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Graphical Abstract

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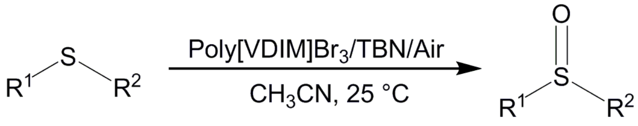

R^1, R^2 = Aryl or Alkyl

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A novel catalytic system poly(1-vinyl-3-dodecylimidazolium tribromide)/TBN for the oxidation of sulfides to sulfoxides with air as oxidant

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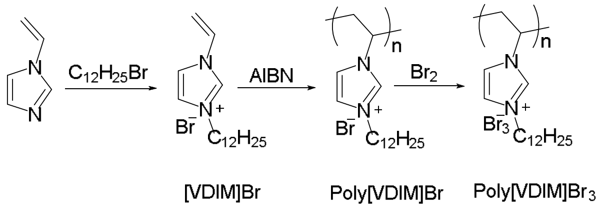
ABSTRACT

A novel and recoverable polymeric ionic liquid, poly(1-vinyl-3-dodecylimidazolium tribromide) (Poly[VDIM]Br_3), was successfully prepared and fully characterized. And a highly efficient metal-free catalytic system Poly[VDIM]Br_3/*tert*-butyl nitrite was developed for the oxidation of sulfides. With air as oxidant, we have successfully achieved 19 kinds of sulfides selectively and efficiently oxidized to corresponding sulfoxides using this catalytic system at room temperature.

Introduction

Selective oxidation of sulfides to sulfoxides is a significant and challenging organic reaction,[1] because the sulfoxide is a kind of important organic synthesis intermediate,[2] which is extensively utilized in medicine, pesticide,[3] heavy metal extraction,[4] oil desulphurization, organic synthesis[5] and other industries.[6,7] Therefore, a great deal of methods have been issued for the oxidation of sulfides to sulfoxides.[8-10] In recent years, as the oxidant, molecular oxygen has been more and more popular,[11] on account of its many outstanding advantages such as environmentally friendly, low cost and by-product as water. Nonetheless, the catalyst was needed to activate molecular oxygen for the oxidation of sulfides. There have been many reports that a dual component catalytic system consisted of bromine-containing and NO_X-containing reagents could successfully achieve the oxidation of sulfides to sulfoxides,[12-14] but most of them suffered from the troublesome drawback—the use of transition metal or acid, which may not environmentally friendly. Consequently, we sought to design a new kind of dual component catalytic system free from the drawback.

As we know, ionic liquids (ILs) are green and recyclable reagents and have attracted tremendous research interest.[15,16] Utilized as monomers, ILs have been frequently employed in the synthesis of polymeric ionic liquids (PILs) over the past few years. And the PILs are described as a novel class of materials combining the unique properties of ILs and the specificities of polymers. As compared to ILs, PILs not only inherit the eminent properties of the ILs, such as superior ionic conductivity, strong solubilizing ability and excellent chemical and electrical stability, but also present intrinsic polymer features and enhanced mechanical stability and durability.[17] Possessing these unique characteristics, PILs are promising candidates for different technological fields, such as materials,[18] catalysts,[19] biotechnology,[20] and surface science.[21] Furthermore, the Br_3^--containing regents which are more stable and benign than Br_2 have been extensively utilized, including phosphorus tribromide[22] and benzyltrimethylammonium tribromide.[23] There were a few reports that the Br_3-containing regents were utilized to oxidize the sulfides,[24,25] but they were used as oxidant, which were not as green as molecular oxygen as the oxidant. In addition, the catalytic mechanism of Br/NO_X systems have been extensively accepted,[26] and *tert*-butyl nitrite (TBN) as a good substitute for NO_X has been reported.[27] And our group have reported related articles of the oxidation of sulfides.[28,29] Accordingly, we designed a kind of Br_3^--containing PIL—poly(1-vinyl-3-dodecylimidazolium tribromide) (Scheme 1), it was not only an eligible substitute for Br_2 but also recoverable.



Scheme 1. Synthesis of the Poly[VDIM]Br_3

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Table 1. Aerobic oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide by Poly[VDIM]Br_3/TBN as the catalyst in different solvents[a]

Entry	Solvent	Time(h)	Yield(%)[b]
1	Acetonitrile	2	>99
2	Dichloromethane	2	3
3	Acetone	2	<1
4	Ethyl acetate	2	16
5	Tetrahydrofuran	2	4
6	n-Heptane	2	17
7	Acetonitrile/H_2O=1:1[c]	2	36

[a] Reaction conditions: methyl phenyl sulfide 10 mmol, Poly[VDIM]Br_3 (0.5 mmol, 0.25 g) , TBN 0.5 mmol, H_2O 1 mL, solvent 20 mL, 25 °C.

