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Research Article

A new platform for the post-functionalization of porous polymer under thermal solvent-free conditions; as a highly efficient and recyclable PTC containing nanocavity

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ABSTRACT

In this work, for the first time, functionalized 3D-network polymer was synthesized through thermal solvent-free method. The synthetic steps include (1) the preparation of ionic liquid (1-methyl-3-(trimethoxysilylpropyl) imidazolium choloride) [pmim]Cl, (2) synthesis of the 3D-network polymer based on calix[4]resorcinarene, and finally (3) immobilization of ionic liquid on the synthesize polymer through one-pot solvent-free conditions. The formation of this cationic porous polymer was confirmed by elemental analysis, scanning electron microscopy (SEM), thermal gravimetric analysis (TGA) and derivative thermogravimetric (DTG). Taken together, the results reveal the successful preparation of the efficient and wondrous mesoporous cationic polymer with the simultaneously merged properties of ionic liquid and polymeric matrix on the basis of calix[4]resorcinarene. Therefore, it provides an efficient heterogeneous catalyst for being applied in the catalytic reaction for achieving synthetic goals.

One-pot conditions, thermal solvent-free pathway, easy reaction handling and work up, green and affordable methodology, gaining high yields of product are the most important advantages of the present method for the synthesis of this polymeric heterogeneous catalyst. The recovered catalyst could be used for several times without any significant loss of activity. The unique features of this catalyst such as superior thermal stability, excellent catalytic activity in terms of yield and reaction time, will be potentially important for its applications in industry.

Keywords: Thermal solvent- free conditions; one-pot reaction; polymer supported ionic liquid; phase transfer catalyst

1. Introduction

Over recent years, science and technology are switching their attention toward environmentally green organic processes [1-3]. Since optimization of existing chemical processes together with the development of novel, environmentally friendly processes depend greatly on improvement of catalyst performance; the catalysis has a strong impact on the development of modern sustainable chemistry.

Today phase-transfer catalysis (PTC), has been investigated widespread during recent decades to synthesis various organic compounds through simpler, cleaner and more affordable routes combined with higher yields and reaction rates.

A large number of reactions can’t proceed well in the considered media, because the reactants are not compatible with each other from the points of phase and solubility. As an easy, feasible and cost-effective method to conquer this problem is the use of catalytic amounts of phase-transfer agents and accordingly enhance the reaction efficiency [4-5].

Use of homogenous phase-transfer catalysis (PTC), poses serious problems such as difficulty in the separation and recovery of the catalyst, disposal of the spent catalyst and corrosion problems. Avoiding these problems homogeneous catalysts can be heterogenized by anchoring them onto the surface of solid supports to develop eco-friendly PTC which could be recovered and reused for the next catalytic cycles [6-7].

Recently, solid-support heterogeneous catalysis has drawn great interest in industrial processes owing to their potential advantages over solution-based homogeneous catalysis, such as the easier operation/purification and recycling catalysts from reaction environments which lead to improved processing steps, better process economics, and environmentally friendly manufacturing. However, compared with the similar homogeneous catalysis, the heterogeneous catalysis usually suffered from decreased reactivity owing to the less effective interactions between catalytic centers and reactants. In order to solve this problem, porous materials have been proposed as a new type of solid-support for heterogeneous catalysis with much higher efficiency in catalyst–reactant interactions [8-11]. In this context, inorganic porous materials, such as mesoporous silica and zeolite have received considerable attention. However, defects such as need to expensive organic surfactants or templates and calcinations at high temperature for obtaining opening channels have restricted their widespread practical applications on an industry scale.

Compared with inorganic supports, a new class of porous materials (porous organic polymers) with a cross-linked amorphous organic framework, have emerged as a sustainable catalyst support owing to their advantages in good dispersion of active sites, pore-surface modifiability and the adsorption of reactant molecules on the material surface [12-14]. Moreover, owing to the inherited nature of the organic pores, the cavities of the organic polymers are the best mimic of the chemical environment in the organic solvent-mediated homogeneous catalysis and thus help in the maintenance of the catalyst reactivity. These features, coupled with their biodegradability and green nature, make porous organic polymers attractive materials to organic and industrial chemistry.

