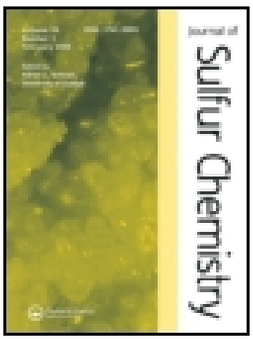

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Epichlorohydrin cross-linked β-cyclodextrin: an environmental method for the synthesis of 2-arylbenzothiazoles derivatives in water

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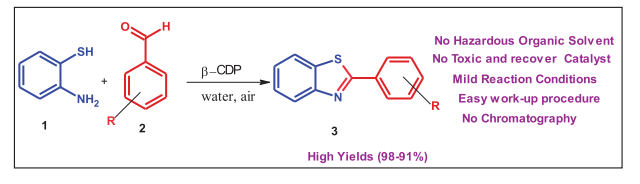
ABSTRACT

In the present study, we report an environmentally benign synthesis of 2-arylbenzothiazoles derivatives from *o*-aminothiophenol and aldehydes in aqueous medium using β-cyclodextrin polymer as a catalyst and air as an oxidant. The polymer showed excellent catalytic activity, recovered, reused six times, and the catalyst efficiency remained unchanged. This suggests that the catalyst is an efficient and green catalyst for the synthesis of 2-arylbenzothiazoles derivatives and the obtained results could be promising for industrial synthesis of 2-arylbenzothiazoles derivatives.



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β-Cyclodextrin polymer; 2-arylbenzothiazoles; environmental; water chemistry; air oxidant and industry

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides composed of 6–8 glucopiranose units (namely α-, β- and γ-CDs) linked by glycosidic bonds. CDs have been introduced into many organic reactions in aqueous solution.[1–8] They are water soluble, non-toxic and hydrophobic in the central cavity. The most significant characteristic of the CDs is their ability to form inclusion complexes with different guest molecules in aqueous solution or in the solid state through host–guest interactions.[9–11] β-CD is the cheapest among the CD family and has been widely used in separation, catalysis and in organic reactions.[12–15] It has played a vital role in activating substrate and improving its selectivity.[16–19] Although β-CD exhibits good catalytic activity in liquid-phase oxidation, the separation of β-CD from the homogeneous system is very difficult. Therefore, β-CD was immobilized on appropriate supports, for example, organic, polymeric and mineral materials

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in order to improve recyclability, easy recovery and cost-effectiveness.[20] Immobilized β-CD not only shows good mechanical properties but also completely retains molecular recognition and catalytic properties of cyclodextrins. One way for producing immobilized β-CD (abbreviated as β-CDP) is through the reaction of β-CD molecules with bifunctional cross-linking agents such as epichlorohydrin (EPI).[21–24]

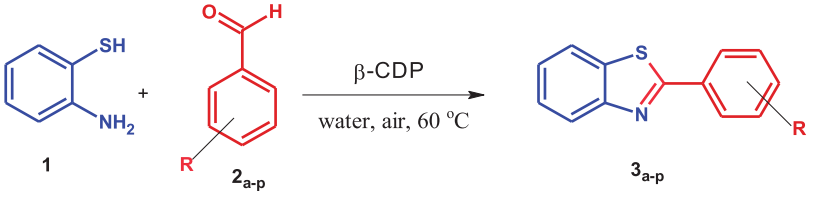
Over the last few years, we are constantly working on development of new tools and methodologies for synthesized bio active compounds by green catalyst.[25–34] On the basis of exhaustive literature review, it has been found that 2-substituted benzothiazole have good potential to exhibit anticancer activity.[35–46] Accordingly, in the present study, we report the synthesis of 2-arylbenzothiazoles derivatives using β-cyclodextrin polymer as a catalyst in an environmentally benign method which includes water as a solvent and air as an oxidant.

2. Results and discussion

In this paper, we have screened β-cyclodextrin polymer as a catalyst in an environmental-friendly synthesis of 2-arylbenzothiazoles derivatives $\mathbf{3_{a-p}}$ from o-aminothiophenol **1** and aldehydes in water using air as an oxidant (Scheme 1). The use of β-CDP in water not only gave high yield, selectivity and lower reaction time but also the whole process turned out to be cheap, speedy, facile and eco-friendly (Table 1).

2.1. Infrared spectroscopy (FTIR) characterization

FTIR spectra of β-CD (a) and β-CDP (b) are shown in Figure 1. FTIR spectrum of β-CDP is similar to that of β-CD, indicating that the frame of β-CD does not change during



Scheme 1. Synthesis of 2-arylbenzothiazoles $\mathbf{3_{a-p}}$.

Table 1. β-CDP as catalyst for the synthesis of 2-arylbenzothiazoles[a] $\mathbf{3_{a-p}}$.

