxides to thiranes, thiocyanohydrins and azidohydrins. These reactions were performed in acetonitrile and aqueous media to produce the corresponding products in high yields and short reaction times. The catalyst can be recovered and reused several times.

**Keywords:** Polymeric cosolvent; Poly (vinylpyrrolidone); Nucleophilic substitution reactions; Ring opening of epoxides.

### Introduction

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis have posed a serious threat to the environment. Consequently methods that successfully minimize the use of organic solvents are the focus of much attention. One of the recently developed methods is to use water as solvent for organic reactions [1, 2]. Unfortunately, its use is limited by the low solubility of organic compounds in aqueous media. One of the most important strategies to overcome this limitation in using water, in order to expand the scope of water-based organic synthesis, has been the utilization of phase transfer catalysts (PTC) such as organic cosolvents especially in biological media [3-5].

It is well known that low molecular weight organic

cosolvents have been used as effective polar PTC for promoting organic reactions [6-8]. Much research has also been done on the preparation of heterogeneous polymeric cosolvent catalysts to be used in organic reactions [9-11]. By virtue of their insolubility, such materials would be particularly attractive since they can be recovered by filtration and used again.

Nucleophilic substitution reactions of different nucleophiles on alkyl halides in the presence of phase transfer catalysts are important and well-studied reactions in organic synthesis. Many papers on PTC and polymeric cosolvent assisted nucleophilic substitution reactions have been reported [12-15].

Epoxides are one of the most versatile intermediates in organic synthesis and a large variety of reagents are known for the ring opening of these compounds [16, 17]. Their electrophilic reactions with different

\* Corresponding author: Tel: +987136460724; Fax: +987136460788; Email: ghasemis@shirazu.ac.ir

nucleophilic anions have been an interesting subject in organic synthesis. Ring opening of 1, 2-epoxides are often carried out under either alkaline or acidic conditions and several different methods have been devised for ring opening of epoxides in the presence of different nucleophilic anions [18, 19]. These reactions may require high temperatures and/or long reaction times, and side reactions such as isomerizations, epimerization and rearrangements may occur in these systems. Ring opening of epoxides in the presence of different homogenous and heterogeneous PTCs such as organic cosolvents have also been reported [20-23].

Furthermore, conversion of epoxides to thiranes is another important organic transformation in organic synthesis. For this purpose several sulfurated agents in the presence of different Lewis acids have usually been used [24]. Preparation of thiranes using cosolvents and polymeric cosolvents has also been reported as a new strategy especially in aqueous media [25].

In continuation of our previous studies on the introduction of polymeric phase transfer catalyst based on modified polyacrylamide resin as a new polymeric quaternary ammonium salt, poly (vinylamine) (PVA) and poly (allylamine) (PAA) [26-28], herein, we report poly (vinylpyrrolidone)-grafted silica as a polymeric cosolvent catalyst. Using polymer grafted silica as a heterogeneous phase transfer catalyst instead of polymeric PTCs have some advantageous. They are environmentally friendly, have excellent stability (mechanical, chemical and thermal), good accessibility and good dispersion of catalytic sites. The efficiency of this heterogeneous cosolvent catalyst investigated in different organic reactions such as nucleophilic substitution reactions of alkyl halides with different nucleophiles, ring opening of epoxides and their conversions to thiranes in organic and aqueous media.

## Materials and Methods

### General information

Substrates were purchased from Fluka and Merck Companies. Aminopropyl silica gel with an average particle size of 0.015-0.035 mm (>400 mesh ASTA) supplied by Fluka. All products were characterized by comparison of their FT-IR and NMR spectra and physical data with those reported in the literature. All yields refer to the isolated products. Progress of reactions was followed by TLC on silica-gel Polygram SIL/UV 254 plates or by GLC on Shimadzu GC 14-A instrument with hydrogen flame ionization detector. FT-IR spectra were run on a Shimadzu FT-IR-8300 spectrophotometer. <sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance DPX instrument (250

MHz) in CDCl<sub>3</sub>. TGA thermograms were recorded on an instrument of Perkin Elmer with N<sub>2</sub> carrier gas and the rate of temperature change of 20 °C/min was used.

### *Preparation of the polymeric cosolvent catalyst*

Catalyst was prepared according to our previous report [29]. Acrylamidopropylsilica was prepared by the reaction between aminopropylsilica (AMPS) and acryloyl chloride according to a previous procedure [30]. Then to a suspension of acrylamidopropylsilica (2.0 g) in fresh 1-vinyl-2-pyrrolidone (4 mL), recrystallized benzoyl peroxide (0.05 g) was added in a 10 mL sealed tube and heated at 90 °C in an oven for 15 h. The product was soxhlet-extracted with CHCl<sub>3</sub> to remove homopolymer and then washed and dried. The amount of poly (vinylpyrrolidone) grafted silica was determined using TGA by measuring the weight loss upon heating the modified silica particles in a nitrogen atmosphere. It was approximately 1.9 mmol PVP/g.