[b] Determined by GC Agilent 6890N and GC-MS.

[c] Volume ratio.

Herein, we report a novel and efficient catalytic system-Poly[VDIM]Br_3/TBN for selective oxidation of sulfides to corresponding sulfoxides under mild and metal-free conditions with air as oxidant (Table 2).

Results and Discussion

Optimization of the reaction solvents

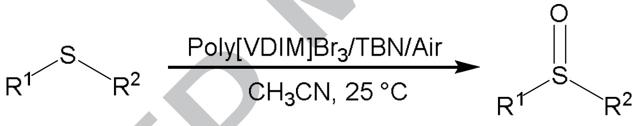
In order to find an appropriate solvent for the oxidation of sulfides to sulfoxides, different solvents for the oxidation of methyl phenyl sulfide as a typical example were screened. The results are summarized in Table 1. As is evident in Table 1, the oxidation reaction proceeds more rapidly in acetonitrile.

The oxidation of sulfides to sulfoxides

With the optimized conditions in hand, we report on the chemoselective oxidation of a variety of aliphatic and aromatic sulfides to their corresponding sulfoxides by Poly[VDIM]Br_3/TBN catalytic system in presence of water in acetonitrile at room temperature with air as oxidant. The results are shown in Table 2.

With this oxidation system, a variety of sulfides were successfully converted to sulfoxides with high conversion rate and it exhibited excellent catalytic efficiency. As was evident in Table 2, there existed obvious difference between the reaction time of different sulfides. Aromatic compounds sulfides with electron-withdrawing groups took more time than those with electron-donating groups. With regard to methyl phenyl sulfide which was aromatic compound, while its benzene ring was connected with the electron-withdrawing groups (-CO-,-X,-NO_2), like entries 5-14, the larger the groups, the time of the reaction may be longer. In addition, the reaction could also be excellently finished when with the electron-donating groups (entries 2-4, 15, 16). Besides, sulfides (entries 12, 14) that were not completely dissolved in acetonitrile probably attributed to considerable molecular volume could also be selectively oxidized to corresponding sulfoxides. With respect to aliphatic compounds

Table 2. Oxidation of sulfides to corresponding sulfoxides[a]

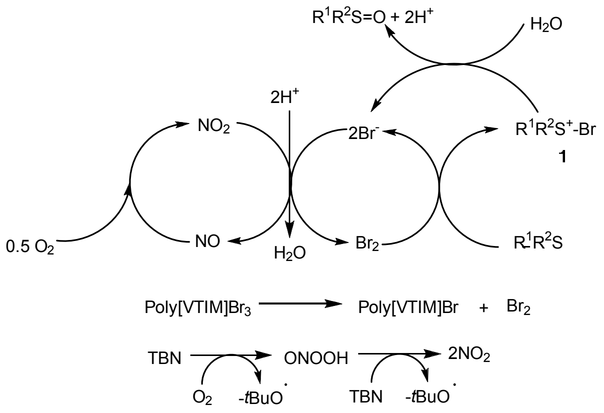


Entry	R^1	R^2	t/h	Conv.(%)[b]	Sel.(%)[b]	Yield(%)[c]
1	Ph-	CH_3	2.5	>99	>99	97
2	4-$CH_3C_6H_4$-	CH_3	2.5	>99	>99	96
3	4-$CH_3OC_6H_4$-	CH_3	2.5	>99	>99	96
4	2-$CH_3OC_6H_4$-	CH_3	2.5	>99	>99	96
5	4-FC_6H_4-	CH_3	3.0	>99	>99	95
6	4-ClC_6H_4-	CH_3	2.5	>99	>99	96
7	2-ClC_6H_4-	CH_3	6.0	>99	>99	96
8	2-BrC_6H_4-	CH_3	5.0	>99	>99	97
9	4-$NO_2C_6H_4$-	CH_3	13	>99	>99	96
10	4-$HCOC_6H_4$-	CH_3	5.5	>99	>99	95
11	4-$CH_3COC_6H_4$-	CH_3	6.5	>99	>99	96
12	4-$PhCOC_6H_4$-	CH_3	8	>99	>99	96
13	4-$CH_3COOC_6H_4$-	CH_3	8	>99	>99	97
14	4-$PhCOOC_6H_4$-	CH_3	8	>99	>99	97
15	Ph-	CH_3CH_2-	2.5	>99	>94	92
16	Ph-	$HOCH_2CH_2$-	5	>99	>91	88
17	-$(CH_2)_4$-		5	>78	>99	71
18	$CH_3CH_2CH_2CH_2$-	$CH_3CH_2CH_2CH_2$-	5	>99	>99	94
19	$CH_3(CH_2)_{11}$-	CH_3	5	>93	>99	89

[a] Reaction conditions: sulfides (10 mmol), Poly[VDIM]Br_3 (0.5 mmol, 0.25 g), TBN (0.5 mmol), H_2O (0.5 mL), CH_3CN (20 mL), air, 25 °C.

