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ORIGINAL PAPER

Polystyrene supported bromoderivative of 2-oxazolidone – an efficient reagent for microwave assisted bromination reactions

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Abstract

We present herein the synthesis and structural characterization of a novel, recyclable and microwave stable polymeric reagent prepared by anchoring bromoderivative of oxazolidone into the 3D matrix of divinylbenzene crosslinked polystyrene and its application for the bromination of alkenes, activated aromatic compounds and for the α-halogenation of ketones under microwave irradiation. The advantages of this protocol include a simple workup procedure, high product yield, shorter reaction time as well as solvent-free reaction pathway. Besides, this new resin was stable under standard laboratory conditions and can be kept for several months without any significant loss of activity.

Keywords Polymer supported reagents · Polystyrene · 2-oxazolidone · Microwave-assisted · Halogenation

Introduction

Bromination is one of the most significant transformations in synthetic organic chemistry and can be achieved by elemental bromine and numerous other bromo compounds [1]. The conventional method of bromination of organic compounds using elemental bromine has the disadvantages of corrosive effect, toxicity, handling difficulty, poor regioselectivity, overbromination and problems in separation of products from the reaction mixture [2–4]. Furthermore, inhalation of bromine vapors causes breathing problems and failure in the respiratory system [5]. Owing to the risky nature of elemental bromine, alternate bromine carriers are developed such as zeolite/KBr/H_2O_2 [6], KBr/BTPPMS [7], KBr/BTPPPD [8], $ZrBr_4$/diaziene [9], IQBC [10] and [BMPy]Br_3 [11]. But, some of these methods include severe reaction conditions and costly reagents, so in the past few decades, a variety of polymer-bound bromine carriers are prepared for organic synthesis [4, 12–17].

Polymer supported reagents have become the subject of extensive and increasing importance in organic chemistry because of their selectivity [18–20], recyclability [21–23], ease of separation of the products [24], little toxicity [25], ease of handling [26] and stability. The nature of the polymeric backbone, solvation and swelling characteristics and overall topology of the macromolecular matrix plays a decisive role in the reactivity of the functional group attached to the polymeric backbone [27]. Takemoto et.al found that the intrinsic chemical reactivity of a supported species can be enhanced by the chemical and structural characteristics of the support [28].

But the efficacy and selectivity of polymer-supported reactions are low related to solution-phase on account of the poor diffusion of the reactants through the polymeric network [29]. This disadvantage which confines its synthetic usefulness can be overwhelmed by running polymer-supported reactions under microwave (MW) conditions. MW assisted organic reactions are fast and as a result, the product and reagent

Highlights

- Divinylbenzene crosslinked polysterene supported bromoderivative of 2–oxazolidone (DVB-PS-OX-Br) is an efficient, recyclable, microwave-safe and an environmentally stable reservoir of bromine
- DVB-PS-OX-Br is used for the bromination of alkenes, activated aromatic compounds and for the α-bromination of ketones under microwave irradiation

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decomposition is avoided, separation of the product from the reaction mixture is simplified, and yields are higher [30]. The use of dry media facilitates organic reactions to happen expeditiously at ambient pressure is another added advantage of MW assisted reactions [31–34].

Organic synthesis based on MW assisted and polymer-supported reagents have arisen independently as a competent strategy for efficient organic synthesis. The ability of a material to absorb microwave energy depends on its dielectric constant (ε') whereas the dielectric loss factor (ε") characterizes its capacity to convert the MW energy into heat. A high dissipation factor ($\tan\delta = \varepsilon'' / \varepsilon'$) is responsible for a high susceptibility to MW energy [35]. Polyethylene, polytetrafluoroethylene and polystyrene are best in the aspect of dielectric properties [36, 37]. However, the mechanical properties of polyethylene and polytetrafluoroethylene are very poor whereas polystyrene has improved rigidity. Polystyrene (PS) crosslinked with divinylbenzene (DVB) is one of the most promising MW transparent polymer [38].