### *Preparation of alkyl thiocyanates, alkyl cyanides, alkyl azides and alkyl aryl ethers*

To a mixture of alkyl halide (1.0 mmol) and NaM (5.0 mmol) (M=SCN, CN, N<sub>3</sub>) in H<sub>2</sub>O (10 mL) was added poly (vinylpyrrolidone)-grafted silica (0.1 mmol, 0.05 g) as a polymeric cosolvent catalyst. The suspension was stirred under reflux condition for the lengths of time. [For the preparation of alkyl aryl ethers, polymeric catalyst (0.1 mmol, 0.05 g) was added to a mixture of alkyl halides (1.0 mmol) and phenol (5.0 mmol) in aqueous NaOH solution (5%, 10 mL)]. On completion of the reaction determined by TLC, using *n*-hexane/ethyl acetate (7:3) as eluent and/or GC, the polymeric catalyst was removed by filtration. The product was obtained upon extraction with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and the pure product was obtained upon evaporation of the solvent. Characterization of products was performed by comparison of their FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and physical data with those of the authentic samples.

### *Preparation of thiocyanohydrins and azidohydrins from epoxides*

To a mixture of epoxides (1.0 mmol) and NaM (M=SCN (3.0 mmol) and N<sub>3</sub> (5.0 mmol)) in CH<sub>3</sub>CN (20 mL) was added poly (vinylpyrrolidone)-grafted silica (0.06 mmol, 0.03 g) as a polymeric cosolvent catalyst. The suspension was stirred under reflux condition for the lengths of time. After completion of the reaction determined by TLC, using *n*-hexane/ethyl acetate (7:3) as eluent and/or GC, polymeric catalyst and excess of salt were removed by filtration. The organic solvent was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The corresponding pure products were obtained upon evaporation of the solvent.

Characterization of products was performed as mentioned above.

## *Preparation of thiranes from epoxides*

To a mixture of epoxides (1.0 mmol), NaSCN (3.0 mmol, 0.23 g) and NaOH (1.5 mmol, 0.06 g) in H<sub>2</sub>O (10 mL), was added poly (vinylpyrrolidone)-grafted silica (0.03 mmol, 0.016 g) as a polymeric cosolvent catalyst. The suspension was stirred at room temperature for the length of time. After completion of the reaction, the procedure outlined in section 2.3 was followed.

### *Reuse of the catalyst*

After completion of the following reactions, the catalyst was isolated by filtration. Then, the spent polymeric catalyst from different experiments was washed with water, methanol and ether and dried overnight in vacuum oven. The resulting solid catalyst was charged into another batch for repeating cycles.

## Results and Discussion

Solvents and cosolvents are one of the widely used PTCs for accelerating phase-separated reactions. Whereas, these catalysts are generally not recovered and lead to tedious work-up procedure, the concept of heterogeneous catalysis has been introduced to overcome these problems. In this regard the design of synthetic polymeric supports which are compatible with both aqueous and organic phases such as polyacrylamide and polyvinylpyrrolidone is significant research area.

Polyvinylpyrrolidone grafted onto silica particles for surface modification has been previously presented

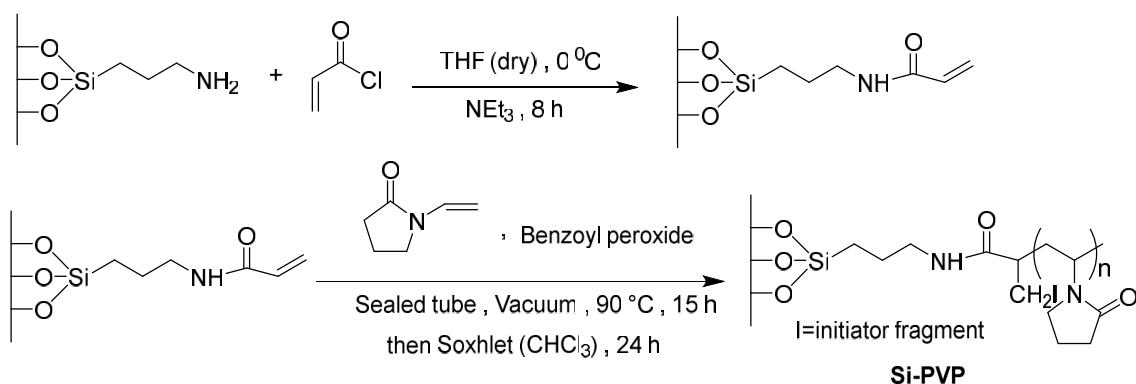
[31]. In this study, we report a catalytic system based of poly (vinylpyrrolidone)-grafted silica as an efficient polymeric cosolvent catalyst. Efficiency of the catalyst was investigated in different organic transformations in aqueous and organic media.

