

## New Insights in Sulfur Dioxide Scavenging: Study of the Reversible Interaction Between Polyamines and Mixed Polyamines-Polyacrylic Acid Polimers with Sulfur Dioxide

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### Highlights

Polyamines (PPI Dendrimers and Hyperbranched PEI) and particularly their mixed polymers with Polyacrylic Acid show great and reversible uptake of SO<sub>2</sub> compared with other amine based materials

### Resumo/Abstract

Sulfur dioxide (SO<sub>2</sub>) is an important atmospheric pollutant, with serious implications for the occurrence of acid rain, human health problems and interference with the normal development of plants. Therefore, there is an urgent need to develop effective SO<sub>2</sub> capture systems. In the present study has been investigated the interaction of gaseous SO<sub>2</sub> and polyamines, namely: i) Polypropyleneimine Dendrimers (generations 1 → 3; PPI-G1; PPI-G2; PPI-G3) and ii) hyperbranched polyethyleneimine (PEIb); as well as the respective mixed polymers of these polyamines with polyacrylic acid (PAA@Polyamine). Unlike the interaction of monomeric amines that form molecular complexes with SO<sub>2</sub>, polyamines generate bisulfite (HO-SO<sub>2</sub><sup>-</sup>) and sulfite (SO<sub>3</sub><sup>2-</sup>) by acid-base reactions between water strongly linked by hydrogen bonds to polyamines and SO<sub>2</sub>, as unequivocally shown by Raman spectroscopy. Interestingly, TGA-MS studies show that upon heating the acid-base reaction is reversible and SO<sub>2</sub> is released. The SO<sub>2</sub> uptake capacity is presented in the Table:

| Polyamine | SO <sub>2</sub> uptake (mmol/g) | PAA@Polyamine | SO <sub>2</sub> uptake (mmol/g) | Ratio |
|-----------|---------------------------------|---------------|---------------------------------|-------|
| PPI-G1    | 3,35                            | PAA@PPI-G1    | 6,54                            | 1,9   |
| PPI-G2    | 4,55                            | PAA@PPI-G2    | 7,54                            | 1,7   |
| PPI-G3    | 4,82                            | PAA@PPI-G3    | 7,90                            | 1,6   |
| PEIb      | 6,12                            | PAA@PEIb      | 8,53                            | 1,4   |

It can be clearly seen that the incorporation of polyamine into the mixed polymer significantly increases the incorporation of SO<sub>2</sub>, especially in mixed polymers containing dendrimers (PAA@PPI-G1 / PAA@PPI-G2). In these cases, we have an increase of 1,9 and 1,7 times respectively for PAA@PPI-G1 and PAA@PPI-G2; and for PAA@PEIb the increase is comparatively smaller but still significant with an uptake increment of 40%.

The polyamines and particularly the mixed PAA@Polyamines show great incorporation of SO<sub>2</sub> compared with other recently reported materials such as silica-supported dendrimers [1], polystyrene polymers with diamines [2] or cross-linked tetramethylguanidine acrylate polymers [3] with absorption maxima of 4,68; 3,40 and 4,06 mmol/g of absorbent material respectively with similar SO<sub>2</sub> gas absorption experiments, therefore mixed polymers are promising platforms for reversible SO<sub>2</sub> uptake.

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