Within this background, we wish to disclose the synthesis and characterization of a new polymeric reagent, divinylbenzene crosslinked polystyrene supported bromo derivative of 2-oxazolidone (DVB-PS-OX-Br) and its efficacy towards bromination reactions under MW irradiation. MW stability and recyclability of the newly synthesized polymeric reagent were also investigated.

Experimental

Materials and methods

The chemicals divinylbenzene ($C_{10}H_{10}$: 130.19 g/mol), styrene (C_8H_8: 104.15 g/mol) and 2-oxazolidone ($C_3H_5NO_2$: 87.07 g/mol) were purchased from Sigma Aldrich Germany. The monomer styrene and the crosslinking agent divinylbenzene were washed with 1% NaOH solution (5 mL × 3) and with distilled water (5 mL × 3) to remove the inhibitor. 2-oxazolidone was used without any additional purification. All other reagents and solvents used were of analytical grade and used as such. Fourier transform infrared spectroscopy (FTIR) of the synthesized resins were recorded in the range 4000–450 cm^{-1} using Perkin Elmer FTIR spectrometer. The surface morphology of the synthesized resin was carried out by SEM JEOL (JSM6390lV) scanning electron microscope. Thermogravimetric analyses were carried out using a Perkin Elmer, Diamond TG/DTA instrument. An Elementar Vario EL III analyzer is used for CHN analysis. Thin-layer chromatography was performed on Silica Gel pre-coated plates (Merck). The products formed in various reactions were analyzed on a Thermo scientific Trace GC 1300 equipped with ISQLT single quadrupole mass spectrometer. Mass spectra were recorded in the EI mode. The proton NMR spectra were recorded on Bruker Advance 400 MHz instrument with TMS as an internal standard. A single-mode microwave synthesis reactor - Anton Paar monowave-300 is used for carrying out MW assisted chemical reactions.

Preparation of polystyrene supported 2-oxazolidone (DVB-PS-OX)

3% DVB crosslinked polystyrene (DVB-PS), its chloromethylated derivative (DVB-PS-Cl), and chloromethyl methyl ether (CMME) were prepared using the reported procedures [39–41]. For preparing DVB-PS-OX, 4 g chloromethylated resin (DVB-PS-Cl) was allowed to swell in dichloromethane (DCM) for 2 h and to the swollen bead, 4 g oxazolidone and 4 mL pyridine were added and refluxed for 24 h at 110 °C. The newly synthesized resin was filtered, washed with acetone and methanol several times. The resin was drained and dried at 80 °C. Yield – 5.5 g.

Preparation of bromo derivatives of polystyrene supported 2-oxazolidone (DVB-PS-OX-Br)

Bromo derivatives of DVB-PS-OX was prepared by the reported procedure [14]. DVB-PS-OX (5 g) in CCl_4 (25 mL), bromine (5 mL) was added and stirred at 0 °C for 4 h at room temperature. The resultant dark orange colored resin on filtration and washing with CCl_4 (5 mL × 5) yielded a stable non-hygroscopic product. The resin was dried in vacuum at 60 °C to give dark orange polymer (DVB-PS-OX-Br). Yield-7.5 g. The bromine capacity of the newly synthesized resin was determined by iodometric titration and was found to be 2.53 mmol/g [14].

Determination of the microwave stability of DVB-PS-OX-Br

The stability of DVB-PS-OX-Br resin towards MW irradiation was examined by heating the resin at two different temperatures (100 °C and 150 °C) in an Anton Parr Monowave300 MW synthesizer at an 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 by iodometric titration [42].

Microwave-assisted bromination reactions using DVB-PS-OX-Br- general procedure

The low molecular weight organic substrate (0.5 g) was dissolved in DCM (1 mL) and a fivefold molar excess of DVB-PS-OX-Br (2.5 g) was added to this. The solvent was allowed to evaporate and the polymeric reagent with the adsorbed substrate was MW irradiated for 5 min at an MW power of 300 W. After every one minute of MW irradiation, the addition of DCM (0.5 mL) followed by evaporation of the solvent was repeated. The reactions were monitored by TLC. After 5 min of MW exposure, the insoluble spent reagent was filtered and washed with more solvent. The collective washings and filtrate were dried over anhydrous sodium sulphate and the conversion and selectivity were found out by GC-MS analysis. The above procedure was repeated with different organic substrates.