The polymeric cosolvent catalyst was designed by the sequence of reactions given in Scheme 1.

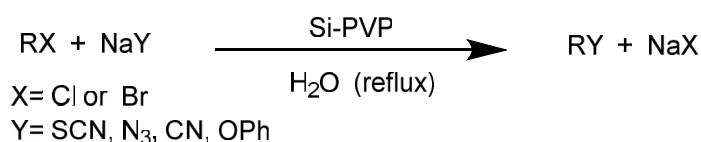
Acrylamidopropylsilica was prepared by reaction between aminopropylsilica (AMPS) and acryloyl chloride according to previous procedure [30]. The FT-IR spectrum of AMPS showed a broad band at 1050–1200 cm<sup>-1</sup> due to SiO and at 3250 cm<sup>-1</sup> corresponding to NH<sub>2</sub> (Figure 1A). In FT-IR spectrum of acrylamidopropylsilica, absorption frequencies of amide group appeared at 1558, and 1662 cm<sup>-1</sup> and double bond at 1627 cm<sup>-1</sup> (Figure 1 B). The appearance of these bands suggests that the reaction between amine groups on the surface of the AMPS and acryloyl chloride have occurred successfully. The free-radical graft polymerization of vinylpyrrolidone onto silica particles was performed using benzoyl peroxide as initiator (Scheme 1). FT-IR spectrum of poly(vinylpyrrolidone)-grafted silica shows the characteristic band of N-C=O at 1670 cm<sup>-1</sup> (Figure 1 C). The amount of grafted poly(vinylpyrrolidone) onto silica was determined by thermogravimetric analysis (TGA) to be 1.9 mmol/g (5.8% water and 20.1% PVP).

The synthetic utility of this modified silica was studied by conversion of alkyl halides to their corresponding thiocyanates, cyanides, azides and alkyl aryl ethers (Scheme 2).

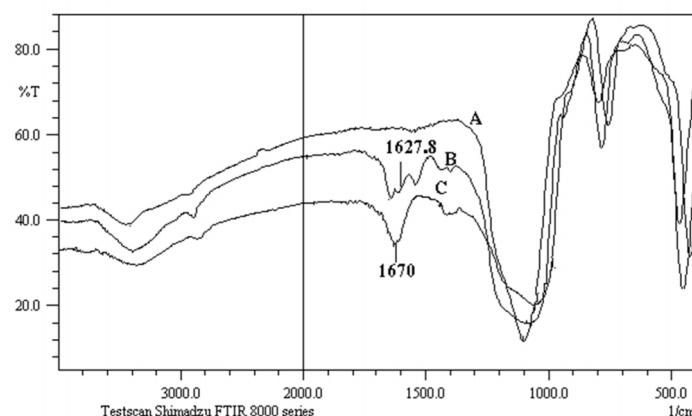
Short reaction times with good to excellent yields



**Scheme 1.** Preparation of poly(vinylpyrrolidone)-grafted silica



**Scheme 2.** Nucleophilic substitution reactions of alkyl halides in the presence of poly (vinylpyrrolidone)-grafted silica



**Figure 1.** FT-IR spectra of (A) aminopropylsilica (B) acrylamidopropylsilica (C) poly (vinylpyrrolidone)-grafted silica

express the effectiveness of the catalyst in accelerating the reactions. The effects of the solvent and molar ratio

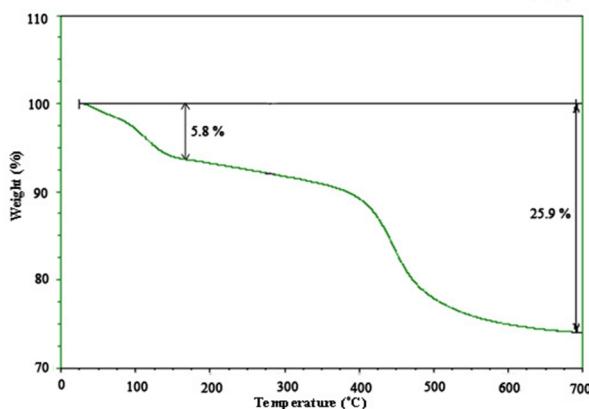
of the catalyst to substrate on the substitution of alkyl halides were investigated. The reaction was carried out