Although a variety of POPs have been reported, some of them suffer from one or more defects in their synthetic or functionalization routes and properties including long reaction times, multiple steps for synthesis, functionalization via copolymerization or further post-polymerization under harsh reaction conditions, the use of expensive catalysts, solubility in various solvents, and low thermal and/or chemical stability. Therefore, developing and applying new porous organic polymers for heterogeneous-type catalytic systems, which may quickly move from the laboratory to green industrial plants, have received increased attention.

3D-Network polymer based on calix[4]resorcinarene could be a good candidate for the development of solid-support porous organic polymers because of their simple synthesis and the unique properties such as straightforward functionalization route via post-functionalization without undergoing copolymerization or further postpolymerization, versatile chemical modification (acylation, alkylation and silylation of hydroxyl group and nucleophilic aromatic substitution on the aromatic rings) and high thermal and chemical stability.

To the best of our knowledge, despite its convenient properties and significant potential for functionalization under mild reaction conditions, there have been no reports on the functionalization of this polymeric structure under thermal solvent-free conditions.

Having the above points in mind, as part of our continuing efforts to develop high performance and environmentally friendly procedures for various important reactions and transformations [15-20] and our new interest in the application of the 3D-network porous polymer based on calix[4]resorcinarene for the preparation of biologically important molecules [21-23], herein, we propose, for the first time, the functionalization of polymeric calix[4]resorcinarene *via* covalently anchored ionic liquid under thermal solvent-free conditions and the investigation of its efficiency as phase transfer catalyst for the synthesis of azidohydrins derivatives through the ring opening of various epoxide.

2. Experimental

2.1. General

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies and used without further purification. Products were characterized by physical data, IR, ^{1}H NMR and^{13}C NMR spectra. IR spectra were obtained on a Bomen MB:102 FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker spectrometer at 400 MHz and 100 MHz, respectively, in $CDCl_3$ or dimethyl sulfoxide (DMSO) with tetramethylsilane as an internal standard. Elemental analyses were performed at a Thermo Finnigan Flash EA 1112 CHNS-Analyzer. The polymer morphology was examined by SEM

(LEO-1455VP). Thermal stability of the functionalized polymer was investigated by NETZSCH STA 409 PC/PG under nitrogen atmosphere (rate of $N_2 \approx$ 1Lit/h).

Monitoring of the reactions and the purity determination of the products were accomplished by TLC on silica gel PolyGram SILG/UV 254 plates.

2.2. Synthesis of calix[4]resorcinarene (1)

Calix[4]resorcinarene was prepared according to the literature procedures [24].

2.3. Synthesis of the 3D-network polymer based on calix[4]resorcinarene (2)

To a magnetically stirred mixture of formaldehyde (42 mmol), and the prepared calix[4]resorcinarene (14 mmol), 40 cm^3 NaOH solution (10%) was added dropwise under an inert atmosphere at room temperature. After completion of NaOH addition, the mixture was heated to 90°C and remained at this temperature for 20 h. Then the reaction mixture was cooled down and the resultant gel was washed consecutively with cold water to make sure that excess alkali was removed. In the following, the gel became acidic in treatment with 0.1 M HCl solution. Finally, the resultant solid product was dried at 100°C for 10 h [25].

2.4. Synthesis of novel functionalized polymer (3) through one-step solvent-free chemical modification

The mixture of 12 mmol (3-chloropropyl)trimethoxysilane and 12 mmol of 1-methylimidazole (freshly distilled) was refluxed at 95 °C for 24 h under nitrogen atmosphere. The reaction mixture was cooled down and 1-methyl-3-(trimethylsilylpropyl) imidazolium chloride ([pmim]Cl) (slightly yellow viscous oil) was obtained with 98 % yield. Then, 0.5 g of the synthesized polymer was added to [pmim]Cl. After heating the slurry at 90 °C for 20 h the solid was isolated by filtration. Owing to the solubility of unreacted ([pmim]Cl) in water, the desired cationic polymer was collected by filtration and washed with deionized water several times before drying at 80 °C.

2.5. Determination of the amount of grafted cationic moieties onto polymer

The amount of grafted cationic moieties onto polymer was achieved by elemental analysis. The amount of grafted imidazolium moieties was generally found to be 2.1 mmol per gram of the dry cationic polymer.