Regeneration of the spent reagent

The spent reagent obtained from different reactions were combined and washed with dichloromethane (2 mL× 5) to remove any trace of the organic substrate or product. Then the bromo group is introduced into the polymer by following the original method [14]. The renewed bromo resin was used for the halogenation of various organic substrates.

Results and discussion

Preparation of DVB-PS-OX-Br

2-oxazolidone was grafted onto DVB-PS-Cl by heating under reflux in the presence of pyridine for 24 h at 110 °C. DVB-PS-OX-Br resin was synthesized by stirring a suspension of the resin DVB-PS-OX in CCl_4 with bromine on a magnetic stirrer for 4 h at room temperature. According to Koshy et al. in polyvinylpyrrolidone-bromine complex, the bromine functionality exists in the form of a tribromide complex [14]. They proposed that the absorbed water may facilitate the formation of bromide ion which can also complex with Br_2 to form tribromide complex. D.H. Lorenz established the structure of the PVP-iodine complex as a triiodide complex based on X-ray analysis and infrared spectroscopic investigation [43]. Based on these we suggest a tribromide structure for our complex (Scheme 1).

FTIR studies

DVB-PS-Cl and DVB-PS-OX were characterized by FTIR spectroscopy. The FTIR spectra of DVB-PS-Cl (Fig.1a) shows a characteristic band for C-Cl stretching at 691 cm^{-1}. The peak at 835 cm^{-1} is typical of the benzene ring of DVB. Another band at 2924 cm^{-1} indicates the presence of the $-CH_2$ group. This is by the data reported by Jincy et.al [44]. The spectrum also shows a band at 3082 cm^{-1} corresponds to aromatic hydrogen. The grafting of DVB-PS-Cl with 2-oxazolidone has been confirmed by the appearance of a new peak at 1642 cm^{-1} in the IR spectrum of DVB-PS-OX (Fig.1b). This stretching band is attributed to the C=O group of the oxazolidone unit [45, 46]. The spectrum also exhibits bands at 1505 cm^{-1} and 1150 cm^{-1}. These bands originate from the C-N stretching and ether group of the oxazolidone ring.

CHN analysis

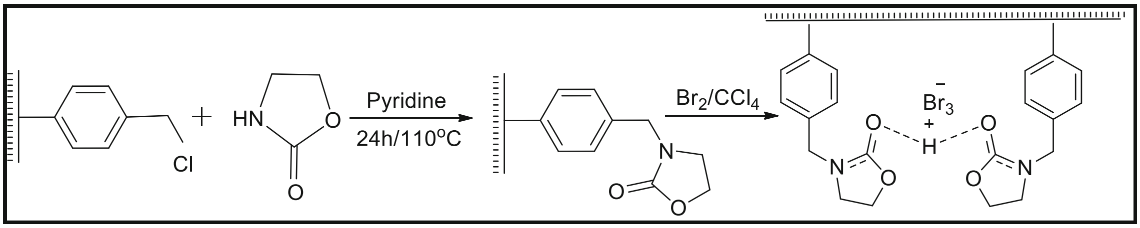
The grafting of 2-oxazolidone to DVB-PS-Cl was again confirmed by CHN analysis. The CHN content of DVB-PS-Cl and DVB-PS-OX are given in Table.1.

Thermogravimetric analysis

The thermal stability of DVB-PS-Cl and DVB-PS-OX was investigated by thermogravimetric analysis. The Thermogram of DVB-PS-Cl (Fig.2, a) shows that it is stable up to 275 °C and undergoes degradation in two steps. Elimination of the chloromethyl group takes place in the first step at 275 °C and in the second step the degradation of the polymer chain starts from about 460 °C. The results are in good agreement with thermal studies reported by Zhao et al. [47]. Thermogram of DVB-PS-OX shows an initial mass loss of 10% due to the removal of absorbed water. The second mass loss of about 21% starting around 190 °C can be attributed to the loss of oxazolidone ring. (Fig.2, b). After that, the polymer chain follows the same degradation pattern as that of the chloromethylated resin.