[b] Determined by GC Agilent 6890N and GC-MS.

[c] Isolated yield.



Scheme 2. Mechanism of the oxidation of sulfides

sulfides (entries 17-19), the oxidation reaction could also achieve with high selectivity and efficiency.

Mechanism

A plausible mechanism for this novel and metal-free catalytic oxidation process can be described by the dual cycle shown in Scheme 2. Firstly, the lone pair electrons on sulfur atom in sulfide are attacked by Br^+ which is derived from Br_2 in the Poly[VDIM]Br_3 and generate the intermediate product **1**. Then the intermediate product hydrolyzes and the corresponding sulfoxide is obtained. What needs to be particularly stated is that H_2O provides the oxygen atom and accelerate the formation of sulfoxide. In addition, the Br^- is continuously reoxidized to Br_2 by NO_2, which is the key for a catalytic amount of Br_2 to oxidize sulfide substrates, the NO_2 is reduced to NO and H^+ is turned to H_2O simultaneously. The NO is easily released from TBN as an efficient NO equivalent and NO can easily be oxidized to NO_2 by O_2 in the air. The coupling of the two cycles form a novel and efficient aerobic sulfide oxidation system.

After the oxidation reaction was terminated, the solid Poly[VDIM]Br generated from the Poly[VDIM]Br_3 could be conveniently isolated by filtration, with the further washing with acetonitrile for three times and vacuum drying at 45 °C for 6 h, and the fresh Poly[VDIM]Br_3 could be uncomplicatedly prepared through it reacting with bromine again according to the preparation steps, which made the whole catalytic reaction more green and thoroughly met the requirements of green chemistry.

With respect to green and sustainable chemistry, it was undeniable that the Poly[VDIM]Br_3/TBN catalytic system was more attractive, because it not only possessed high selectivity and efficiency for the oxidation of sulfides to sulfoxides without using any metal and acid at room temperature but also hardly generated potentially deleterious byproduct like sulfones. In addition, as an ideal regent, the Br_3^- in the Poly[VDIM]Br_3 was an exceedingly stable state relative to Br_2, and Poly[VDIM]Br was still a good "carrier" for the Br_2.

Characterization of Poly[VDIM]Br_3

The FT-IR spectra of [VDIM]Br, Poly[VDIM]Br and Poly[VDIM]Br_3 were illustrated in Fig. 1. The [VTIM]Br (curve a) exhibited several characteristic peaks. The peaks at 3092 (C-H), 1642 (C=C), 960 (C-H) and 915 cm^{-1} (C-H) showed the existence of the $-HC=CH_2$ of imidazole side chain, and those at 3144 (C-H), 1551 (C=N), 1466 (C=C) and 1172 cm^{-1} (C-N) showed the existence of the imidazole ring. The peaks at 816, 769, and 625 cm^{-1} were derived from in-plane and out-of-plane rings C–H bending for imidazole. Moreover, the bands at 2922 ($-CH_2$), 2853 ($-CH_2$), 1466 ($-CH_2/-CH_3$), 1377 ($-CH_3$) and 722 cm^{-1} ($-CH_2-$) were assigned to the long carbon side chain. After [VTIM]Br through polymerization (curve b), the intensity of the peaks at 1642, 960 and 915 cm^{-1} were too weak to be observed which indicated the unsaturated carbon-carbon double bond had disappeared. After Poly[VDIM]Br reacting with Br_2 (curve c), the intensity of the peaks at 825, 739 and 648 cm^{-1} were remarkably enhanced. The existence of the Br_3^- was proved by Raman spectra.

The Raman spectra of Poly[VDIM]Br and Poly[VDIM]Br_3 were presented in Fig. 2. It was evident that there was no distinctive characteristic peaks in the Raman spectra of Poly[VDIM]Br (curve a). As compared to it, the Poly[VDIM]Br_3 clearly showed two characteristic peaks at 163 and 210 cm^{-1} (curve b), in agreement with previous report.[30] The harmonic vibrational frequency of Br_2 was about 325 cm^{-1}. As was obvious in the curve b, there was no peak at 325 cm^{-1}, indicating that there was no free bromine in the Poly[VDIM]Br_3. Therefore, the collective evidence strongly suggests that the formation of the Poly[VDIM]Br_3 through the FT-IR and Raman spectra.