2.6. General procedure for the Synthesis of azidohydrin derivatives in the presence of novel phase transfer catalyst (2)

NaN_3 (2 mmol) was added to a mixture of epoxides (1 mmol) and functionalized polymer (0.025 g) in water (1.5 mL). The suspension was magnetically stirred at 60 °C for the lengths of time shown in Table 1. After completion of the reaction as judged by TLC (using *n*-hexane/ ethyl acetate (4:2) as eluent), the catalyst was removed by filtration. The products were obtained upon extraction with ethyl acetate (3×5 mL). The extract was dried over $CaCl_2$, and then solvent was evaporated under high vacuum to give the azidohydrins.

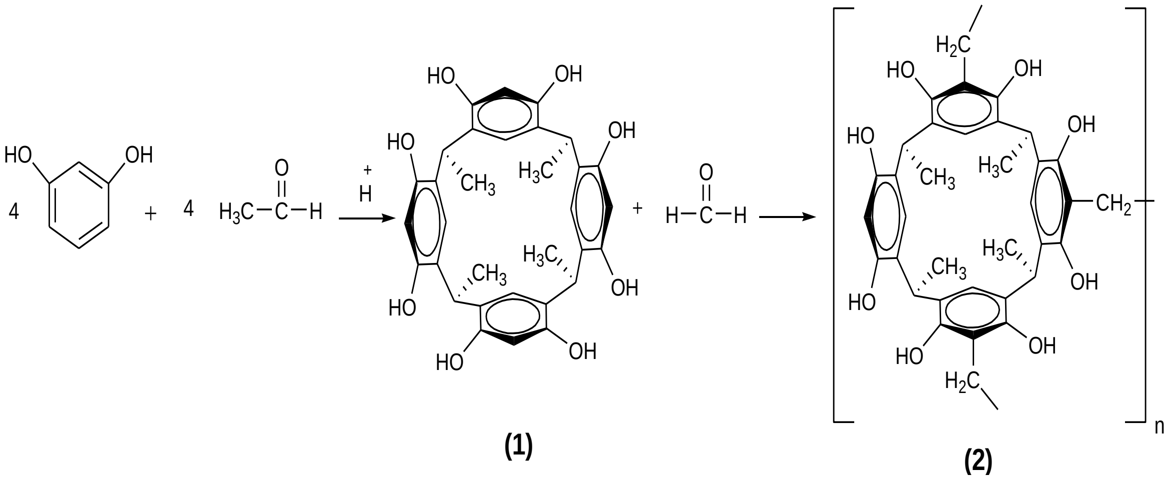
The recovered catalyst was washed with water, ethanol and ethyl acetate, respectively. Then was dried under vacuum and reused for the next reaction.

3. Results and discussion

As stated earlier, the search for more efficient catalytic systems that might combine the advantages of both homogeneous and heterogeneous catalysis is one of the most exciting challenges of modern chemistry. Considering this fact, we have chosen the immobilization of ionic liquid (1-methyl-3-(trimethoxysilylpropyl) imidazolium choloride) [pmim]Cl on to the 3D-network polymer based on calix[4]resorcinarene *via* two post-functionalization steps under one-pot thermal solvent-free conditions.