SEM analysis

Figure 3(a,b) shows the SEM images of DVB-PS-OX at various magnification. The SEM micrographs show that the particles are spherical and almost uniform in size. The average particle size measured from the SEM image is observed to be 51.82 μm. The particle size distribution was shown in the histogram (Fig. 3,c).



Scheme 1 Preparation of polystyrene supported bromoderivatives of 2-oxazolidone

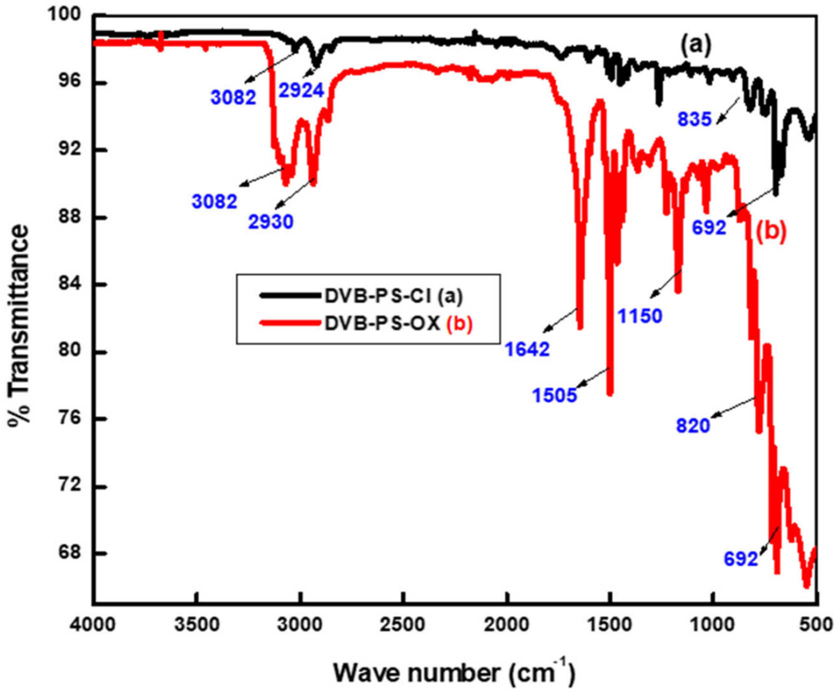


Fig. 1 – IR spectra of (**a**) DVB-PS-Cl and (**b**) DVB-PS-OX

Determination of the microwave stability of DVB-PS-OX-Br

The bromo resin DVB-PS-OX-Br should be stable to MW irradiation to perform synthetic reactions under MW conditions. To study the stability of DVB-PS-OX-Br polymer towards MW irradiation, 1 g of the bromo resin was MW irradiated at an MW power level of 300 W for about 5 min at two different temperatures (100 °C and 150 °C). After 1,2,3,4 and 5 min, a definite amount of the resin was taken out and its bromine capacity was estimated iodometric titration. The bromine capacity was found to be 2.48 mmol/g after 1 min of MW irradiation and there is only a decrease of 0.4 mmol/g in bromine efficiency after 5 min at 100 °C. When the temperature was elevated to 150 °C, the bromine capacity was found to be 1.93 mmol/g after 1 min of MW irradiation and there is a rapid fall in the bromine efficiency after 2 min. It may be because of the more vigorous release of bromine at high temperatures. Moreover, the resin gets charred after 3 min. Therefore we carried out all organic reactions at 100 °C for about 5 min at an MW power of 300 W.

