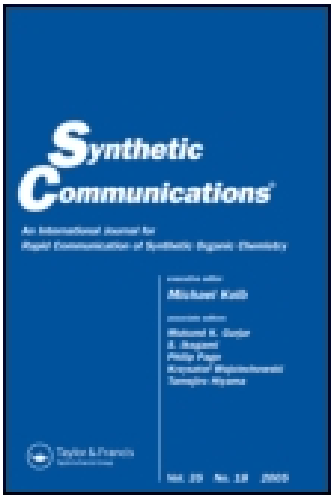

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# Selective Oxidation of Sulfides to Sulfoxides With Poly[4-Hydroxy(tosyloxy)iodo]styrene

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# Selective Oxidation of Sulfides to Sulfoxides With Poly[4-Hydroxy(tosyloxy)iodo]styrene

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**Abstract:** Sulfides can be selectively converted to corresponding sulfoxides in excellent yields under mild conditions by linear and 1% cross-linked poly[4-hydroxy(-tosyloxy)iodo]styrene (PSHTIB).

**Keywords:** Poly[4-hydroxy(tosyloxy)iodo]styrene, sulfide, sulfoxide

Oxidation of sulfides is an important method for preparing sulfoxides and sulfones. Trifluoroperacetic acid,[1] sodium bromite,[2] an $MeNO_2$ solution in dilute $HNO_3/H_2SO_4$,[3] mercury(II) oxide–iodine reagent,[4] and iodic acid[5] are frequently used as oxidation reagents. At present, many low-molecular-mass hypervalent iodine reagents that can selectively oxidize

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sulfides to the corresponding sulfoxides are available, for example phenyliodo diacetate,[6] iodosobenzene (PhI=O),[7] hydroxy(tosyloxy)iodobenzene (HTIB, Koser's reagent),[8] and dichloroiodobenzene.[9]

Characteristics of these reagents include ease of preparation, low toxicity, mild reaction conditions, high selectivity, and reasonable cost. However, the oxidation product is easily contaminated with iodobenzene after reaction.

Recently, Togo and coworkers reported a method for the oxidation of sulfides to sulfoxides and sulfones that employs recycling of poly[(4-diacetoxyiodo)styrene] in chloroform–water (1%).[10] Their method is credited with overcoming the product-contamination drawback inherent in the use of low-molecular-mass hypervalent iodine reagents.

We studied the environmentally benign reagents poly[4-hydroxy(tosyloxy)-iodo]styrene (PSHTIB) and poly[(4-diacetoxyiodo)styrene],[11] and describe the utility of the former as an oxidizing reagent for sulfides in this communication.

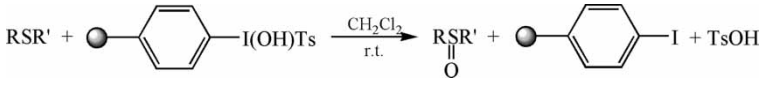
Linear PSHTIB and 1% cross-linked PSHTIB was prepared using a method reported previously.[12] The loading capacities (measured by iodometry) of linear PSHTIB and 1% cross-linked PSHTIB were 1.91 mmol/g and 1.72 mmol/g, respectively.

Linear PSHTIB (1.3 g) or 1% cross-linked PSHTIB (1.5 g) in dichloromethane reacted with sulfides (2 mmol) at room temperature to produce the corresponding sulfoxides (Scheme 1) (Table 1).

Our results showed that both hypervalent iodine reagents had high selectivity and produced single sulfoxides, the yields of which approached those obtained using low-molecular-mass hypervalent reagents. The polyiodobenzene formed from PSHTIB was easily separated from the reaction products by filtration, avoiding the inconvenience of separating and refining iodobenzene formed from HTIB. In addition, the recycled reagent contained almost the same functional group as the original reagent. The polystyrene-supported hypervalent iodine reagents conform to environmental and economic criteria.[13]

## EXPERIMENTAL

Linear polystyrene was purchased from J & K Chemical Ltd. (Peking). Cross-linked polystyrene (1%, 200–400 mesh) was obtained from Nankai Share Group (Tianjin). Melting points were determined by a capillary method and are uncorrected. Elemental analyses were performed using a PE 2400




