



## Preparation and structural characterization of sodium polyphosphate coacervate as a precursor for optical materials



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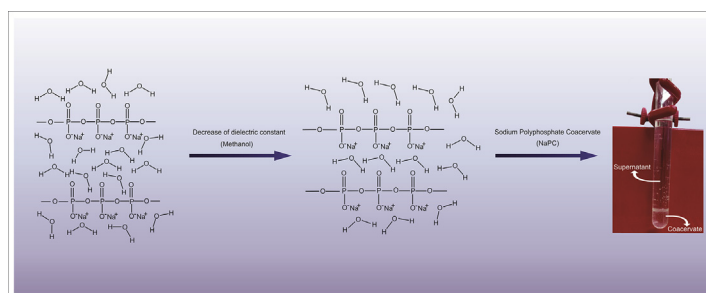
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### HIGHLIGHTS

- Sodium Coacervates Polyphosphates (NaPC) were prepared.
- Methanol reduces the dielectric constant and it leads to coacervation process.
- NaPC can be used as soft Glass-Materials precursors.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This paper describes the preparation of Sodium Polyphosphates Coacervates (NaPC) through the direct addition of different methanol molar fractions to a sodium polyphosphate solution. The presence of methanol reduces the dielectric constant medium and it promotes the coacervate formation. Rheology measurement shows that the NaPC viscosity is dependent on a methanol molar fraction, which is caused by the dielectric constant reduction of the water-methanol mixture. Raman spectra for the lyophilized NaPC show that the symmetric P-O<sub>t</sub> stretching mode is more sensitive than the symmetric P-O<sub>b</sub> stretching mode, due to the approach of the adjacent polyphosphate chains. The <sup>31</sup>P NMR spectra also confirm a decrease in the Q<sup>2</sup>/Q<sup>1</sup> ratio because of the methanol content. Besides, we have obtained transparent soft Glass-Materials to melt NaPC at 800 °C.

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## 1. Introduction

Polyphosphate Coacervates (PC) are colloidal systems obtained by polyphosphate solutions destabilization through the addition of electrolytes or solvents solutions featuring a lower dielectric

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constant than water [1]. “Coacervates”, is a word derived from Latin, in which “co” (together) and “acerv” (a heap) [2–4]. They are formed by the interaction between aqueous sodium polyphosphates solutions and different cations, including  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Al}^{3+}$ , and lead to a separation of phases [5–10]. The most viscous phase, richer in colloids, is called coacervate, while the less viscous is called supernatant [1]. The interaction between the metaphosphate chains and the metal ions  $\text{Ca}^{2+}$  and  $\text{Eu}^{3+}$  has been studied in water through  $\text{Eu}^{3+}$  luminescence, FTIR and  $^{31}\text{P}$  NMR spectroscopy [11]. Two main families of sites can be identified for the metal ions in the aqueous polyphosphate colloidal system: (1) cagelike sites provided by polyphosphate chains and (2) a family which emerges followed by the saturation of cagelike sites. The occupation of this second family leads to supramolecular interactions between polyphosphate chains and a consequent destabilization of the colloidal system [11].

The coacervation process may be also induced by the addition of a low molecular weight solvent [2,4]. According to the method proposed by Umegaki et al. it is necessary the adding of 10% in volume of methanol in the solution to obtain the liquid–liquid phase separation and formation of the coacervates [1]. Willots et al. studied the coacervation process as an alternative route for glasses preparation. He highlights the use of ethanol as a solvent for the phase separation process [12]. Silva et al. prepared a great amount of transparent amorphous materials using the coacervation process of sodium polyphosphate or Graham Salt containing  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$  applying methanol to reduce the dielectric constant of the mixture [5,13]. The proposal and understanding of the coacervation process on the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  coacervates using 10% of methanol was also studied through X-ray Absorption Spectroscopy (EXAFS analysis) and Raman Spectroscopy [14]. Concerning the applications, coacervates have a great potential for bone substitution [15,16], incorporation of organic compounds [17], drug delivery systems [18], biomedical applications [19], optical devices [20] and absorption of heavy metal ions [21].

Saegusa et al. studied the effect of the addition of three different alcohols in the preparation of lipid vesicles using the coacervation process [22]. In this study, Saegusa et al. prepared lipid vesicles (liposomes) using the coacervation process by the addition of methanol, ethanol and 1-propanol in the phospholipid water system to determine the optimum conditions for the formation of coacervation. Umegaki and Kanazawa researched the viscosities of magnesium and calcium highpolyphosphates coacervates in the range of 20 °C–90 °C without addition of ethanol [6]. The results showed that magnesium and calcium highpolyphosphates coacervates presented Newtonian behavior in different temperatures. The addition of water to magnesium highpolyphosphates decreased the viscosity while no degradation of the polyphosphate chains in solution was observed.