**Table 1.** Substitution of alkyl halides with nucleophiles in the presence of poly (vinylpyrrolidone)-grafted silica in H<sub>2</sub>O<sup>a</sup>

No	Substrates (RX)	Time				Yields (%) <sup>b</sup>			
		SCN <sup>-</sup>	CN <sup>-</sup>	N <sub>3</sub> <sup>-</sup>	PhO <sup>-</sup>	SCN <sup>-</sup>	CN <sup>-</sup>	N <sub>3</sub> <sup>-</sup>	PhO <sup>-</sup>
1		8 min	40 min	30 min	5 min	95	93	90	93
2		15 min	90 min	45 min	10 min	90	90	90	90
3		8 min	40 min	30 min	5 min	95	95	95	90
4		15 min	2 h	45 min	10 min	90	90	97	85
5		20 min	70 min	50 min	20 min	93	80	95	90
6		1 h	1 h	60 min	5 h	95 (85,15) <sup>c</sup>	90	95	-
7		17 h	-	-	2 h	75	-	-	92
8		16 h	-	-	2 h	70	-	-	85
9		15 h	-	-	1 h	70	-	-	90
10		10 h	-	-	1.5 h	65	-	-	80
11		12 h	-	-	2 h	75	-	-	100 <sup>d</sup>
12		12 h	-	-	3.5 h	80	-	-	70 (80,20) <sup>e</sup>

<sup>a</sup> All of the reactions were carried out under reflux condition. Molar ratio of poly (vinylpyrrolidone)-grafted silica to alkyl halide was 0.1:1;

<sup>b</sup> All products are obtained after 100% conversion of substrates and yields refer to the isolated products; <sup>c</sup> Structures and regiochemical ratios determined for the products by <sup>13</sup>C-NMR. <sup>d</sup> 100% conversion to cyclohexene (elimination product) by GC; <sup>e</sup> 70% conversion include substitution product (80%) and elimination product (20%) by GC.



**Figure 2.** Thermogravimetric analysis (TGA) of poly (vinylpyrrolidone)-grafted silica

in different solvents such as EtOAc, THF, *n*-hexane, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, H<sub>2</sub>O, and CH<sub>3</sub>CN. Acetonitrile and water proved to be the best due to the polar nature of the catalyst and its compatibility with both organic and aqueous phases. Thus, we choose water as a green and cheap media. Molar ratio of the polymeric catalyst to alkyl halide was optimized for each nucleophile in water and was found to be 0.1:1.

The corresponding alkyl thiocyanates were obtained in good to excellent yields in water without the formation of any alkyl isothiocyanates except in the case of Ph<sub>3</sub>CCl (Table 1, entry 6). The characteristic <sup>13</sup>C-NMR and FT-IR absorption bands for thiocyanates and isothiocyanates appeared at about 111 ppm, 2160 cm<sup>-1</sup> (sharp), and 132 ppm, 1950-2100 cm<sup>-1</sup> (broad) respectively.

Conversion of alkyl halides to alkyl cyanides and alkyl azides were obtained in good to excellent yield in water respectively using polymeric cosolvent catalyst. Benzylic alkyl halides were reacted readily with cyanide and azide ions, but conversion of aliphatic substrates to their corresponding products was very slowly and are not complete in acceptable times (Table 1, entry 7-12). This is probably due to the lower nucleophilicity of

cyanide and azide ion compared to thiocyanide.

The reaction of different alkyl halides with sodium phenoxide which is produced *in situ* during the reaction of phenol with aqueous solution of sodium hydroxide was performed effectively in high yields and in a short reaction time in aqueous media (Table 1). O-Alkylation has been predominated entirely in these reactions and no C-alkylation product was observed. Primary alkyl halides give their corresponding ethers successfully, but secondary alkyl halides give also elimination product. Cyclohexyl bromide gives elimination product entirely (Table 1, entry 11) and cyclopentyl bromide gives a mixture of substitution and elimination products (Table 1, entry 12). Tertiary alkyl halide failed to react due to the steric hindrance (Table 1, entry 6).