*Scheme 1.*

***Table 1.*** Results of the oxidation

| Product | Yield[a] (lit.) | Yield[b] | Mp (°C) (lit.) | IR $\nu/cm^{-1}$ |
|---|---|---|---|---|
| PhS(O)Ph | 100 | 95 | 70–71 (MeOH) (70.4)[2] | 1583, 1442, 1039, 695 |
| PhS(O)Bn | 91 (100)[8] | 90 | 120–121 (MeOH) (123) [2] | 1495, 1038, 747, 694 |
| $Bn_2SO$ | 100 (100)[8] | 95 | 133–134 (MeOH) (132–3)[4] | 1494, 1456, 1032, 776, 701 |
| PhS(O)Et | 88 (95)[8] | | | 2978, 1478, 1045, 751, 695 |
| PhS(O)Bu-n | 82 (97)[8] | | | 2960, 1448, 1038, 750, 695 |
| BnS(O)Bu-n | 86 (94)[8] | | | 1494, 1456, 1032, 776, 701 |
| $(Bu\text{-}n)_2SO$ | 71 | | 33 (MeOH)(34)[2] | 2960, 1380, 1028 |
| $(CH_2)_4SO$ | 78[4] | | | 2934, 1444, 1031 |
| PhS(O)Ph | 96[c] | 91[d] | 70–71 (70.4) | 1582, 1443, 1040, 693 |
| PhS(O)Bn | 88[c] | 88[d] | 120–121 (123) | 1494, 1039, 747, 695 |

[a]By applying linear PSHTIB.
[b]By applying 1% cross-linked PSHTIB.
[c]By applying linear PSHTIB recycled.
[d]By applying 1% cross-linked PSHTIB recycled.

(Perkin-Elmer) instrument. IR spectra were recorded using an FT-IR1730 (Perkin-Elmer) instrument.

## General Procedure for Oxidation of Sulfides

### Oxidation of Sulfides with Linear PSHTIB

Sulfide (2 mmol) was added to linear PSHTIB (1.3 g) in dichloromethane (25 ml) at room temperature. After removing the solvent, anhydrous ethanol (15 ml) was added to the residue and the poly(4-iodostyrene) was recovered by filtration. The filtrate was evaporated, and dichloromethane (15 ml) was added to the residue, which was then washed with 5% sodium hydroxide solution (10 ml). The organic layer was dried over anhydrous magnesium sulfate and concentrated, yielding the products.

### Oxidation of Sulfides by 1% Cross-linked PSHTIB

Oxidation of sulfides by 1% cross-linked PSHTIB was carried out using the procedure described for linear PSHTIB.

### Regeneration of PSHTIB

Regeneration of 1% Cross-linked Poly[4-hydroxy(tosyloxy)iodo]styrene

Recovered 1% cross-linked poly(4-iodostyrene) (5.5 g) was washed with dichloromethane (100 ml) using a scorbutic extractor, yielding neat 1% cross-linked poly(4-iodostyrene) (5.3 g). This was treated using a method described previously[12] to obtain 1% cross-linked poly[(4-diacetoxyiodo)-styrene] (6.8 g) and poly[4-hydroxy(tosyloxy)iodo]styrene (7.5 g). IR (KBr) 3417, 1176, 1015, 814, 673 $cm^{-1}$. Anal. found: S, 5.38%. Its loading capacity was 1.68 mmol/g.

Regeneration of Linear Poly[4-hydroxy(tosyloxy)iodo]styrene

Methanol (200 ml) was added slowly to the recovered linear poly(4-iodostyrene) (4.5 g) in chloroform (70 ml) to yield neat linear poly(4-iodostyrene) (3.5 g), which was treated by a previously reported method[12] to obtain poly[(4-diacetoxyiodo)styrene] (4.8 g) and linear poly[4-hydroxy(tosyloxy)-iodo]styrene (5.4 g). IR (KBr) 3407, 1180, 1016, 816, 675 $cm^{-1}$. Anal. found: S, 6.12%. Its loading capacity was 1.93 mmol/g.

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