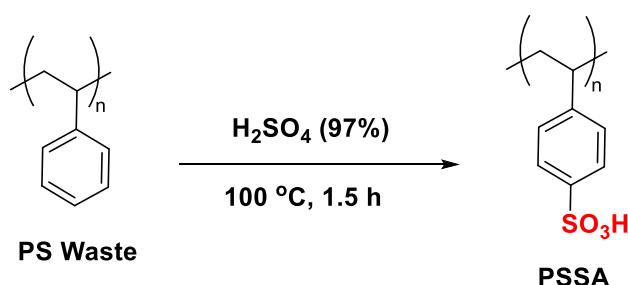


## Experimental Protocol for the Preparation of Polystyrene Sulfonic Acid (PSSA)



**Reference:** RSC Sustainability, 2026,4, 1986-1995. <https://doi.org/10.1039/D5SU00927H>

### WATH OUR STEP-BY-STEP VIDEO OF THIS PROTOCOL

1 g of expanded polystyrene (PS) waste is first dissolved in the minimum amount of ethyl acetate in a beaker. The resulting solution is transferred to a round-bottom flask, and the solvent is evaporated using a rotary evaporator with a water bath set at 35 °C. The flask is left connected to the rotavapor for an additional 20–30 minutes to ensure complete removal of the solvent.

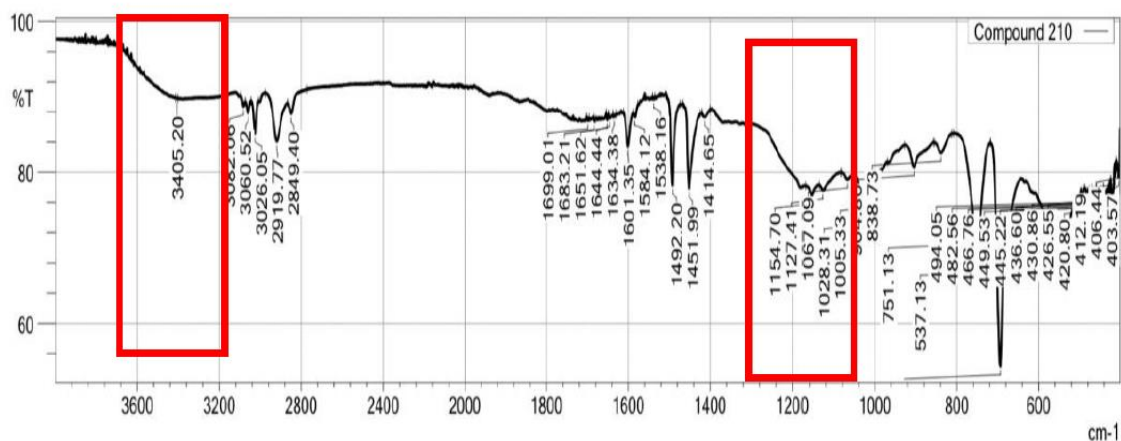
The reduced PS is then scraped from the walls of the flask using a spatula and evenly distributed across the bottom to minimise volume. The flask is clamped to a stand, and 10 mL of concentrated sulfuric acid is added along with a Teflon-coated magnetic stirring bar.

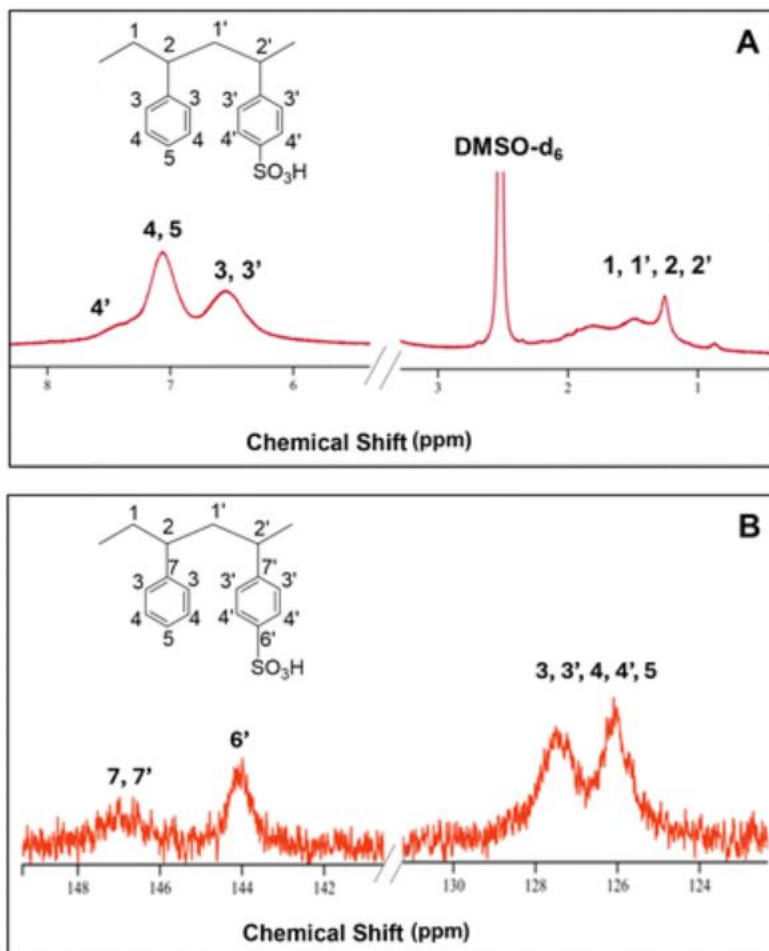
The reaction mixture is heated at 100 °C for 1.5 hours using a heating block. It is recommended to use a glass rod during the reaction to help submerge any PS fragments not fully in contact with the acid. **Note: Do not use a metal spatula, as it will dissolve in hot sulfuric acid.**

