



Efficient preparation, uses, and recycling of a polymer-bound sulfonylhydrazide scavenger



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ABSTRACT

Polymer-bound sulfonylhydrazide was prepared from commercial sulfonic acid resin through a straightforward, one-step synthetic route avoiding chlorosulfonic intermediates. The simplex self-directing optimization method was used to determine rapidly the ideal operating conditions under microwave irradiation. Polymer-bound sulfonylhydrazide has found an application as scavenging agent in winemaking therefore, this clean preparative approach is expected to be more acceptable by wine-makers. An efficient recycling protocol of the used supports has also been established.

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1. Introduction

Polymer-supported scavengers have become a widespread tool in organic chemistry for the rapid and efficient purification of complex mixtures.¹ Sulfonylhydrazide-functionalized polystyrene bead (SHPS) is a well-acknowledged scavenger for the removal of aldehydes and ketones (Fig. 1).² SHPS have been used recently for the complete removal of reducing glycans through their aldehyde functional group from complex mixtures for HPLC/MS analysis.³ Sulfonylhydrazide resin was also used as a linker for carbonyl compounds in a 'catch and release' strategy for the preparation of a series of 1,2,3-thiadiazoles.⁴ It has also been used as generator of polymer-supported diimide for pericyclic reactions,⁵ and for protein extraction in aqueous media.⁶

Sulfur dioxide is now considered a toxic chemical by most of the world health authorities. However, it remains an irreplaceable additive in enology for wine conservation, combining antioxidant and antibacterial properties. Sweet white wines retain particularly high SO₂ levels due to their high sulfur dioxide binding power. We have previously developed a unique method for reducing this binding power by removing some of the carbonyl compounds responsible,

which are naturally present in these wines. The method retained was selective liquid–solid removal, using phenylsulfonylhydrazide grafted on porous polymer supports as a scavenging agent. The results obtained showed that the method was efficient for removing carbonyl compounds and significantly reduced the binding power of the wines under conditions intended to conserve their organoleptic qualities.^{7–9}

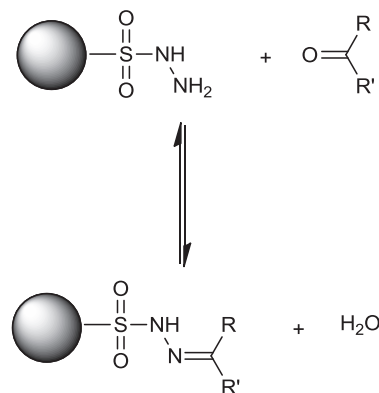


Fig. 1. Scavenging reaction using polymer-bound sulfonylhydrazide.

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In order to use the process on an industrial scale, we needed to develop an efficient, clean, and cheap synthetic route to access this scavenger in large quantities, as commercially available SHPS is far too expensive (about 5000 USD/kg) for a practical application in winemaking process.

Polymer-supported sulfonylhydrazide is usually obtained from sulfonic resin by chlorination with thionyl chloride, followed by hydrazine hydrate treatment (Fig. 2).¹⁰ Another reaction involves the chlorosulfonation of polystyrene/divinylbenzene (PS/DVB) beads followed by treatment with hydrazine hydrate in polar media (Fig. 3).¹¹

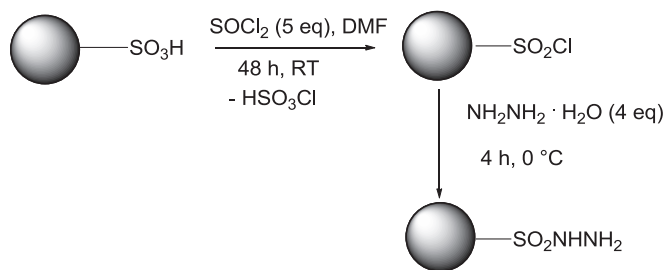


Fig. 2. Classical synthetic route to polymer-bound sulfonylhydrazide.

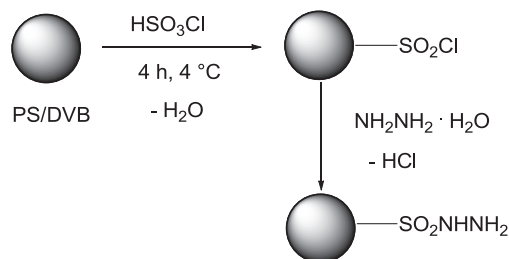


Fig. 3. Second classical synthetic route to polymer-bound sulfonylhydrazide.