Momeni and Filiaggi studied the rheological properties of the polyphosphate coacervates, which demonstrated themselves as Newtonian liquids. Their low shear rates and viscosity are directly related to the chain length of the sodium polyphosphate and divalent cation type ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Ca}^{2+}$ ) for the material preparation. The study shows a small fraction exchange of  $\text{Ca}^{2+}$  for  $\text{Sr}^{2+}$  or  $\text{Ba}^{2+}$  allowing the obtaintion of more elastic coacervates with higher viscosity than that having only calcium coacervates [23].

In this paper, we studied the influence of different methanol molar fractions on the coacervation process of a sodium polyphosphate solution, without the presence of di- or trivalent metallic ions. Furthermore, a glass derived from sodium coacervate was prepared in order to demonstrate its potential as a new precursor for optical materials. We studied the structural and spectroscopic properties of the sodium coacervates by means of rheological measurements, scanning electronic microscopy (SEM),

energy dispersive X-Ray spectroscopy (EDS), Raman spectroscopy,  $^{31}\text{P}$  solid-state nuclear magnetic resonance (NMR), X-ray diffraction and differential scanning calorimeter (DSC).

## 2. Experimental procedure

### 2.1. Coacervate preparation

Sodium polyphosphate coacervates, NaPC, were prepared according to the methodology proposed earlier by Umegaki et al. [1]. Different molar fractions ( $x = 4.25; 8.17; 11.8; 15.1; 18.2; 23.7$  and 30.8%) of methanol (Synth P.A) were slowly added to a 4 mol L<sup>-1</sup>  $\text{Na}(\text{PO}_3)_n$  solution (Merck), under constant stirring. Samples were renamed as described in Table 1

### 2.2. Coacervate characterization

The viscosity behavior of the coacervates was studied by rheological measurements using TA instruments AR2000 rheometer at 25 °C. For each sample, flow curves were measured at the increasing shear rate from 0.1 to 100 s<sup>-1</sup>. The flow curves were fitted by Power's law ( $\sigma = k \dot{\gamma}^n$ ) to obtain flow behavior ( $n$ ); consistency index ( $k$ ); and coefficient of determination ( $r^2$ ). The appearance viscosity ( $\eta_{\text{ap}}$ ) of samples was determined by the average viscosity values of the viscosity curves.

After coacervation, samples were frozen in a biofreezer at -20 °C for 24 h and subsequently they were lyophilized in a L101 LIOTOP freezer-dryer for 12 h. The structural and spectroscopic properties of the lyophilized sodium coacervates were studied by the following techniques:

Raman scattering spectra were recorded at room temperature in a frequency range of 200–1500 cm<sup>-1</sup> in a HORIBA Jobin Yvon model LabRAM HR micro Raman apparatus equipped with a 632.8 nm laser delivering 17 mW.

Differential scanning calorimetry (DSC) measurements for both NaPC lyophilized sodium coacervates and coacervate glass were carried out in a temperature range from 25 to 600 °C at a heating rate of 10 °C min<sup>-1</sup> using the DSC Q600 equipment from TA Instruments. In such conditions, samples were encapsulated in aluminum crucibles under a flowing nitrogen atmosphere (70 mL min<sup>-1</sup>) and estimate error is  $\pm 2$  °C for  $T_g$  and  $T_x$ .

Powder X-ray diffraction measurements were carried out with a Siemens Kristalloflex diffractometer operating with a Ni filtered  $\text{CuK}\alpha$  radiation source, step scanning was performed at  $2\theta$  angle ranging 10–80° with a step pass of 0.01° and a step time of 2 s.

SEM images and energy dispersive X-ray spectroscopy (EDS) for the samples NaPC4.25 and NaPC30.8 were obtained using the field emission scanning electron microscope JEOL JSM-7500F.

Solid state NMR experiments were carried out at room temperature on a Bruker Avance III 400WB HD spectrometer, using a 4 mm MAS-NMR probe at a spinning speed of 14 kHz.  $^{31}\text{P}$  NMR measurements were carried out at 162.0 MHz, using 90° pulses of

**Table 1**  
Compositions of the NaPC prepared by addition of different methanol molar fractions.

Samples	Methanol molar fractions (x%)
NaPC4.25	4.25
NaPC8.17	8.17
NaPC11.8	11.8
NaPC15.1	15.1
NaPC18.2	18.2
NaPC23.7	23.7
NaPC30.8	30.8

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