Polymer supported bromoderivatives of 2-pyrrolidone: an efficient reagent for the microwave assisted conversion of *trans*-cinnamic acid to *trans*- β -bromostyrene

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Abstract

Here a novel polymeric reagent was synthesised by anchoring bromoderivatives of pyrrolidone into the 3D matrix of divinylbenzene cross linked polystyrene and successfully employed for the decarboxylative bromination of *trans*-cinnamic acid to *trans*- β -bromostyrene under microwave exposure. 100% conversion and selectivity in a concise period of time under solvent-free condition and simple workup procedure are the foremost attraction of this method. The prepared polymeric reagent exhibited good cyclic stability without any significant reduction in bromine content and satisfactory storage stability under normal laboratory condition.

Graphic abstract

Keywords Polymer-supported reagents · Polystyrene · 2-Pyrrolidone · Microwave assisted · Halogenation · *Trans*-cinnamic acid · *Trans*- β -bromostyrene

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1 Introduction

Bromination is undoubtedly one of the remarkable and challenging transformations in organic chemistry and can be done utilising bromine and various other bromo compounds [1]. In organic synthesis, the use of molecular bromine is recognised. But there are several disadvantages associated with the conventional procedure of bromination of organic compounds with elemental bromine. The main drawbacks are handling difficulty, corrosive effect, toxicity, over-bromination and difficulties with separation of products from the reaction mixture [2–4]. Moreover elemental bromine can affect breathing even in little concentration, and significant quantities of bromine can upset the respiratory system [5]. So in the past few decades, a legion of polymer-bound bromine carriers are developed in order to overcome the hazardous nature of bromine [6–11]. The main benefits of these polymeric reagents are their high selectivity [12–14], stability, recyclability [15–17], low toxicity [18], ease of handling [19] and ease of separation of the heterogeneous catalyst from the reaction mixture by simple filtration [20]. Even though a wide range of polymeric reagents are used such as clay polymer nanocomposites resin [4], piperidine and piperazine reagents [6], polyvinylpyrrolidone reagents [8–11, 18, 20, 21, 50], polyvinylpyridine reagents [7, 17, 22], still polystyrene is one of the most common polymeric reagents used in organic synthesis [23, 24]. In addition to polymers, various other heterogeneous catalysts are also used in organic synthesis [25–28].

However, the efficiency and selectivity of polymer-supported reactions are low compared to the solution phase because of the poor diffusion of the reactants through the polymeric network [29]. This drawback, which limits its synthetic utility, can be overcome by carrying out polymer-supported reactions under microwave (MW) conditions. MW assisted reactions which are an alternative source of energy are speedy, and as a result, the product and reagent decomposition are avoided, and the separation of the product from the reaction mixture is simplified with higher yields [30–32]. Moreover, the reaction can be performed under the solvent-free condition and can avoid the possibility of explosion [33–35]. The use of dry media facilitates organic reactions to happen expeditiously at ambient pressure is another added advantage of microwave-assisted reactions [36–38].

To date, methods used for the preparation of β -bromostyrene are limited in number. The classical method involves the synthesis by catalytic Hunsdiecker reaction (CHR) of cinnamic acid, but the isolated yield

obtained is only 73% [39]. Corvari et al. [40] reported the synthesis of β -bromostyrene from *trans*-cinnamic acid. However, in this approach, a mixture of *cis* and *trans* isomers are obtained. Strom et al. [41] made an extension of Corvari and Mestdagh works and prepared *trans*- β -bromostyrene through a different route. The drawback of this method is that it involves a sequence of reactions. Another work described the synthesis of both *cis* and *trans* isomers of β -bromostyrene through decarboxylative elimination of 2,3-dibromo-3-phenylpropanoic acid [42]. A novel stereoselective method was developed by Shastin and co-workers for the synthesis of β -bromostyrene starting from hydrazones of aromatic aldehydes and bromoform in the presence of CuCl [43]. Tang et al. [44] synthesised *cis*- β -bromostyrene from cinnamic acid through β -lactone intermediates. Szyling et al. [45] described a one-pot procedure via borylative coupling/halodeborylation for the synthesis of (*E*)- or (*Z*)- β -arylvinyl bromides from styrenes and vinyl boronates. In another work, the stereoselective synthesis of an aryl vinyl in a speedy microscale reaction of *trans*-4-methoxycinnamic acid with *N*-bromosuccinimide in dichloromethane was reported [46]. However, neither of the methods described above are speedy nor use a polymer-bound reagent under MW condition for the synthesis of *trans*- β -bromostyrene.