The disadvantages of these synthetic routes are that they require the use of toxic reagents and/or solvents, which may be detrimental for wine chemistry applications.

In this study, we examined a cleaner and straightforward access to polymer-supported sulfonylhydrazide, starting from commercial PS/DVB sulfonic resin. We also investigated the recycling of the polymer-supported sulfonylhydrazide obtained after the scavenging reaction.

2. Results and discussion

Microwaves have been recently reported to convert efficiently several carboxylic acids into their hydrazide derivatives ($R\text{-CONHNH}_2$).¹² Furthermore, we have shown in a previous paper that sulfonic acid functions grafted on lignin beads could be directly converted into sulfonylhydrazide under microwave irradiation¹³ (Fig. 4). The reaction can be performed in aqueous media with only a slight excess of hydrazine hydrate as sole reagent.



Fig. 4. Microwave synthesis of polymer-bound sulfonylhydrazide.

Therefore, we decided to try this method on a commercially available PS/DVB sulfonic resin, Dowex™ monosphere 650C, as it meets the requirements of FDA Food Additive Regulation 21 CFR 173.25. The SO_3H loading of the resin was estimated to be 4.50 ± 0.05 mmol/g.

We were interested to find rapidly the optimal conditions of hydrazination under microwave irradiation. Thus, we used a rational approach for the optimization of the values of the different parameters involved in the reaction. Amongst the various methodologies developed by experimental strategists, the self-directing method (also called the simplex method) first presented by Spendley et al.¹⁴ appeared to be most attractive from a synthetic chemist's point of view, being mathematically simple and easy to implement. The simplex method, under its more or less sophisticated improvements, has found numerous applications in biochemistry,¹⁵ material chemistry,¹⁶ analytical chemistry,¹⁷ and in organic synthesis.^{18–20}

The sequential simplex method of optimization is a strategy that rapidly and efficiently locates the region of the optimum by varying all factors simultaneously.²¹ A simplex is a geometric figure defined by a number of points (experiments) equal to one more than the number of variables (dimensions). A self-directing optimization begins with a patterned set of experiments for all of the interesting variables. The pattern is a triangle for two variables, a tetrahedron for three variables, or a simplex (i.e., a multidimensional triangle) for four or more variables. Once this pattern has been run, the experiment that produced the worst result is identified. This experiment is then discarded and replaced by a new experiment according to a definite rule. In this work, we determined the position (parameters) of the replacement point by the simple rule: "Twice the average of the best points minus the worst point" as proposed by Hendrix.²² When this replacement experiment has been run, the worst point of the new set is identified and discarded yet again. This will continue until no further improvement is observed.

To conduct the optimization, it is first necessary to select the parameters that are expected to have the greatest influence on the yield of the reaction. In our case, four parameters were selected: the reaction temperature (T), the reaction time (t), the pH of the aqueous solution, and the molar ratio hydrazine hydrate/polymer-supported sulfonic acid (R). Limits were imposed on each parameter in order not to reach too drastic operating conditions. Imposed limits of the chosen system were as follows: $30\text{ °C} < T < 200\text{ °C}$; $15\text{ min} < t < 120\text{ min}$; $0 < \text{pH} < 14$; $1 < R < 4$.

Since our system had four variables, the self-directing optimization started with a set of five experiments carried out randomly in the experimental domain limited by the imposed range of values for each variable. The loading of sulfonylhydrazide moieties grafted on support was then determined for each experiment and the yield calculated from the initial sulfonic acid resin loading. The results obtained are reported in Table 1. Besides, the remaining SO_3H loading of the resin was also determined for each experiment. The values obtained matched very well the difference—initial SO_3H loading minus sulfonylhydrazide loading, which validates the sulfonylhydrazide titration method.

The worst grafting yield was obtained with the third experiment. So, point **3** was replaced by a new one (point **6**) using the Hendrix's process (Table 2). This method was repeated until no significant improvement of the yield was observed (Table 3).

Point **5** has now become the worst point and was replaced by point **7**. Successive replacements allowed reaching the highest accessible yield (87%) for point **10**. Nonetheless, the experimental conditions for that experiment were rather harsh: reaction time $t=103.5$ min; reaction temperature $T=175\text{ °C}$; $\text{pH}=14$; $\text{NH}_2\text{NH}_2/\text{SO}_3\text{H}$ molar ratio $R=5.5$.

Further replacements did not improve that value; the self-directing optimization was thus stopped at point **14**. At that

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