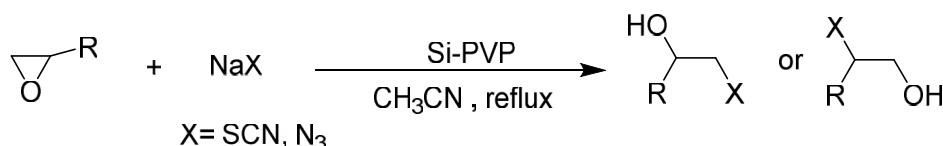
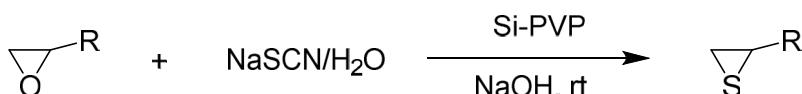
In order to get an insight into the role of poly (vinylpyrrolidone)-grafted silica as a polymeric cosolvent catalyst in this type of transformation, a series of reactions were performed on *p*-nitrobenzyl chloride with NaN<sub>3</sub> in the presence of catalysts A-E [silica gel (A), aminopropyl silica gel (B), acrylamidopropylsilica gel (C), poly (vinylpyrrolidone) (D), and poly (vinylpyrrolidone)-grafted silica (E)] (Table 2). Obviously, in the absence of any catalyst reaction

**Table 2.** Comparison the efficiency of different catalysts on the reaction of *p*-nitrobenzyl chloride with NaN<sub>3</sub> in H<sub>2</sub>O using different kinds of catalysts

Entry	Catalyst <sup>a</sup>	Time	Conversion (%) <sup>b</sup>
1	-	48 h	40
2	A	10 h	100
3	B	10 h	100
4	C	9 h	100
5	D	8 h	100
6	E	50 min	100

<sup>a</sup> The types of catalysts were: silica gel (A), aminopropyl silica gel (B), acrylamidopropylsilica gel (C), poly (vinylpyrrolidone) (D), and poly (vinylpyrrolidone)-grafted silica (E);

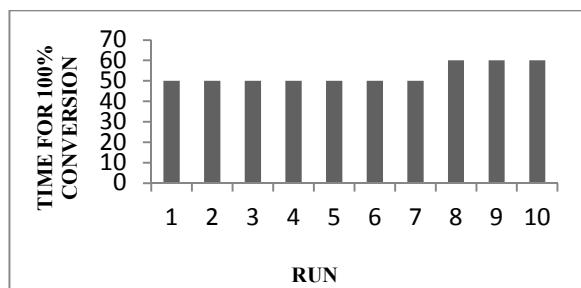
<sup>b</sup> Conversion based on the *p*-nitrobenzyl chloride.

**Scheme 3.** Ring opening of epoxides in the presence of poly (vinylpyrrolidone)-grafted silica**Scheme 4.** Conversion of epoxides to thiranes in the presence of poly (vinylpyrrolidone)-grafted silica

occurred with very low speed (Table 2, entry 1). However, the reaction proceeded in the presence of all of these five catalysts; the rate of reaction was highest in the case of poly (vinylpyrrolidone)-grafted silica (E) (Table 2, entry 6). It may be due to the availability and accessibility of the poly (vinylpyrrolidone) moiety because of grafting on the surface of silica. All of these experimental facts lead us to believe that poly (vinylpyrrolidone)-grafted silica (E) is a good catalyst for nucleophilic substitution reactions. It seems that with this catalyst the reaction proceeds smoothly in the vicinity of the catalyst.

Isolation of the supported catalyst was easily performed by filtration. The resulting isolated catalyst was used for the reaction of *p*-nitrobenzyl chloride with NaN<sub>3</sub> in H<sub>2</sub>O. This catalyst was used successfully in ten subsequent cycles without considerable loss in its efficiency. The time for 100% conversion of *p*-nitrobenzyl chloride to *p*-nitrobenzyl azide was reduced from 50 min to 60 min only after seventh run (Figure 3). The FT-IR spectrum of the used catalyst was found to be the same as the original one and can be kept for months.

Furthermore, the synthetic utility of this modified silica was studied by conversion of epoxides to their corresponding thiocyanohydrins and azidohydrins respectively (Scheme 3).

**Figure 3.** Reusability of poly (vinylpyrrolidone)-grafted silica in the reaction of *p*-nitrobenzyl chloride with NaN<sub>3</sub> in H<sub>2</sub>O

The effects of the solvent and molar ratio of the catalyst on the ring opening of epoxides were investigated. The reaction was carried out in different solvents such as THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, EtOH, H<sub>2</sub>O, and CH<sub>3</sub>CN under reflux condition for conversion of styrene oxide to thiocyanohydrin and azidohydrin. Acetonitrile proved to be the best solvent. Molar ratio of the polymeric catalyst to the substrate was optimized and was found to be 0.06:1. By employing optimized condition, the reaction of different epoxides to thiocyanohydrins and azidohydrins was performed effectively in high yields and in a short reaction time in acetonitrile (Table 3). Except for the reaction of styrene oxide which give a small percentage of the other regioisomer (Table 3, entry 1), the reaction of other epoxides were characterized to be highly regioselective and only one isomer was obtained.