Herein we report the stereoselective conversion of *trans*-cinnamic acid to *trans*- β -bromostyrene by a new, efficient polymeric reagent, divinylbenzene (DVB) crosslinked polystyrene supported bromo derivatives of 2-pyrrolidone (DVB-PS-PY-Br) under MW condition. This work has been organized into two parts. The preparation of DVB-PS-PY-Br constitutes the first part of the work and the second part includes the decarboxylation of *trans* cinnamic acid followed by the formation of *trans*- β -bromostyrene using the newly synthesised polymer-supported reagent under MW condition.

2 Materials and methods

Divinylbenzene (DVB), styrene and 2-pyrrolidone were acquired from Sigma Aldrich Germany. All other solvents and reagents used were of reagent grade. A Perkin Elmer Spectrum Version 10.4 was used for taking the IR spectra, and the measurements were done in the range 4000–450 cm^{-1} . The morphology of the synthesised resin was investigated by transmission electron microscopy using a JEOL JEM-2100 microscope. Thermogravimetric analyses were done using a Perkin Elmer, Diamond TG/DTA instrument. The presence of nitrogen and bromine in the sample were confirmed by energy dispersive X-ray spectroscopy using JEOL JSM-6390 scanning electron

microscope with EDX attachment. CHN analyses were carried out using Elementar Vario EL III analyser. The progress of the chemical reaction was examined by thin layer chromatography (TLC) with Merck precoated silica plates. GC–MS analyses were recorded on a ThermoScientific Trace GC 1300 equipped with mass ISQLT single quadrupole mass spectrometer. EI mode is used in recording the Mass spectrum. ^1H NMR spectra were recorded on Bruker Advance 400 MHz instrument with TMS as an internal standard. A single mode MW synthesis reactor—Anton Paar monowave-300 is used for carrying out MW assisted chemical reaction.

2.1 Preparation of polystyrene supported 2-pyrrolidone resin (DVB-PS-PY)

3% DVB crosslinked polystyrene (DVB-PS), its chloromethylated derivative (DVB-PS-Cl) and chloromethyl methyl ether (CMME) were prepared using the standard procedures [47–49]. 2 g chloromethylated polystyrene resin (DVB-PS-Cl) was dispersed in dichloromethane and allowed to swell for 2 h. To the swollen bead, 2 g pyrrolidone and 2 mL pyridine were added and refluxed for 24 h at 110 °C. The polystyrene supported 2-pyrrolidone resin obtained was washed with acetone and methanol. The resin was again washed in a soxhlet apparatus using methanol as solvent and allowed to dry at 80 °C and designated as DVB-PS-PY. Yield: 3.1 g.

2.2 Preparation of bromo derivatives of polystyrene supported 2-pyrrolidone (DVB-PS-PY-Br)

Bromination of DVB-PS-PY was carried out as per the reported procedure [50]. Bromine (2 mL) was added to a suspension of the resin DVB-PS-PY (2.5 g) in CCl_4 (25 mL), and magnetically stirred for 4 h at 0 °C. The resultant product on filtration and washing with CCl_4 (10 mL $\times$ 3) followed by vacuum drying yielded a stable dark orange coloured non-hygroscopic product designated as DVB-PS-PY-Br. Yield: 3.2 g.

2.3 Determination of bromine efficiency of DVB-PS-PY-Br

About 100 mg of DVB-PS-PY-Br was added to 20 mL dimethylformamide in an iodine flask at 0 °C. To this suspension, 1 g potassium iodide was added and retained in the dark with intermittent shaking. The iodine which was liberated during the reaction was titrated against std. $\text{Na}_2\text{S}_2\text{O}_3$ (0.05 M) solution until all the brown colour was disappeared in solution. This procedure was repeated two or three times until all the complexed halogen has reacted.

From the titre value, the bromine capacity can be calculated [50].

2.4 Determination of the MW stability of DVB-PS-PY-Br

The MW stability of DVB-PS-PY-Br was investigated by heating the resin at varying temperatures (100 °C and 150 °C) in an Anton Parr Monowave300 MW synthesiser at a MW power level of 300 W for about 5 min. After 1, 2, 3, 4 and 5 min, a certain amount of the resin was taken out, and its bromine efficiency was found out iodometrically [51].

2.5 Microwave assisted conversion of *trans*-cinnamic acid to *trans*- β -bromostyrene using DVB-PS-PY-Br

A five-fold molar excess of DVB-PS-PY-Br (2.5 g) was impregnated with a solution of cinnamic acid (0.5 g) in dichloromethane (1 mL). The solvent was evaporated, and the functional polymer with the adsorbed substrate was MW irradiated for 5 min at an MW power of 300 W in an Anton Parr Monowave300 MW synthesiser. After every 1 min of MW irradiation, the addition of dichloromethane (0.5 mL) followed by evaporation of the solvent was repeated. The progress of the reaction was followed by thin layer chromatography. After the reaction was completed, the insoluble spent reagent was separated by filtration and washed with dichloromethane. The collective filtrate and washings were dried over anhydrous sodium sulphate followed by evaporation of solvent to get the final product. GC–MS and spectral analysis were done for the characterisation of the product.