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

Functional Polymer	Total % of elements		
	Nitrogen	Carbon	Hydrogen
DVB-PS-Cl	0	79. 68	6.14
DVB-PS-OX	3.70	67.00	6.83

Microwave-assisted halogenation reactions using DVB-PS-OX-Br

The novel method of synthesis of organic compounds always remains popular in synthetic organic chemistry [48, 49]. Our new resin, DVB-PS-OX-Br, is a safe and an environmentally stable reservoir of bromine. The resin is found to be effective for the bromination of olefinic and activated aromatic compounds and also for α-bromination of ketones under MW irradiation. The slow release of bromine from the reagent improves the safety of the experiments. The solvent-free condition further adds on to green chemistry protocols.

The various organic substrates undergo bromination by the reagent, time taken; products, conditions, conversion and selectivity are given in Table 2. As shown in Table 2, several olefinic compounds (entries 1–4) undergo bromination when MW irradiated with DVB-PS-OX-Br. Decarboxylative bromination leading to the formation of β-bromostyrene was observed for cinnamic acid. For cinnamaldehyde, instead of addition across the double bond, the substitution of bromine took place at the double bond. Styrene and cyclohexene are very efficiently converted to styrene dibromide and dibromocyclohexane on reaction with DVB-PS-OX-Br. We could achieve 100% conversion and selectivity for cinnamic acid, styrene and cyclohexene. Activated aromatic compounds were also treated with DVB-PS-OX-Br (Table 2 entries 6–7). Methyl substituted phenol smoothly reacted with

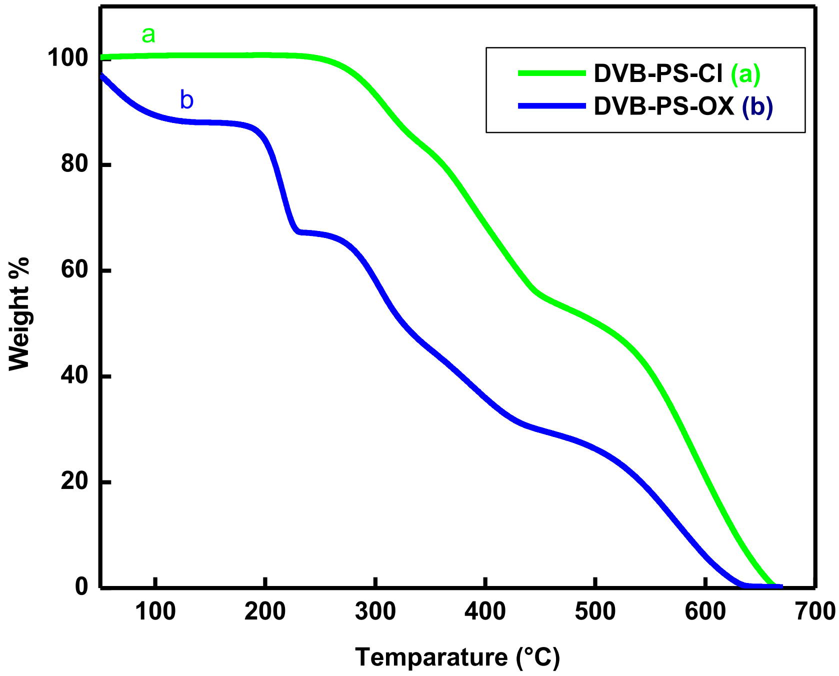


Fig. 2 –TGA of (**a**) DVB-PS-Cl and (**b**) DVB-PS-OX

reagent and gave the corresponding mono brominated product (selectivity-95%) whereas the bulky substituted phenol afford its dibrominated product (selectivity-80%) and mono brominated product (selectivity-16%). We have also studied the bromination of activated aniline such as N,N-dimethyl aniline (Table 2, entry-5) and obtained parabrominated

