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# Water dynamics in poly(vinyl pyrrolidone)–water solution before and after isothermal crystallization

S. Cerveny [a,*], S. Ouchiar [b], G.A. Schwartz [a], A. Alegria [a,c], J. Colmenero [a,c,d]

[a] Centro de Física de Materiales (CSIC-UPV/EHU), Materials Physics Center, Paseo Manuel de Lardizabal 5, 20018, San Sebastian, Spain
[b] Synthèses Organométalliques et Catalyse, Unite´ de Catalyse et Chimie du Solide, UMR CNRS 8181, USTL-ENSCL, Cite´ Scientifique, 59652 VilleneuVe d'Ascq, France
[c] Departamento de Física de Materiales, Universidad del País Vasco (UPV/EHU), Facultad de Química, Apartado 1072, 20018, San Sebastián, Spain
[d] Donostia Internacional Physics Center, Paseo Manuel de Lardizábal 4, 20018, San Sebastián, Spain

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ABSTRACT

In this work we have studied the low-temperature dynamics of water molecules after isothermal crystallization at different temperatures ($T_c$) and times ($t_c$) of an aqueous solution of poly(vinyl pyrrolidone) (PVP) by broadband dielectric spectroscopy (BDS) and optical microscopy. Three different water concentrations ($c_w$ = 45, 50 and 55 wt.%) were explored. Two major different phases were observed by optical microscopy during crystallization: one related with the core ice formed during crystallization and the other one related with the amorphous phase. Between them a rich interface was also seen. By BDS, two dielectric processes (I and II) are observed in the amorphous samples whereas, in the partially crystallized samples a third relaxation (process III) emerges in the dielectric spectra. Process II is related with the rotational dynamics of water molecules in the amorphous phase with similar characteristics to that found in the complete amorphous solutions whereas the process III is attributed to the rotation of water molecules at the interface between the ice cores and the amorphous water–PVP phase. Typical characteristics of these processes on the relaxation map are discussed.

## 1. Introduction

The behaviour of frozen aqueous solutions of polymers or sugars has been the subject of considerable study since it is involved in several fields of the food industry, biomedical technologies as well as in protocols of pharmaceuticals storage [1,2]. In spite of the fact that in all these fields it is relevant to know how molecular movements of the matrix and the water molecules are affected by freezing the solution, up to our knowledge there are no literature results concerning the dynamics of these solutions after isothermal crystallization. However, some studies related to water dynamics during non-isothermal crystallization in different solutions have been reported. For instance, the dynamics of glycerol–water solutions [3,4] was studied in a semicrystalline environment by dielectric spectroscopy. In this case, three relaxation processes were found (attributed to water–glycerol domains, interfacial water and ice). In addition, the dynamics of poly (vinyl pyrrolidone)–water solution during non-isothermal crystallization was also studied in the literature [5,6] showing a discontinuous temperature dependence of the relaxation times.

On the other hand, water dynamics in amorphous solutions of hydrophilic systems in the low-temperature range of 130–250 K have been previously investigated by dielectric spectroscopy [5–10]. From these studies, it is well-known that a relaxation process associated with the reorientation of the water molecules in the solution is observed (the so-called Process II in references [7–10]). The temperature dependence of the relaxation times are usually Arrhenius-like below the glass transition temperature ($T_g$) of the solution, suggesting that in this temperature range water motions are restricted by the glassy matrix. In addition, at temperatures higher than $T_g$, a systematic deviation of the Arrhenius behaviour is observed and attributed to the fact that water molecules can move in an unhindered or unobstructed medium [5–10].

In this work we address the behaviour of water dynamics after isothermal crystallization i.e. in a semicrystalline environment. To do that, we analyze the water dynamics before and after isothermal crystallization at different crystallization temperatures ($T_c$) and crystallization times ($t_c$) in samples of poly(vinyl pyrrolidone)–water solutions (water concentration, $c_w$ = 45, 50 and 55 wt.%). As the response of water molecules in this amorphous material is well-characterized [5], we are able to compare the dielectric response of water molecules in a partially crystallized environment with that in the amorphous material and to discuss how the water dynamics is affected by crystallization.

## 2. Experimental

Poly(vinyl pyrrolidone) (PVP) in aqueous solution at a water concentration of $c_w$ = 55 wt.%, was purchased from Aldrich Chemical

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* Corresponding author. Tel.: +34 943018808; fax: +34 943015800.
*E-mail address:* scerveny@ehu.es (S. Cerveny).

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and was used without any further purification. The weight-average molecular weight $M_w$ of the dry polymer is 160,000 g/mol. Different water concentrations were reached by evaporating water from the sample as received under normal room conditions. In this way, additional samples with $c_w = 50$ and 45 wt.% were obtained.

Optical microscopy measurements were performed using a LEICA 5500DM equipped with a Linkam heating-cooling stage. The images were obtained and processed with a Leica Image Processing software.

A broadband dielectric spectrometer, Novocontrol Alpha analyzer, was used to measure the complex dielectric function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, $\omega = 2\pi f$, in the frequency ($f$) range from $f = 10^0$ Hz to $f = 10^7$ Hz. In this way each spectrum was collected in a time that does not exceed 1 min. The samples were placed between parallel gold-plated electrodes with a diameter of 30 mm and thickness of 0.1 mm (Teflon spacer). The sample temperature was controlled with stability better than 0.1 K. In this work, the dielectric response was described by using a sum of empirical Cole–Cole functions [11]

$$\varepsilon^*(\omega, t_c) = \varepsilon_\infty + \sum_j \frac{\Delta\varepsilon_j}{\left[1 + \left(i\omega\tau_j\right)^{\alpha_j}\right]} \qquad (1)$$

where $\Delta\varepsilon_j = \varepsilon_s - \varepsilon_\infty$, with $\varepsilon_\infty$ and $\varepsilon_s$ being the un-relaxed and relaxed values of the dielectric constant, $\tau_j$ as the characteristic relaxation time and $\alpha$ as the shape parameter ($0 < \alpha \leq 1$) which describe the symmetric broadening of the relaxation. As we will show in the next section, we chose two or three CC functions to describe the dielectric spectra of amorphous and semicrystalline samples respectively.