2.6 Regeneration of the spent reagent

The spent reagent obtained was washed with dichloromethane (2 mL $\times$ 5) to eliminate any trace of the organic product or substrate. Then the bromine functionality is introduced into the polymer by following the original procedure. The renewed bromo resin can again be used for the halogenation reactions [51].

3 Results and discussion

2-Pyrrolidone was grafted onto DVB crosslinked chloromethylated polystyrene by heating under reflux in the presence of pyridine for 24 h at 110 °C. Bromo derivatives of polystyrene-supported 2-pyrrolidone resin was synthesised by stirring a suspension of the DVB-PS-PY resin in CCl_4 with Br_2 for 4 h at room temperature. According

Scheme 1 Formation of bromo derivatives of polystyrene supported 2-pyrrolidone (DVB-PS-PY-Br)

Fig. 1 FTIR spectra of **a** DVB-PS-Cl, **b** DVB-PS-PY and **c** DVB-PS-PY-Br

to Koshy et al. [50] in polyvinylpyrrolidone-bromine complex, the bromine functionality exists in the form of a tribromide complex (Scheme 1).

The grafting of the 2-pyrrolidone ring to the chloromethylated resin was confirmed by FTIR-spectroscopy, CHN analysis, EDX spectroscopy and TG analysis.

DVB-PS-Cl, DVB-PS-PY and DVB-PS-PY-Br were characterised by FTIR spectroscopy. The FTIR spectrum of DVB-PS-Cl (Fig. 1a) shows a band at 677 cm^{-1} corresponds to C-Clstr. The spectrum also shows a band at 2924 cm^{-1} corresponds to aromatic hydrogen. The chemical modification of DVB-PS-Cl with 2-pyrrolidone has been confirmed by the appearance of a new peak at 1649 cm^{-1} in the IR spectrum of DVB-PS-PY (Fig. 1b) due to C=O stretching of amide carbonyl from the pyrrolidone unit. The spectrum also shows bands at 1495 cm^{-1} and 1179 cm^{-1} due to the C-N stretching frequency of N-C=O and N-C bonds of the pyrrolidone unit. A shift in absorption frequency from 1649 to 1636 cm^{-1} , 1495 to 1492 cm^{-1} and 1179 to 1159 cm^{-1} in the spectrum of DVB-PS-PY-Br (Fig. 1c) can be attributed to the interaction of bromine functionality with the oxygen of the carbonyl group of the pyrrolidone unit.

Table 1 CHN data of DVB-PS-Cl and DVB-PS-PY

Sample no	Sample name	Total N%	Total C%	Total H%
1.	DVB-PS-Cl	0	79.68	6.14
2.	DVB-PS-PY	3.62	65.94	6.72

Fig. 2 TGA curves of **a** DVB-PS-Cl and **b** DVB-PS-PY

CHN analysis of DVB-PS-Cl and DVB-PS-PY again confirms the attachment of pyrrolidone ring to the chloromethylated resin. The CHN content of DVB-PS-Cl and DVB-PS-PY are given in Table 1.

The thermal stability of the synthesised polymers was investigated by thermogravimetric analysis (TGA). The chloromethylated resin is found to be stable up to 275 °C (Fig. 2a) and shows two-stage decomposition. In the first stage, the elimination of the chloromethyl group ($-\text{CH}_2\text{Cl}$) takes place around 275 °C . The second degradation is attributed to the decomposition of the polymer chain from about 460 °C . This is in accordance to the data published by Zhao et al. [52]. Thermogram of polystyrene supported 2-pyrrolidone shows an initial mass loss of 10% due to the removal of absorbed water. The second mass loss starts around 220 °C and may be due to the decomposition of the pyrrolidone ring (Fig. 2b). After that, the resin shows

a similar degradation pattern as that of the chloromethylated resin.

EDX spectroscopy elucidates the chemical nature of the synthesised resin DVB-PS-PY. The EDX profile displayed sharp peaks at the energy of 0.2 keV and 2.6 keV for carbon and chlorine respectively. The weak peak for nitrogen was also observed, which strongly indicates the presence of all these elements in the synthesised resin (Fig. 3).

Figure 4a, b depicts the SEM images of DVB-PS-PY. It is found that the particles are spherical-shaped and almost uniform in size. The average particle size measured from the SEM image is observed to be 53.26 μm . The particle size distribution is shown in the histogram (Fig. 4c).

