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Analysis Method

^{1}H time domain NMR real time monitoring of polyacrylamide hydrogels synthesis

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ABSTRACT

Synthesis reactions of polyacrylamide based hydrogels were automatically monitored *in situ* by time-domain nuclear magnetic resonance, through a steady-state pulse sequence. Four hydrogel formulations with different amounts of monomer and crosslinking agent were tested and the proposed method demonstrated sensitivity to each formulation without the need for *a priori* calibration of the spectrometer, even when the hydrogels exhibited substantially different structural characteristics. The results obtained by the proposed method were compared for validation with those generated by traditional reaction monitoring methods, such as UV–Vis spectroscopy, and exhibited similar results, suggesting that time-domain nuclear magnetic constitutes an interesting alternative for the monitoring of solution crosslinking reactions.

1. Introduction

The efficient control of a chemical reaction depends on knowledge of the evolution of factors such as concentration of reagents and products and the kinetics of the process itself. When aiming at the modeling of more efficient processes, both on pilot and industrial scale, the knowledge and prediction of changes in those and other parameters is key in the optimization of reactional conditions [1,2].

Spectroscopic and chromatographic techniques are commonly applied to the monitoring of a chemical reaction. They are applied in the verification of the reaction's kinetics and yield of desired products [3,4]. Traditionally, the characterizations are carried out on aliquots taken from the reactor, which are diluted or manipulated according to the analysis method [5]. However, the removal of material from the reaction medium and its subsequent transport to where the characterization equipment is located can be inconvenient, dangerous or introduce errors in the measurement of the property of interest. These factors compromise the reproducibility of the measure and add hindrances to the control of variation in quality to each reaction batch [2]. Real-time *in situ* monitoring of a given chemical reaction is a possible solution to those issues. Among the spectroscopic techniques, proton nuclear magnetic resonance (^{1}H NMR) relaxometry is becoming more and more an established experimental technique used for the characterization of different materials, in particular polymer based systems [6–10].

The monitoring of chemical reactions was attempted on simple molecules with distinct signals by detection of abundant nuclei (^{1}H and ^{19}F) on high (500 MHz, proton Larmor frequency) and medium field NMR spectrometers (45 MHz, proton Larmor frequency) with relatively high success rates [11–13]. Some research groups have used low magnetic field NMR (around 20 MHz, proton Larmor frequency) to follow reactions involving polymeric systems that exhibit an intense change in their molecular mobility during the chemical process [14,15]. However, the chemical reaction monitoring methods reported in the literature using NMR as the main tool lack applicability in common situations involving polymeric materials (chemical crosslinking reactions in solution, for example), mainly because of their technical requirements, such as a low viscosity medium or reactions of simple molecules.

In this work we investigated the feasibility of a method for monitoring cross-linking polymerization reactions of a hydrogel based on chemically cross-linked polyacrylamide (XPAam), by means of proton time-domain nuclear magnetic resonance (^{1}H TD-NMR) in a low field spectrometer (23 MHz for protons) through steady state relaxation constants determination via the Carr-Purcell

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Continuous Wave Free Precession pulse sequence (CP-CWFP). Structure-properties relationship of the samples were studied via proton Multiple Quantum (^{1}H MQ) probing and fast field cycling proton spin-lattice dispersion profiles (FFC), as we aimed to understand the influence of distinct polymerization conditions on the operational parameters of the proposed method.

2. Experimental

2.1. Materials and samples' preparation

The monomer, acrylamide (Aam, electrophoresis grade, 99+% pure, Sigma-Aldrich), cross-linking agent, *N,N′*-methylenebisacrylamide (MBAam, 99% pure, Sigma-Aldrich), radical initiatior system comprised of ammonium persulfate (APS, 99% pure, Sigma-Aldrich) and *N,N,N′,N′*-tetramethylenediamine (TEMED, 99% pure, Sigma-Aldrich) were used as received.

All gel samples studied were obtained by aqueous solution radical polymerization, as per the formulations shown in Table 1.

The typical procedure was to polymerize and crosslink the Aam with MBAam at room temperature (27 °C) in a sealed vessel. The water used on the reaction was previously degased by N_2 flow for 10 min, to remove the oxygen and avoid its inhibitor effects on the polymerization process. The zero time (t_0) established as the start of the reaction was the moment the TEMED was incorporated into the solution.