Moreover, conversion of epoxides to thiranes was performed with aqueous sodium thiocyanate in H<sub>2</sub>O using NaOH at room temperature in the presence of this polymeric cosolvent catalyst (Scheme 4).

Molar ratio of the polymeric catalyst to the substrate was optimized for this reaction and was found to be 0.03:1. Under this condition, different oxiranes converted to their corresponding thiranes readily. The results are tabulated in Table 4.

### Conclusion

In conclusion, a polymeric cosolvent catalyst based on poly (vinylpyrrolidone)-grafted silica was designed and applied in different organic transformations. Utilizing this catalyst is cheap due to its recovery from reaction mixture and its preparation is easy. Short reaction times, high yields, easy purification of the products, recyclability of the catalyst and use of water as a green reaction media are other characteristic of the process.

**Table 3.** Conversion of epoxides to thiocyanohydrins and azidohydrins in the presence of poly (vinylpyrrolidone)-grafted silica in  $\text{CH}_3\text{CN}$ <sup>a</sup>

No	Substrates	Products	Time (min)		Yield (%) <sup>b</sup>	
			SCN <sup>-</sup>	N <sub>3</sub> <sup>-</sup>	SCN <sup>-</sup>	N <sub>3</sub> <sup>-</sup>
1			180	240	(75+10)	(80+10)
2			480	570	90	90
3			300	600	80	85
4			120	420	75	75
5			240	330	90	90
6			150	360	85	85
7			120	210	80	90
8			150	270	85	85

<sup>a</sup> All of the reactions were carried out under reflux condition. Molar ratio of poly (vinylpyrrolidone)-grafted silica to epoxide was 0.06:1; <sup>b</sup> All products are obtained after 100% conversion and yields refer to the isolated products.

**Table 4.** Conversion of epoxides to thiranes in the presence of poly (vinylpyrrolidone)-grafted silica using NaSCN/NaOH in  $\text{H}_2\text{O}$ <sup>a</sup>

No	Substrates	Products	Time (min)	Yield (%) <sup>b</sup>
1			30	90
2			150	87
3			120	90
4			240	90
5			105	89
6			120	86
7			150	90
8			180	90

<sup>a</sup> All of the reactions were carried out under room temperature. Molar ratio of poly (vinylpyrrolidone)-grafted silica to alkyl halides was 0.03:1;

<sup>b</sup> All products are obtained after 100% conversion and yields refer to the isolated products.

### Acknowledgment

The authors gratefully acknowledge the partial support of this study by Shiraz University Research Council.

