2º BRAZILIAN SYMPOSIUM ON NANOTECHNOLOGY ENGINEERING
Exploring the interfaces of the nanometric world
September 30th to October 4th 2024

REAL-TIME MONITORING OF SOL-GEL PROCESS BY ^{1}H NMR RELAXATION FOR SYNTHESIS OF SILICA NANOPARTICLES

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Keywords: *sol-gel process. NMR relaxation. real-time monitoring.*

The sol-gel process is a chemical method for obtaining various nanoparticles. Although it has many advantages and possibilities for structural control of the final product, the reaction kinetics are generally complex [1]. Proton nuclear magnetic resonance (NMR) relaxation has become popular as a non-invasive tool for monitoring fast chemical reactions, capable of performing real-time acquisitions and providing data about kinetics and different stages of the synthesis, based on relaxation times [2]. In this work, NMR relaxation was tested for the first time in monitoring the synthesis of silica nanoparticles (SiO_2) in aqueous sol-gel with alkaline catalysis.

The alkoxide precursor used was a 5% w/v solution of 3-methacryloxypropyltrimethoxysilane (MPTMS) and NaOH (0.01 M) as an alkaline catalyst. Two compositions were prepared. Composition 1: 300 µL MPTMS + 550 µL distilled water + 150 µL 0.01 M NaOH. Composition 2: 200 µL MPTMS + 750 µL distilled water + 50 µL 0.01 M NaOH. Both compositions had a total volume of 1 ml. Relaxation measurements were performed on a Maran ULTRA NMR at 0.5 T (23.4 MHz for ^{1}H) at room temperature. Transverse relaxation times (T_{2*}) obtained by Solid Echo were acquired every 2 min. A total of 360 measurements were made during the sol-gel process for each composition.

Each relaxation signal was fitted with the equation below:

$$A(t) = F_i \exp\left[\left(\frac{-t}{2T_{2*}^{i}}\right)^2\right] + F_b \exp\left[\left(\frac{-t}{T_{2*}^{b}}\right)\right] + k$$

Where $T_{2*}{}^{i}$ and F_i are the relaxation times and the percentage of solvents (water and alcohol) at the nanoparticle interface and $T_{2*}{}^{b}$ and F_b are the relaxation times and the percentage of bulk solvents (far from the interface). Figure 1 shows an example of a fit for one of the relaxation signals obtained in this study.

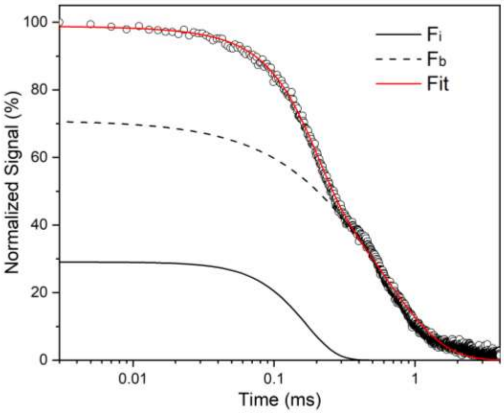

Figure 1: Relaxation signal obtained by Solid Echo and decomposition into two components.

The combination of 360 measurements provided a profile of the evolution of the sol-gel process (Figure 2).

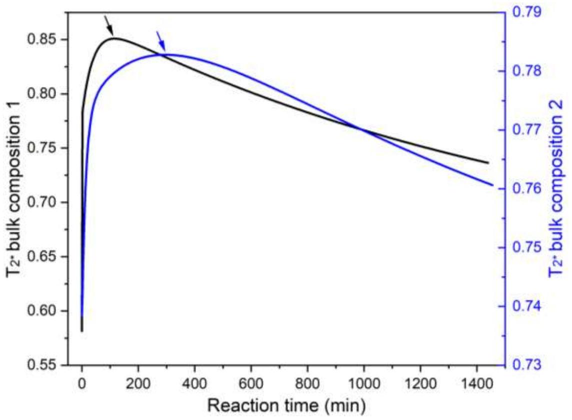

Figure 2: Real-time monitoring of the sol-gel process based on T_{2*}^{b} values.

The first region (rapid increase of T_{2*}^{b}) is related to the first hydrolysis and polycondensation reactions. The second region (slower increase of T_{2*}^{b}) is related to the growth of the clusters. The third region (decrease of T_{2*}^{b}) is related to the gel formation. And the maximum point can be attributed to the gel point for each composition. As expected, the more dilute sample has a longer gel point.

From the transverse relaxation, it was possible to visualize the main stages of the sol-gel process, including the gel point.

Therefore, proton NMR relaxation was able to monitor in real time a sol-gel process for the synthesis of SiO_2 nanoparticles, for two different compositions. An increase in 200 µL of distilled water extended the gel point time by approximately 200 min. In addition, the transverse relaxation time of the solvents far from the interface was more sensitive during the reactions, allowing the identification of the main steps. Since this NMR relaxation methodology was used as an unprecedented method, adjustments may be made in future work for other formulations.

REFERENCES

1. Singh, Lok P. et al. **Advances in colloid and interface science**, v. 214, p. 17-37, 2014.
2. Rodrigues, E. J. R. et al. **Polymer International**, v. 67, n. 6, p. 675-683, 2018.

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