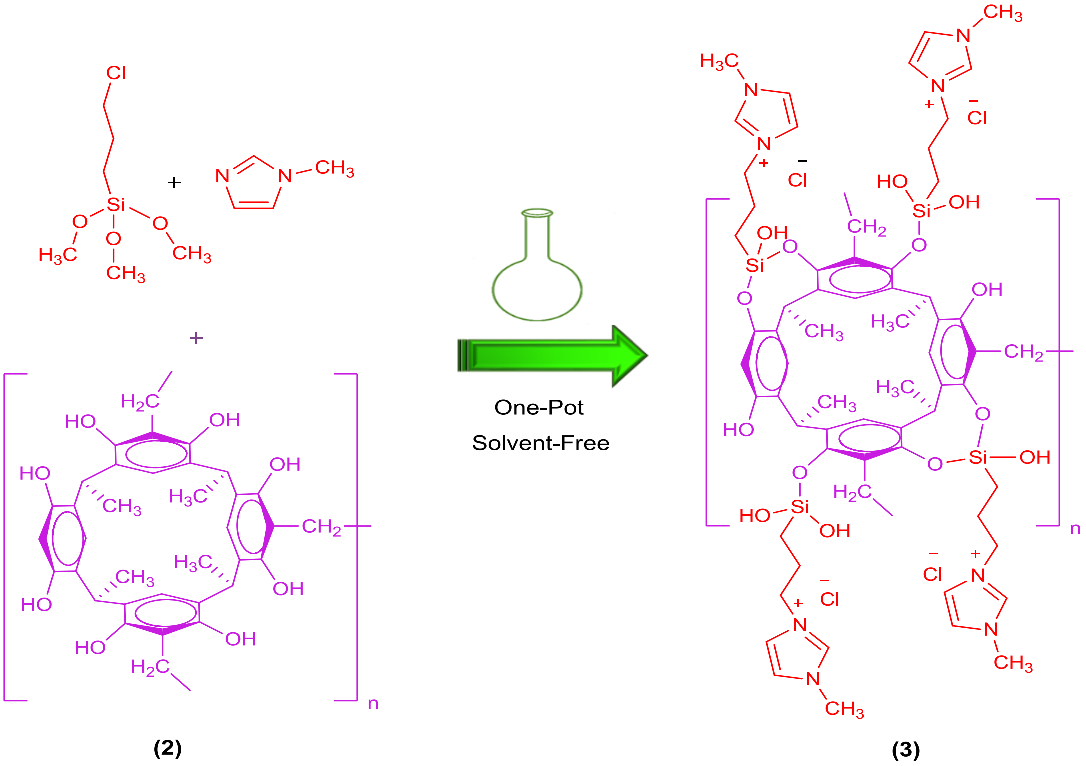
To achieve this objective, the 3D-network polymer **2** was prepared by the reaction of resorcinol and acetaldehyde, followed by polycondensation of calix[4]resorcinarene **1** with formaldehyde [8], the synthesis steps are depicted in Scheme 1.

The structure of compound **1** was established unambiguously from spectroscopic (IR, ^{1}H NMR, ^{13}C NMR) data (See Supplementary Material). Formation of polymer **2** was also confirmed and characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and scanning electron microscope (SEM) [24-26] (Available in Supplementary Material).



Scheme 1 Synthesis of calix[4]resorcinarene (**1**) and the3D-network polymer (**2**).

Subsequently, the prepared polymer **2** was treated with 1-methyl imidazole and (3-chloropropyl) trimethoxysilane to undergo a condensation reaction, yielding cationic polymer **3** in one-pot solvent free conditions (Scheme 2). The loading amount of the cationic moieties on polymer was determined by elemental analysis. The nitrogen analysis of supported IL **3** (N, 5%) indicates that 2.1 mmol of imidazolium moieties was grafted on to the surface of per 1 g of the polymer. The formation of **3** was also confirmed by SEM, TG and DTG analysis.



Scheme 2 Synthesis of cationic polymer (**3**) containing imidazolium moieties through one-step solvent-free chemical modification of (**2**).

In order to gain insight into the morphology of the synthesized polymer **3**, scanning electron microscopy was used (Fig 1).

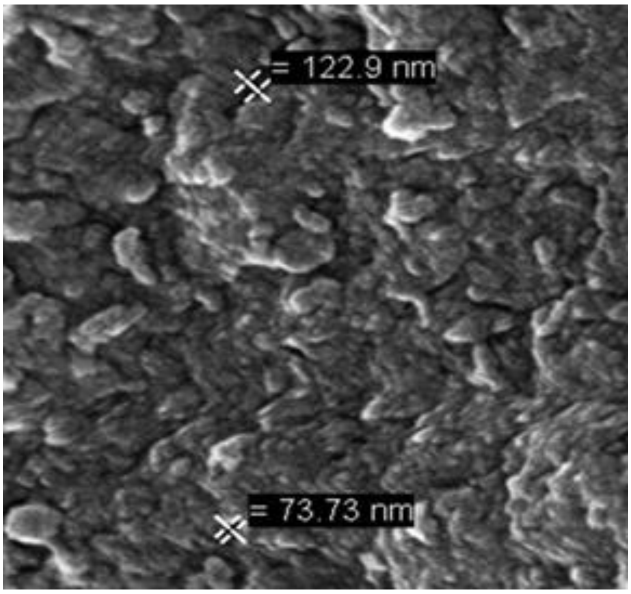


Fig. 1 SEM image of synthesized polymer **3**.

Since the cationic polymer **3** shows smaller pores (about 73-123 nm in diameter) than polymer **2** (300 nm in diameter, See Supplementary Materials), it can be concluded that ILs are successfully grafted to the polymeric backbones.