### References

1. (a) Li C. J. Organic reactions in aqueous media-with a focus on carbon-carbon bond formation. *Chem. Rev.* **93**: 2023-2035 (1993).
- (b) Lindstrom U. M. Stereoselective organic reactions in water. *Chem. Rev.* **102**: 2751-2772 (2002).
2. (a) Li C. J., and Chen L. Organic chemistry in water. *Chem. Soc. Rev.* **35**: 68-82 (2006).
- (b) Dicks A. P. A review of aqueous organic reactions for the undergraduate teaching laboratory. *Green Chem. Lett. Rev.* **2**: 9-21 (2009).
3. Yang R. L., Li N., and Zong, M. H. Using ionic liquid cosolvents to improve enzymatic synthesis of arylalkyl  $\beta$ -d-glucopyranosides. *J. Mol. Catal. B-Enzym.* **74**: 24-28 (2012).
4. Gonzalo G., Rodríguez C., Rioz-Martínez A., and Gotor V. Improvement of the biocatalytic properties of one phenylacetone monooxygenase mutant in hydrophilic organic solvents. *Enzyme Microb. Tech.* **50**: 43-49 (2012).
5. Kundu A., Dasmandal S., Majumdar T., and Mahapatram A. Effect of cosolvents in the presence of sodium dodecyl sulfate micelles on the rate of alkaline hydrolysis of tris(2,2'-bipyridine)iron(II) complex. *Colloid Surface A*, **452**: 148-153 (2014).
6. Mikolakozik M., Grejszczak S., Zatorski A., Montanari F., and Cinquini M.  $\alpha$ -Phosphoryl sulphoxides and sulphones: New catalysts in two-phase alkylation of ketones. *Tetrahedron Lett.* **37**: 3757-3760 (1975).
7. Fowleski A. F., and Whitesides G. M. SN2 displacements and reductive coupling of ketones with olefins in N, N-diethylacetamide and N-ethylpyrrolidone. *J. Org. Chem.* **44**: 2369-2377 (1979).
8. Landini D., and Maia A. Phase transfer catalysis (PTC): search for alternative organic solvents, even environmentally benign. *J. Mol. Catal. A: Chem.* **204**: 235-243 (2003).
9. Regen S. L., Mehrota A., and Singh A. Poly(acrylamide)-based solid-phase cosolvents. *J. Org. Chem.* **46**: 2182-2184 (1981).
10. Mahdavi H., Amani J., and Rahimdoost N. Triphenylphosphine oxide on non-cross-linked maleimide-styrene copolymer support: As a novel stable phase transfer catalyst. *Catal. Commun.* **9**: 2532-2535 (2008).
11. (a) Debnath K., Pathak S., and Pramanik A. Facile synthesis of ninhydrin and isatin based hydrazones in water using PEG-OSO<sub>3</sub>H as a highly efficient and homogeneous polymeric acid-surfactant combined catalyst. *Tetrahedron Lett.* **54**: 4110-4115 (2013).
- (b) Maia A., Landini D., Leska B., and Schroeder G. Silicon polypodands: a new class of efficient solid-liquid phase-transfer catalysts. *Tetrahedron*, **60**: 10111-10115 (2004).
12. Jadhav V. H., Jeong H. J., Lim S. T., Sohn M. H., Song C. E., and Kim D. W. Polymer-supported oligoethylene glycols as heterogeneous multifunctional catalysts for nucleophilic substitution. *Tetrahedron*, **69**: 3577-3583 (2013).
13. Jia Z., Zhen T., Zhang X., and Gu Q. Preparation of phase-transfer catalytic porous membrane by  $\gamma$ -ray irradiation grafting and its application in nucleophilic substitution reaction. *J. Membrane Sci.* **448**: 74-80 (2013).
14. Benaglia M., Cinquini M., Cozzi F., and Tocco G. Synthesis of a poly(ethylene glycol)-supported tetrakis ammonium salt: a recyclable phase-transfer catalyst of improved catalytic efficiency. *Tetrahedron Lett.* **43**: 3391-3393 (2002).
15. (a) Davarpanah J., and Kiasat A. R. Nanomagnetic double-charged diazonobiacyclo [2.2.2] octane dichloride silica as a novel nanomagnetic phase-transfer catalyst for the aqueous synthesis of benzyl acetates and thiocyanates. *Catal. Commun.* **42**: 98-103 (2013).
- (b) Jadhav V. H., Kim J. Y., Chi D. Y., Lee S., and Kim D. W. Organocatalysis of nucleophilic substitution reactions by the combined effects of two promoters fused in a molecule: oligoethylene glycol substituted imidazolium salts. *Tetrahedron*, **70**: 533-542 (2014).
- (c) Łęska B., Pankiewicz R., Schroeder G., and Maia A. Application of a new class  $\beta$ -podands in solid-liquid phase transfer catalysis. *J. Mol. Catal. A: Chem.* **269**: 141-148 (2007).
16. (a) Firouzabadi H., Iranpoor N. Jafari A. A. and Makarem S. Aluminumdodecatungstophosphate (AlPW<sub>12</sub>O<sub>40</sub>) as a reusable Lewis acid catalyst: Facile regioselective ring opening of epoxides with alcohols, acetic acid and thiols. *J. Mol. Catal. A: Chem.* **250**: 237-242 (2006).
- (b) Firouzabadi H., Iranpoor N., and khoshnood A. Aluminum tris (dodecyl sulfate) trihydrate Al(DS)<sub>3</sub>·3H<sub>2</sub>O as an efficient Lewis acid-surfactant-combined catalyst for organic reactions in water: Efficient conversion of epoxides to thiranes and to amino alcohols at room temperature. *J. Mol. Catal. A: Chem.* **274**: 109-115 (2007).
17. Sharghi H., Nasseri M. A., and Niknam Kh. Phenol-containing macrocyclic diamides as new catalysts in the highly regioselective conversion of epoxides to  $\beta$ -hydroxy thiocyanates. *J. Org. Chem.* **66**: 7287-7293 (2001).
18. Trikittiwong P., Sukpirom N., and Chavasiri W. Regioselective epoxide ring opening mediated by iron oxide-pillared clay. *J. Mol. Catal. A: Chem.* **378**: 76-81 (2013).
19. Shah A. K., Prathap K. J., Kumar M., Abdi S. H. R., Kureshy R. I., Khan N. H., and Bajaj H. C. Fe(OH)<sub>3</sub> nano solid material: An efficient catalyst for regioselective ring opening of aryloxy epoxide with amines under solvent free condition. *Appl. Catal. A: Gen.* **469**: 442-450 (2014).
20. (a) Sharghi H., Salimi Beni A., and Khalifeh R. Synthesis of some novel thioxanthene-fused azacrown ethers and their use as new catalysts in the efficient, mild, and regioselective conversion of epoxides to  $\beta$ -hydroxy thiocyanates with ammonium thiocyanate. *Helv. Chim. Acta*, **90**: 1373-1385 (2007).
- (b) Kiasat A. R., and Zayadi M. Polyethylene glycol