Entry	No	R	Time (hour)	Yield (%)[b]	Entry	No	R	Time (hour)	Yield (%)[b]
1	**3a**	H	2	98	9	**3i**	4-OH	2	92
2	**3b**	4-Cl	2	97	10	**3j**	2-OH	3	90
3	**3c**	4-Br	2	96	11	**3k**	2-Cl	3	93
4	**3d**	4-F	2	96	12	**3l**	2-NO_2	3	96
5	**3e**	3-CH_3	3	95	13	**3m**	2-MeO	3	95
6	**3f**	4-NMe_2	2	94	14	**3n**	2-pyridyl	4	92
7	**3g**	4-NO_2	2	98	15	**3o**	2-Furyl	4	91
8	**3h**	4-MeO	2	97	16	**3p**	2-thienyl	4	90

[a]Reaction conditions: **1**(1 mmol), **2a** (1.2 mmol) and catalyst (1 g) in 25 ml water.
[b]Isolated yields.

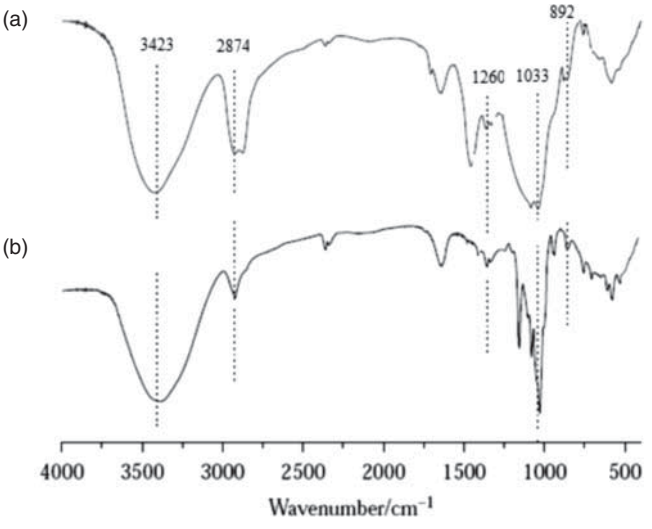


Figure 1. FTIR spectra of β-CD (a) and β-CDP (b).

Table 2. The effect of the reaction temperature for synthesis 2-phenylbenzothiazole[a] **3a**.

Entry	Temperature	Conversion[b] (%)	Yield[c] (%)
1	40	66	50
2	50	71	56
3	60	95	98
4	70	95	98

[a]Reaction conditions: **1**(1 mmol), **2a** (1.2 mmol) and catalyst (1 g) in 25 ml water.
[b]Consumption of o-aminothiophenol.
[c]NMR yield.

the course of immobilization. The peaks of β-CDP at 3423 and 2874 cm^{-1} are stronger than those of β-CD, and the increased intensity may be attributed to the presence of more $-OH$ and $-CH_2$ groups in the β-CDP. The FTIR spectrum of β-CDP showed the characteristic peaks at 1260 and 721 cm^{-1}, indicating the presence of the expoxy group in β-CDP. The peak at 1033 cm^{-1} in the β-CDP was assigned to the C—O or C—O—C stretching in the β-CDP. The increase in the band intensity at around 1033 cm^{-1} might be β-CD. In addition, the peak at 892 cm^{-1} in the β-CDP was the characteristic bands of α-(1,4)-glucopyranose in β-CD.[47] Therefore, it could be concluded that β-CD had been immobilized successfully onto β-CDP.

2.2. The effect of reaction temperature

The effects of the reaction temperatures on the yield of 2-phenylbenzothiazole and the conversion of o-aminothiophenol are shown in Table 2.

As shown in Table 2, the synthesis of 2-phenylbenzothiazole promoted by β-CDP is highly sensitive to the reaction temperature. At 50°C, both the conversion and the yield were low. As the reaction temperature was increased to 60°C, both the conversion and yield increased. Further increase in the reaction temperature was not beneficial to the yield anymore and 60°C was chosen as the optimal reaction temperature.

Table 3. The effect of the amount of β-CDP for synthesis 2-phenylbenzothiazole[a] **3a**.

Entry	Amount of β-CDP (g)	Conversion (%)[b]	Time (h)	Yield (%)
1	0	56	2	12
2	0.2	68	2	31
3	0.5	77	2	65
4	1	95	2	98
5	2	95	2	98
6	3	95	2	98

[a]Reaction conditions: **1**(1 mmol), **2a** (1.2 mmol) and catalyst (1 g) in 25 ml water.
[b]Consumption of o-aminothiophenol.