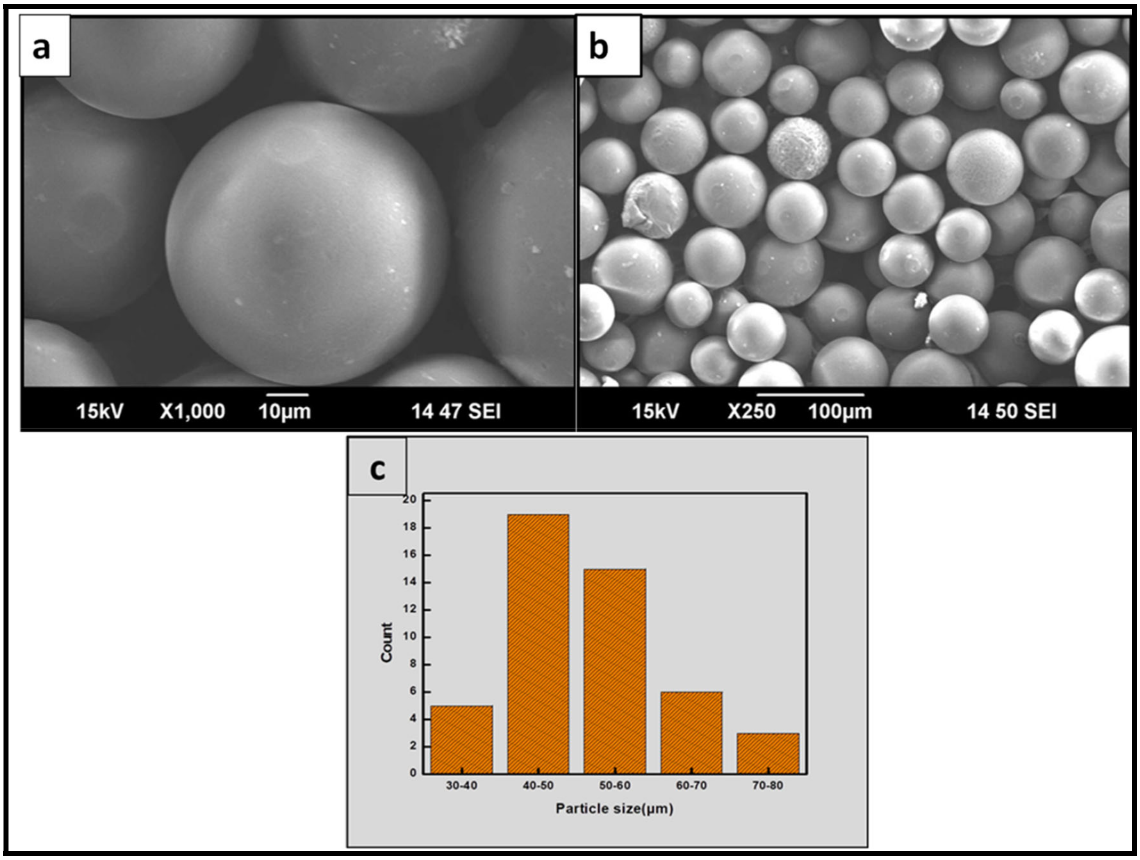
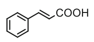
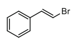
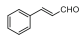
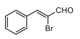
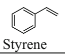
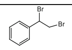
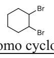
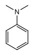
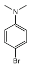
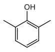
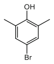
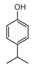
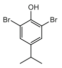
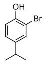
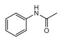
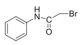


Fig. 3 –SEM images of DVB-PS-OX under different magnification (**a**, **b**) and particle size histogram (**c**)

Table 2 Bromination reactions using DVB-PS-OX-Br

Entry	Substrate	^{a}MW/300 W/5 min.		
		Product	^{b}Conversion (%)	^{b}Selectivity (%)
1.	 Cinnamic acid	 Bromo styrene	100	100
2.	 Cinnamaldehyde	 α-Bromo cinnamaldehyde	32	100
3.	 Styrene	 Styrene dibromide	100	100
4.	 Cyclohexene	 Dibromo cyclohexane	100	100
5.	 N,N-dimethyl aniline	 4-Bromo-N,N-dimethylaniline	40	100
6.	 2,6-Dimethyl phenol	 4-Bromo-2,6-Dimethyl phenol	100	95
7.	 4-tert-butyl phenol	 2,6-Dibromo-4-tert-butyl phenol	100	80
		 2-Bromo-4-tert-butyl phenol		16
8.	 Acetanilide	 α-Bromoacetanilide	20	100