After the reaction, the mixture is cooled in an ice-water bath, and ice-cold water is slowly added. A rubbery solid precipitates, which is then filtered under vacuum and washed thoroughly with deionised water until the filtrate reaches neutral pH.

The solid is dried overnight in an oven at 70 °C, yielding a yellowish-white product. The resulting PSSA is insoluble in deuterated solvents and is characterised by FTIR spectroscopy. The number of acidic sites is [determined by titration with a 0.01 M NaOH solution using phenolphthalein as an indicator.](#)

Typical yields range from 0.9 to 1.2 g of PSSA, with degrees of sulfonation between 30% and 45%.





An approximation of the degree of sulfonation of polystyrene sulfonic acid (PSSA) can be calculated by determining the number of acidic protons from the sulfonic acid ( $-\text{SO}_3\text{H}$ ) groups present in the polymer. While this method provides a useful estimate, the precise sulfur content should ideally be determined by elemental analysis. Nevertheless, calculating the number of active acid sites allows us to evaluate the catalytic potential of PSSA in organic synthesis.

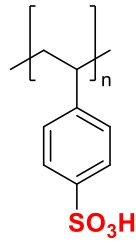
The degree of sulfonation is determined by titrating a sample of PSSA with a 0.01 M NaOH solution in water, using phenolphthalein as an indicator. Since PSSA is not soluble in water, the titration is performed as a suspension. The colour change can be slow and may lead to false positives, so the titration should only be considered complete if the pink colour (typical of phenolphthalein in basic solution) persists for 15–20 minutes. For better visibility, it is recommended to place a piece of white paper under the conical flask during titration.

To calculate the degree of sulfonation, we consider the mass of the repeating unit of a fully para-sulfonated polystyrene resin. The molar mass of this unit is 184.02 g/mol, meaning that 1 g of fully sulfonated PS contains:

$$1000 \text{ mg} / (184.02 \text{ mg/mmol}) \sim 5.4 \text{ mmol.}$$

$$1000 \text{ mg} \times 1 \frac{\text{mmol}}{184.02 \text{ mg}} \sim 5.4 \text{ mmol}$$

Meaning that a fully sulfonated resin has 5.4 mmol of  $\text{H}^+$  in 1g of resin.



**Repeating unit of PSSA**

(mass of 184.02 g/mol, C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>S<sub>2</sub>)

In a typical protocol, 20 mg of PSSA are suspended in 20 mL of distilled water in a small conical flask. Two drops of phenolphthalein solution are added as an indicator, and the resin is titrated with 0.01 M NaOH. If the titration endpoint is reached at 4.75 mL of NaOH, the degree of sulfonation is calculated as:

$$0.01 \frac{\text{mmol}}{\text{mL}} \times 4.75 \text{ mL} \times \frac{1}{0.02} \text{ g} = 2.37 \text{ mmol of H}^+ \text{ per gram of resin}$$

$$0.01 \text{ mmol/mL} \times 4.75 \text{ mL} \times 1/0.02 \text{ g} = 2.37 \text{ mmol of H}^+/\text{g of resin}$$

Given the theoretical maximum of 5.4 mmol/g, then the percentage of sulfonation is:

$$\frac{2.37}{5.4} \times 100 = 43.8 \sim \mathbf{44\% \textit{ sulfonation}}$$

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