Thermal behavior of the achieved functionalized polymer **3** was investigated by thermo-gravimetric analysis at a heating rate of 10 °C per minute under nitrogen atmosphere (Fig. 2). The TG curve indicates an initial weight loss of 6% up to 100 °C due to the adsorbed water and organic solvent in polymeric support which is common in the cases of immobilized catalysts onto organic or inorganic supports [27-31].Complete loss of the IL chains is seen in the range of 320-380 °C. Weight loss in the temperature range of 500–800 °C can be assigned to the decomposition of the polymeric support. Thus, the TGA and DTG curves also convey the obvious information that IL chains are successfully grafted to the polymeric backbones.

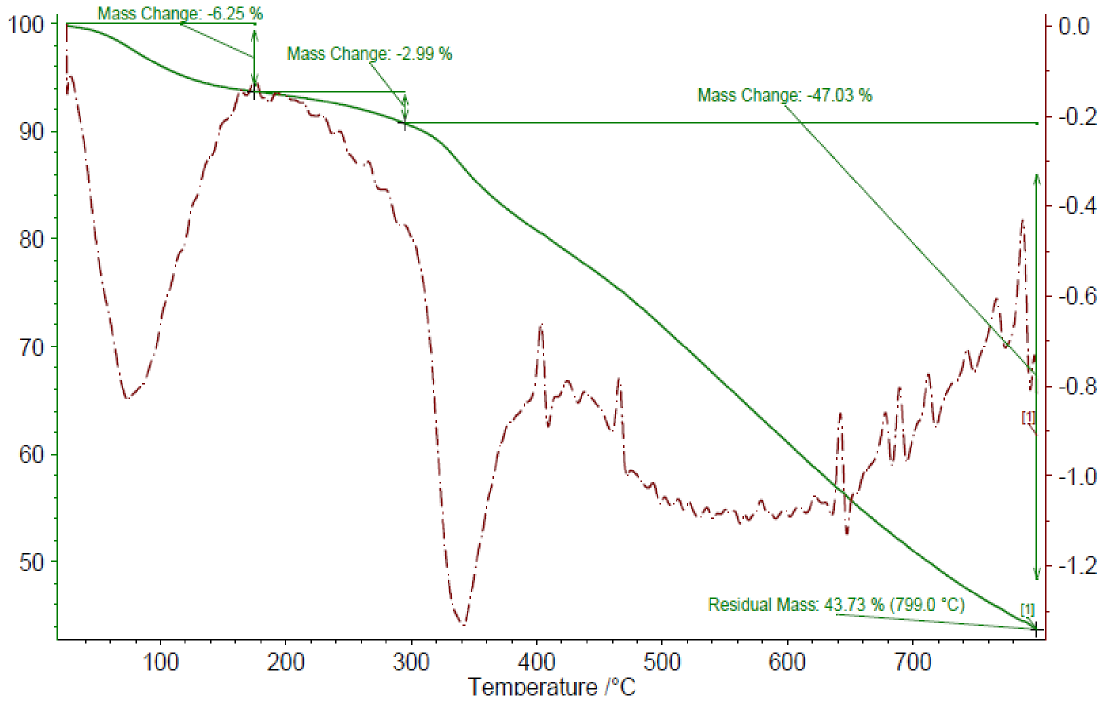


Fig. 2 TGA and DTG curves of cationic polymer **3**.

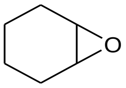
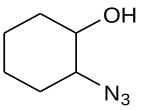
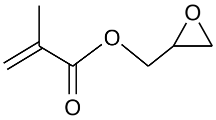
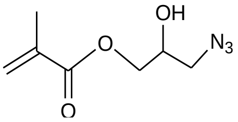
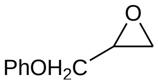
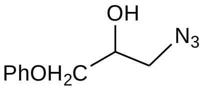
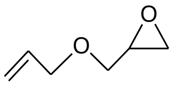
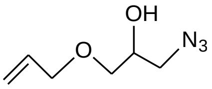
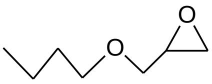
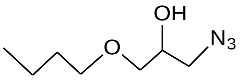
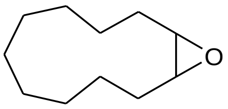
It is noteworthy that, the synthesized cationic polymer (**3**) is effectively insoluble in various solvents, including H_2O, CH_3OH, EtOH, DMSO, DMF, CH_3CN, CH_2Cl_2 and $CHCl_3$.