Transmission electron microscopy is a potent tool to reveal the surface morphology and size of the particles. The transmission electron microscopic images of

DVB-PS-PY show the micro porous nature of the particle. The existence of concentric rings in selected area electron diffraction (SAED) pattern shows the crystalline nature of the synthesised DVB-PS-PY. (Fig. 5).

The reagent DVB-PS-PY-Br should be stable towards microwave irradiation in order to perform synthetic reactions under microwave conditions. The stability of DVB-PS-PY-Br towards microwave irradiation was studied by exposing the bromoresin to MW irradiation at two different temperatures (100 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$) in an Anton Parr Monowave300 microwave synthesiser for varying time intervals (1, 2, 3, 4 and 5 min) and the bromine efficiency was determined iodometrically after each time interval. The bromine capacity was found to be 2.5342 mmol/g after 1 min and there is only a decrease of 0.7 mmol/g in bromine efficiency after 5 min of MW irradiation at 100 $^{\circ}\text{C}$.

Fig. 3 EDX spectra of DVB-PS-PY

Fig. 4 SEM images of DVB-PS-PY under different magnification (a, b), particle size histogram (c)

Fig. 5 TEM of DVB-PS-PY under different magnification (**a**, **b**) and SAED pattern (**c**)

Fig. 6 Histogram of bromine capacity of DVB-PS-PY-Br in different cycles

It is found that there is a tendency for the resin to get charred after 5 min of MW irradiation at 100 °C. When the temperature was raised to 150 °C, the bromine capacity was found to be 2.4342 mmol/g after 1 min of MW irradiation, but there is a sudden decrease in the bromine efficacy after 2 min of MW irradiation. It may be due to the more vigorous release of bromine at high temperature. More over charring of the resin occurred after 3 min of MW exposure. So we performed the reaction at 100 °C for about 5 min at an MW power of 300 W (Fig. 6).

The DVB-PS-PY-Br complex was found to be effective for the microwave assisted conversion of *trans*-cinnamic acid to *trans*- β -bromostyrene and the reaction was found to be completed within 5 min of microwave irradiation. The solvent-free condition further adds on to green chemistry protocols. Another advantage of this method is that no column chromatography is needed for the purification of the product. The product can be easily obtained from the

reaction mixture by simple filtration and evaporation of the solvent. The GC–MS analysis of the product shows a 100% conversion and selectivity. ^1H NMR spectral analysis further confirms the product. Coupling constants are used to identify the *trans* product. The spectral data of the product is: $^1\text{HNMR}-(\text{CDCl}_3)-\delta$, ppm-[(7.830 + 7.790)/2], 7.81 (1H, d, $J = 16$), 7.551–7.569 (2H, m), 7.421–7.416 (3H, m), [(6.485 + 6.445)/2], 6.465 (CH-Br, d, $J = 16$). MS (EI) (m/z)-183, 103, 77, 51. The value of coupling constant 16 Hz corresponds to the *trans* isomer. The proposed mechanism for the conversion of *trans*-cinnamic acid to *trans*- β -Bromostyrene based on the tribromide structure is given in Scheme 2.

Recyclability is one of the main benefits of polymer-supported reagents over monomeric reagents. The spent PS-DVB-PY-Br complex obtained after bromination reactions can be recycled back to the original reagent by washing with dichloromethane followed by treatment with Br_2 in CCl_4 . In the current study, the reagent has been reused up to five times very efficiently. The bromine capacity of the regenerated resin was found to be almost the same even after five cycles of regeneration and reuse.

4 Conclusion

In conclusion we have prepared a novel recyclable and microwave stable polymeric reagent divinylbenzene crosslinked polystyrene supported bromoderivatives of 2-pyrrolidone and studied its halogenating efficacy towards the selective conversion of *trans*-cinnamic acid to *trans*- β -bromostyrene under microwave irradiation. Reports regarding the aforesaid conversion are only limited in number, and moreover this may be the first report that utilizes a polymeric reagent for the conversion. We could achieve 100% conversion and selectivity within a comparatively shorter reaction time, and simple workup procedure under solvent-free condition makes the study

Scheme 2 Mechanism of the formation of *trans*-β-bromostyrene

attractive. The slow discharge of bromine from the polymeric reagent under microwave condition improves the safety of the experiment and the usage of microwave energy rapidly decreases the time needed for the synthesis. This bromoresin was recyclable for about five cycles without much loss in bromine efficiency. Moreover, the synthesized resin was stable under standard laboratory condition and can be kept for an extended time without any significant loss of activity.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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