- immobilized on silica gel as a new solid–liquid phase-transfer catalyst for regioselective azidolysis of epoxides in water: An efficient route to 1,2-azido alcohols. *Catal. Commun.* **9**: 2063-2067 (2008).
- (c) Adam F., Appaturi J. N., and Ng E. P., Halide aided synergistic ring opening mechanism of epoxides and their cycloaddition to CO<sub>2</sub> using MCM-41-imidazolium bromide catalyst. *J. Mol. Catal. A: Chem.* **386**: 42-48 (2014).
21. Thomas C., Brut S., and Bibal B. Quaternary ammoniums and a cationic sodium complex as supramolecular catalysts in ring-opening of epoxides by amines. *Tetrahedron*, **70**: 1646-1650 (2014).
22. Lupi V., Albanese D., Landini D., Scaletti D., and Penso M. Synthesis of 2,6-disubstituted morpholines through regioselective oxiranes ring opening by tosylamide under PTC conditions. *Tetrahedron*, **60**: 11709-11718 (2004).
23. Mombani Godajdar B., Kiasat A. R., and Mahmoodi Hashemi M. Synthesis, characterization and application of magnetic room temperature dicationic ionic liquid as an efficient catalyst for the preparation of 1,2-azidoalcohols. *J. Mol. Liq.* **183**:14-19 (2013).
24. (a) Bandgar B. P., Patil A. V., Kamble V. T., and Totre J. V. An efficient synthesis of thiiranes from oxiranes using fluoroboric acid adsorbed on silica gel (HBF<sub>4</sub>-SiO<sub>2</sub>) as a catalyst under mild conditions in the absence of solvent. *J. Mol. Catal. A: Chem.* **273**: 114-117 (2007).  
 (b) Bandgar B. P., Joshi N. S., and Kamble V. T. 2,4,6 Trichloro-1,3,5-triazine catalyzed synthesis of thiiranes from oxiranes under solvent-free and mild conditions. *Tetrahedron Lett.* **47**: 4775-4777 (2006).
- 25.(a) Das B., Reddy V. S., and Krishnaiah M. An efficient catalyst-free synthesis of thiiranes from oxiranes using polyethylene glycol as the reaction medium. *Tetrahedron Lett.* **47**: 8471-8473 (2006).
- (b) Surendra K., Srilakshmi Krishnaveni N., and Rama Rao K. A new and efficient method for the synthesis of thiiranes from oxirane-β-cyclodextrin complexes and thiourea in water. *Tetrahedron Lett.* **45**: 6523-6526 (2004).
26. Tamami B., and Ghasemi S. Nucleophilic substitution reactions using polyacrylamide-based phase transfer catalyst in organic and aqueous media. *J. Iran. Chem. Soc.* **5**: 26-32 (2008).
27. Tamami B., and Kolahdoozan M. Synthesis of thiiranes from oxiranes in water using polymeric cosolvents. *Tetrahedron Lett.* **45**: 1535-1537 (2004).
28. Mahdavi H., and Tamami B. Synthesis of 2-nitroalcohols from epoxides using quaternized amino functionalized cross-linked polyacrylamide as a new polymeric phase transfer catalyst. *React. Funct. Polym.* **64**: 179-185 (2005).
29. Tamami B., Allahyari H., Ghasemi S., and Farjadian F. Palladium nanoparticles supported on poly (N-vinylpyrrolidone)-grafted silica as new recyclable catalyst for Heck cross-coupling reactions. *J. Orgmet. Chem.* **696**: 594-599 (2011).
30. Macquarrie D. J., and Fairfield S. E. The Heck reaction at a silica surface. Functionalisation of simple organo-modified silicas. *J. Mater. Chem.* **7**: 2201-2204 (1997).
31. Chaimberg M., Parnas R., and Cohen Y. Graft polymerization of polyvinylpyrrolidone onto silica. *J. Appl. Polym. Sci.* **37**: 2921-2931 (1989).