2.2. Theoretical background for carr purcel-continuous wave free precession pulse sequence

The pulse sequence known as Carr-Purcell-Continuous Wave Free Precession (CP-CWFP) (Fig. 1a) consists of a 90° radiofrequency pulse train with the same phase and a precession angle equal to $\psi = (2n + 1)\pi$, where n is an integer, spaced apart by an interval (Tp) of less than twice the system's $T_2{}^*$ value. The first pulse of the sequence disrupts the thermal equilibrium magnetization (M_0). After a waiting period equal to Tp, a train of pulses causes the appearance of an oscillation in the magnetization, evolving to a steady state (M_S) with a time constant T* (Fig. 1b).

In the steady state, the magnetization has a constant amplitude in time, depending only on the values related to the longitudinal (T_1) and transverse (T_2) relaxation constants, as can be seen in Equation (1) [16]:

$$M_S = \frac{M_0.T_2}{T_1 + T_2} \tag{1}$$

T* has the following dependence with T_1 and T_2:

$$T^* = \frac{2.T_1.T_2}{T_1 + T_2} \tag{2}$$

By rearranging Eqs. (1) and (2), it is possible to extract the T_1 and T_2 constants from a single CP-CWFP experiment by simply determining the value of T* through an exponential fit to the curve obtained experimentally.

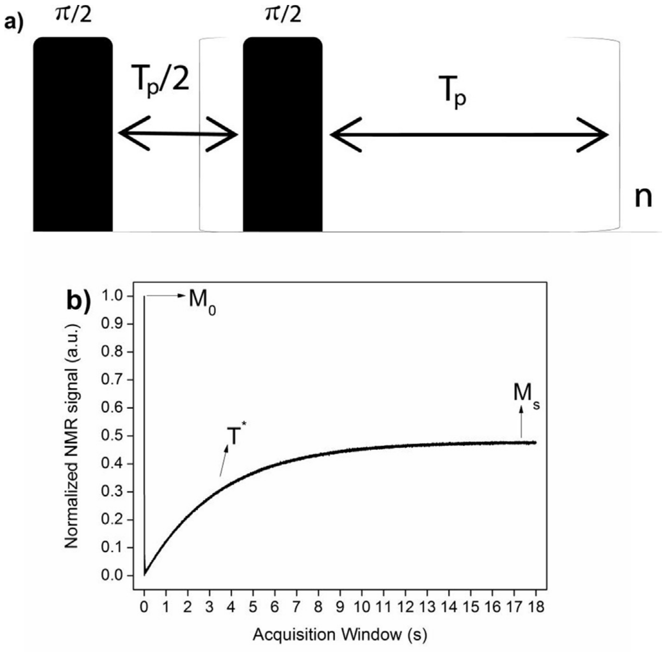

Fig. 1. a) CP-CWFP pulse sequence scheme; b) CP-CWFP signal of a sample of distilled water. The plot positions of the relevant constants are indicated.

$$T_1 = \frac{\frac{T^*}{2}}{\frac{M_s}{M_0}} \tag{3}$$

and

$$T_2 = \frac{\frac{T^*}{2}}{1 - \left(\frac{M_s}{M_0}\right)} \tag{4}$$

2.3. CP-CWFP polymerization monitoring

The reaction monitoring by TD-NMR was performed in a Maran Ultra spectrometer with an electromagnet operating at 0.54 T (23.4 MHz, proton Larmor frequency), equipped with an air flow temperature control unit (±0.1° C) and employing the CP-CWFP pulse sequence. The acquisition parameters were set to a 90° pulse with duration of 7.5 µs, a T_p of 300 µs, with four repetitions per experiments, spaced by an interval of 20 s. The equipment's frequency offset was set to 2.500 KHz.

These parameters allow for an 18 s observation window (greater

Table 1
Samples' formulations.

Sample	Polymer solution concentration[a]	Nominal cross-linking degree	Monomer mass	Cross-linking agent mass[b]	APS solution volume[c]	TEMED volume
XPAam 3%	3% (m/m)	2,6% (m/m)	0,1800 g	0,0047 g	0,03 mL	0,003 mL
XPAam 6%	6% (m/m)	2,6% (m/m)	0,3600 g	0,0094 g	0,03 mL	0,003 mL
XPAam 12%	12% (m/m)	2,6% (m/m)	0,7200 g	0,0187 g	0,03 mL	0,003 mL
XPAam 18%	18% (m/m)	2,6% (m/m)	1,0800 g	0,0281 g	0,03 mL	0,003 mL

[a] Deionized water volume was fixed at 6 mL.
[b] With respect to monomer mass.
[c] A 10% (w/w) water solution.