2.3. The effect of the amount β-CDP

The effect of amount of the catalyst, that is, β-CDP on the yield of 2-phenylbenzothiazole $\mathbf{3_a}$ and the conversion of o-aminothiophenol were investigated by varying the catalyst loading from 0 to 3 g. As shown in Table 3, β-CDP exhibited higher catalytic activity for synthesis of 2-phenylbenzothiazole compared with that in blank experiment, where no catalyst was used. The conversion of o-aminothiophenol increased with the amount of catalyst, which might be attributed to the increased number of hydrophobic cavity in β-CDP. Maximum conversion (ca. 95%) was obtained using 1.0 g of β-CDP, further increase in the catalyst amount negatively affects the yield of 2-phenylbenzothiazole. This is the first example to use β-CDP as a catalyst in water to restrain the conversion while improving the selectivity and this method is particularly effective to enhance the selectivity for those reactions in which the side reactions can happen smoothly without β-CDP. The optimal amount of β-CDP used in the reaction is 1.0 g is shown in Table 3.

2.4. Effect of stirring speed

Stirring speed has a great influence on the synthesis 2-phenylbenzothiazole by β-CDP catalysis. The effect of stirring speed was investigated in the range of 100–800 rpm. The results showed that the conversion of o-aminothiophenol significantly increased with an increase in stirring speed. The conversion corresponding to a stirring speed of 500 rpm was up to 94%, much higher than 45% at a stirring speed of 100 rpm. Beyond this point (500 rpm), an increase in stirring speed had no significant influence on the conversion of o-aminothiophenol. These results indicated that the conversion of o-aminothiophenol was strongly dependent on the dispersion extent of the organic phase in aqueous phase, which promoted the mass transfer between the two phases to improve the selectivity of 2-phenylbenzthiazole.

2.4.1. Scale-up experiment

Besides, in order to verify the efficiency of the catalytic system, a scale-up experiment for the synthesis of 2-phenylbenzothiazole catalyzed by β-CDP in water under the above optimum reaction conditions was carried out as shown in Scheme 1. The isolated yield of 2-phenylbenzthiazole was 98%. In comparison with the prior reports, the current process realized the clean synthesis of 2-phenylbenzothiazole and provided high yield to

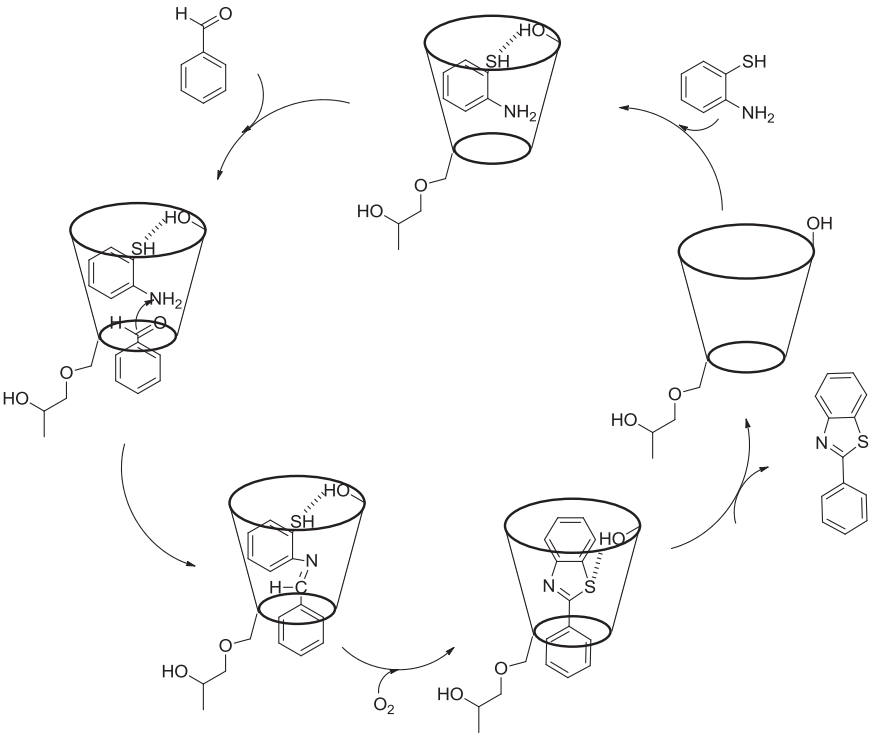


Figure 2. The possible reaction mechanism.

the product under mild reaction conditions, which is very important to preserve natural essence of 2-phenylbenzothiazole during the reaction process.