These features render it suitable for conducting chemical transformations in various reaction media as an efficient heterogeneous catalyst.

In light of the aforementioned points and importance of azidohydrins as precursors in the synthesis of vicinal amino alcohols, carbohydrates, nucleosides, lactames and oxazolines [32-33], we became interested to evaluate the ability of this cationic polymer (**3**) as PTC in nucleophilic substitution reaction of epoxides with sodium azide for the synthesis of these valuable compounds in water.

To develop suitable reaction conditions, 2,3-epoxypropyl methacrylate was chosen as a model compound and parameters including temperature, molar ratio of the reagent/substrate and amount of catalyst were examined in detail. After some experiments, it was found that the use of 2 equiv. of NaN_3 per epoxide in the presence of the catalyst **3** (0.025 g) at 60˚C were the best conditions.

Table 1 Reaction of various epoxides with sodium azide in the present of the representative catalyst in water

Entry	Substrate	Product	Time (min.)	Yield (%)
1			4	95
2			10	96
3			30	81
4			10	87
5			50	85
6		-	360	0

Successful reaction optimization with promising results encouraged us to generalize the scope of this procedure. (Entry 1-5, Table 1).

The reactions of all epoxides with sodium azide were found to be highly regioselective and only one isomer (I) was obtained (Entry 1-5, Table 1). It is noteworthy that no evidence for the formation of diol as by-product was observed. Hence, all products were obtained in pure form without further purification. The structure of products was established unambiguously from spectroscopic (IR, ^{1}HNMR, ^{13}CNMR) data and by direct comparison with authentic samples [26, 34].

The promoting effect of catalyst was definitely confirmed by the reaction of model compound with sodium azide, without adding catalyst or in the presence of the initial calix[4] resorcinarene under optimized reaction conditions. TLC analysis of the reaction mixture did not show completion of the reaction after 8 h [26].

In order to show the merit of this novel catalyst, Table 2 compares our results obtained from the model reaction in the presence of **3** with the same results reported in literature. To our delight, heterogeneous catalyst **3** exhibited significantly higher catalytic activity in terms of the reaction time and amount of catalyst (Entry 1, Table 2).

Table 2 Comparison of azidolysis of model compound with different catalysts in water

Entry	Catalyst	Catalyst (g)	Reagent / Substrate (mmol)	Tem.	Time (h)	Yield (%)
1	**(3)**	0.025	2	60	0.16	96
2	Cationic calix[4]resorcinarenes [35]	0.03	2	70	0.33	94
3	3D-network porous polymer based on calix[4]resorcinarenes [26]	0.1	3	80	1.40	84
4	Dowex-PEG$_{300}$ [34]	0.1	1.2	reflux	1.5	90
5	SiO_2-PEG [36]	0.1	3	reflux	2	90
6	Poly[N-(2-aminoethyl)acrylamido]-trimethyl ammonium iodide [37]	0.2	5	r.t	12	95

Under these results, we expect that this cationic catalyst (**3**) will be a suitable alternative to the existing catalysts.

4. Conclusion

In the present study we disclose a new and fascinating approach for the synthesis of supramolecular imidazolium salts based on polymetic skeleton. A survey of the literatures indicate that, this is the first report on the one-pot solvent-free synthesis of this porous cationic polymer via silylation of hydroxyl groups on the upper rim of calix[4] resorcinarene without the use of acidic or basic catalyst. The reaction procedure is convenient, involving simple experimental procedure and product isolation, thus dispense with expensive chromatographic purification steps. Hence, the procedure opens a novel entry to the convenient synthesis of a number of functionalized porous polymer based on calix[4] resorcinarene.

Following the synthetic strategy, the application of this cationic polymer as PTC for the preparation of azidohydrins was investigated. The catalytic activity of this valuable compound could be attributed to the synergetic effect of methylimidazolium cation and cavity of skeleton.

Unique properties, such as uniform reaction site and significant potential for functionalization, allow one to optimize the properties of this polymer for immobilization of desired catalyst *via* post-functionalizations without undergoing copolymerizations or further post-polymerization modifications. Thus, this study also, suggests that the porous polymer based on calix[4] resorcinarene can be used as an important and versatile green solid support for a variety of catalysts.

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