[a] All microwave reactions were carried out at 300 W for 5 min in cycles of 1 min

[b] Conversion and selectivity were obtained from GC-MS analysis

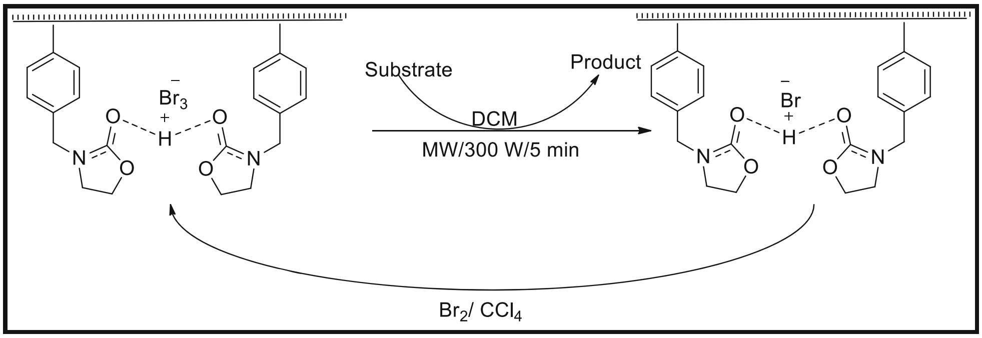
product in moderate yield (conversion-40%, selectivity-100%). In the α-bromination of acetanilide a low yield of the corresponding α-brominated isomer was formed (Table 2, entry-8).

One of the significant features of this polymeric reagent is the probability of recycling. The spent PS-DVB-OX-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 (Scheme.2). In the current study, the reagent has been reused up to five times very competently. The bromine capacity of the regenerated resin was found to be almost the same even after five cycles of regeneration and reuse. The bromine capacity of the resin in different cycles is shown in the histogram (Fig.4).

Conclusion

We have prepared and characterized an innovative, powerful, recyclable and microwave stable polymeric reagent, divinylbenzene crosslinked polystyrene supported bromoderivatives of 2-oxazolidone and studied its behavior to

Scheme 2 Regeneration of DVB-PS-OX-Br



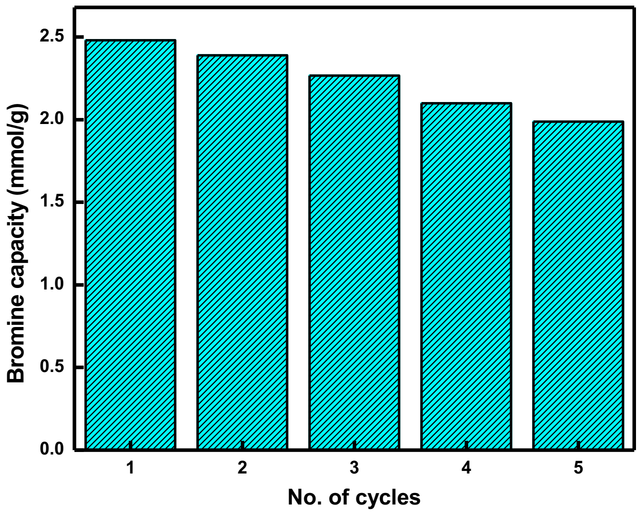


Fig. 4 Histogram of bromine capacity of DVB-PS-OX-Br in different cycles

act as an efficient halogenating agent under microwave irradiation. The major benefits of this method are shorter reaction time and a simple workup procedure. Moreover, the reagent has the advantage of improved shelf-life and recyclability. The use of microwave heating considerably decreases the reaction time and reduces environmental pollution through the usage of solvent-free reaction protocols. Besides, this new 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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Data availability Not applicable.

Compliance with ethical standards

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

Code availability Not applicable.

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