2.5. Reaction mechanism

The mechanism for β-CDP catalysed synthesis 2-phenylbenzothiazole based on above experimental results has been proposed in Figure 2. β-CD in the β-CDP and o-aminothiophenol can form the inclusion complex via intermolecular hydrogen bonding O—H O at the second rim of β-CD still retained in the cavity. Then, benzaldehyde entered into the cavity from the primary side, with the aldehyde group pointed towards the secondary side to react with amidine resulting in the formation of a Schiff's base. The oxidative cyclodehydrogenation of reaction intermediate, that is, the Schiff's base using air as an oxidant occurred inside the β-CD cavity and finally resulted in the 2-phenylbenzothiazole formation.[17,18]

2.6. Reusability of the catalyst

The insoluble β-CDP could be easily recycled by centrifugation after the reaction. The recovered β-CDP was washed successively with ethanol and deionised water. After drying, the catalyst was reused for the next run under the same condition. The results indicated that the catalytic activity was not affected significantly over the consecutive cycles. The catalyst

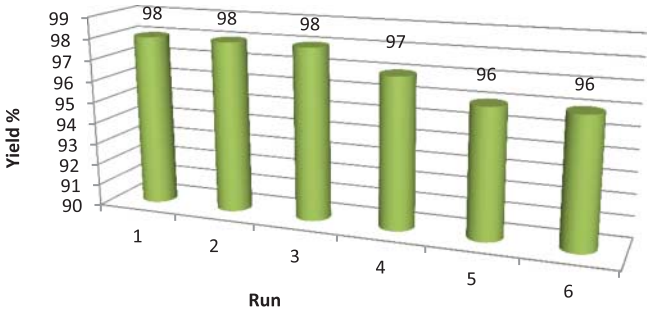


Figure 3. Recyclability of β-CDP in the model reaction.

was reused for six cycles and it retains the catalytic activity and the selectivity during recycling experiments (cf. Figure 3).

3. Conclusion

This work provides an easy access to efficient synthesis of 2-arylbenzothiazoles derivatives under mild reaction conditions with easy recovery of the catalyst β-CDP. This water-mediated reaction is mild, easy to handle, economic and eco-friendly. This method is bestowed with merits such as high yield, cost-effectiveness, biomimetic, neutral aqueous-phase conditions and environmentally benign nature. These advantages of the catalyst made it preferential for the synthesis of 2-arylbenzothiazoles derivatives in the industrial process.

4. Experimental

4.1. Catalyst preparation

According to the previous report,[48–51] a typical procedure for the preparation of β-CDP was described as follows: β-CD (5 g, 0.44 mmol) was mixed with 8 mL NaOH (50%, w/w) solution and mechanically stirred for 20 min till β-CD was completely dissolved. Then, 15 mL epichlorohydrin (EPI) was slowly added to the reaction mixture. The reaction mixture was polymerized at 65°C under vigorous stirring (200 r.min^{-1}). After stirring for about 1–2 h, precipitate could be observed, and the viscosity of the solution was also increased. The solution was mixed with 100 ml acetone, and the insoluble polymers were poured into water. The resultant product was filtrated, and further washed with acetone in a Soxhlet extractor for 24 h. After drying in oven at 80°C for 12 h under vacuum, the polymer product was crushed and granulated to 160–250 μm in diameter. The content of β-CDP in immobilized β-CDP, measured by the phenolphtalein decoloration method according to the literature report,[52] was found to be 50%.

4.2. Catalyst characterization

The FTIR spectra of samples were measured by KBr pellet. All the infrared spectra were recorded on a Shimadzu DR-8001 spectrometer with wave numbers ranging from 400 to 4000 cm^{-1}.

4.3. General procedure for the synthesis of 2-arylbenzothiazole

For a typical reaction run, o-aminothiophenol (1 mmol, 125 mg) was dissolved in deionised water (25 mL) at 60°C in a 100 mL 3-necked round bottom flask fitted with a reflux condenser and magnetic stirrer. β-CDP (1 g) was added to the vessel and the mixture was heated to 60°C in an oil bath with electric heater. Substituted aldehyde (1.2 mmol) was added to the reaction system and it was stirred for 2 h at 60°C. The progress of the reaction was monitored by TLC. When the reaction was finished, the mixture was extracted with ethyl acetate and dried over anhydrous sodium sulfate. Then, ethyl acetate was removed in vacuum. All of the products are known compounds and characterized easily by comparison with melting point, IR and ^{1}H NMR spectral data reported in literature.[53–56]

4.4. Scale-up experiment

The large-scale reaction experiment was performed under the following optimum reaction conditions: a mixture of β-CDP (100 g) and 250 ml deionised water was stirred at 60°C. Subsequently, o-aminothiophenol (100 mmol) was added. After 1 h, 120 mmol of benzaldehyde was added, the reaction system was then stirred for 2 h. After the reaction, the solution was extracted by ethyl acetate, and crude product was obtained in 98% yield.

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