Finally, differential scanning calorimeter (DSC) measurements were made by using a Q2000 TA Instrument.

## 3. Results and discussion

### 3.1. Calorimetric response

A typical DSC scan showing the heat flow of PVP–water solution with $c_w = 55$ wt.% during cooling and heating (at a rate of 10 K/min) is given in Fig. 1. It is evident that it is possible to avoid crystallization on cooling obtaining a glass phase at low temperatures. However, the heating scan in Fig. 1 shows a glass transition ($T_{g,onset} = 205$ K) followed by a cold crystallization in the temperature range of 230–250 K. After that, a broad melting is observed in the temperature range between 250 and 270 K. The $T_g$ of all the samples was determined as the onset of the heat flow step. The inset of Fig. 1 shows the calorimetric response of dry PVP. In this case, no crystallization at all is observed and consequently the only component in this mixture that presents crystallization is the water. Therefore in this work we are dealing with the behaviour of water molecules during the crystallization of water itself.

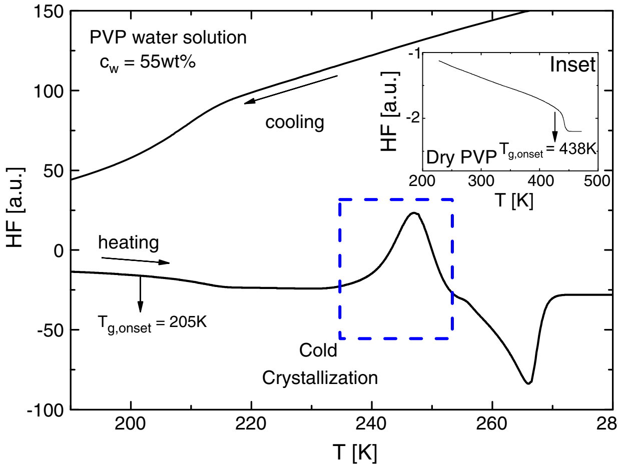

**Fig. 1.** Heat flow measured by DSC during cooling and heating at a rate of 10 K/min of PVP–water solution with $c_w = 55$ wt.%. A cold crystallization is observed in the temperature range of 230–255 K (dotted box). $T_{g,onset}$ represents the onset of the glass transition temperature ($T_g$). Inset: DSC scans of dry PVP where no crystallization is observed.

### 3.2. Optical microscopy

In order to analyze both the ice morphologies and the crystallization kinetics, optical microscopy measurements were performed (magnification 20×). The samples were quickly cooled at a rate of 40 C/min down to 170 K. After that, the samples were heated again up to the desired crystallization temperature ($T_c$) and were held (during $t_c$) to observe the behaviour during crystallization. Spherulitic-like structures with very similar morphologies were observed for all water concentration and temperatures explored. Fig. 2 shows the evolution of the ice cores formed during isothermal crystallization. At $t_c \approx 10$ min, small spherulitic-like structures of ice (opaque) appear in the samples and an increment in the diameter with crystallization

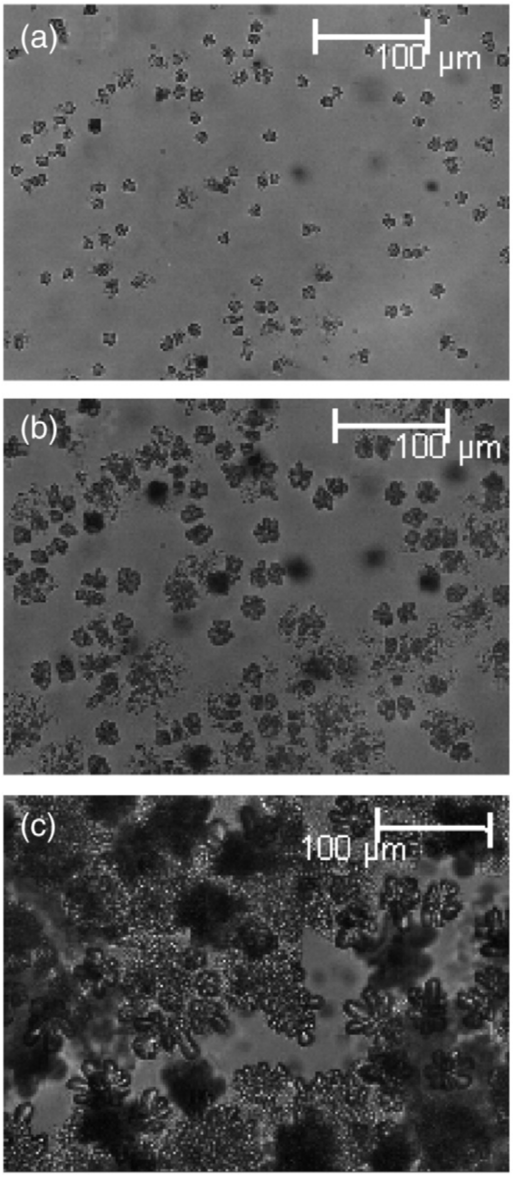

**Fig. 2.** Evolution of ice diameter during crystallization at $T_c = 215.15$ K and $t_c = 12$, 70 and 348 min respectively for a solution with $c_w = 55$ wt.%.