Thermal stabilities of Poly[VDIM]Br and Poly[VDIM]Br_3 were investigated by TG analysis in Fig. 3. The decomposition temperature of the Poly[VDIM]Br (curve a) was about 275 °C, indicating a nice thermal stability. The weight loss of Poly[VDIM]Br was nearly 63.7% in the temperature range 275-335 °C, which was attributed to the decomposition of C-C bonds including carbon backbone in the main and side chain. There was nearly no mass loss after 335 °C, which was mostly due to the strong electrostatic interaction between the polymeric cation and the Br-anion. In contrast, the decomposition temperature of Poly[VDIM]Br_3 (curve b) was about 189 °C and 275 °C, respectively. And they had similar shape of curves after 275 °C, indicating that there probably existed the same substance when temperature up to 275 °C. By the synthetic step, Poly[VDIM]Br_3 was synthesized by Poly[VDIM]Br and Br_2. Therefore, what could be deduced was that Br_2 was firstly released and Poly[VDIM]Br_3 was decomposed into Poly[VDIM]Br at about 189 °C. In addition, it was certain that Poly[VDIM]Br and Br_2 were not simply physically adsorbed and Poly[VDIM]Br_3 was really synthesized. And this observation confirmed the rationality of the chemical structure of Poly[VDIM]Br_3 shown in Scheme 1.

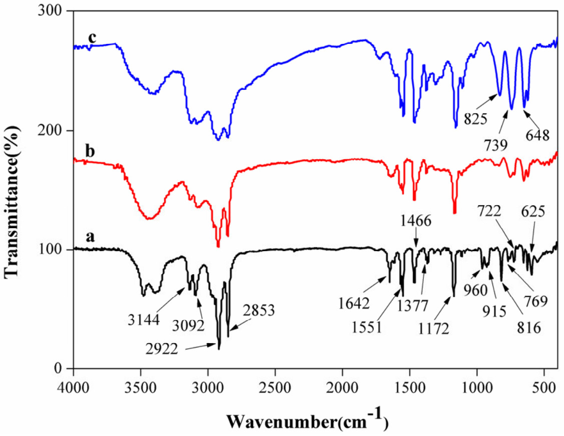


Figure 1. FT-IR spectra of (a) [VTIM]Br, (b) Poly[VDIM]Br and (c) Poly[VDIM]Br_3

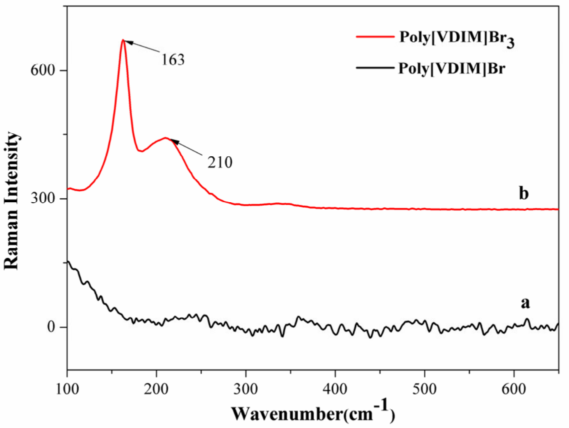


Figure 2. Raman spectra of (a) Poly[VDIM]Br and (b) Poly[VDIM]Br$_3$

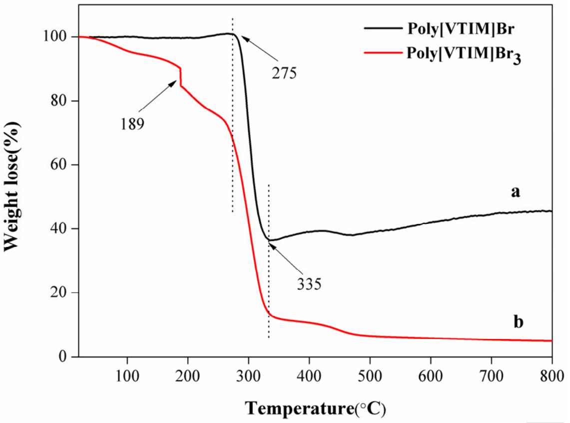


Figure 3. TG curves of (a) Poly[VDIM]Br and (b) Poly[VDIM]Br$_3$

Conclusion

In summary, a novel and recoverable PIL-Poly[VDIM]Br$_3$ was successfully prepared and fully characterized through TGA , FT-IR and Raman spectra. The Poly[VDIM]Br$_3$/TBN catalytic system equipped with high selectivity and efficiency was developed for the aerobic oxidation of 19 kinds of sulfides at room temperature. More importantly, the Poly[VDIM]Br$_3$ was readily prepared from green solvent ionic liquid, easily isolated from reaction mixture and renewable, which met the requirements of green chemistry.

Acknowledgments

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Supplementary Material

Supplementary data (^{1}H NMR, ^{13}CNMR spectra of all compounds) associated with this article.

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Highlights

1. The catalytic system exhibits high selectivity for the oxidation of sulfides to sulfoxides.
2. Excellent yield of sulfoxide was obtained with air as oxidant under mild conditions.
3. The polymeric ionic liquid can be easily isolated and recoverable after the completion of the oxidation reaction.