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Ultralow Field Overhauser Images of Calcium Alginate Gel Formation

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We present magnetic resonance images of the formation of an alginate gel as calcium ions diffuse, through a dialysis membrane, into a sodium alginate solution. Instead of conventional magnetic resonance imaging in a high magnetic field, we employed the electronic Overhauser effect in an imaging mode to enhance the proton signal at a field of only 16 mT. The high sensitivity of the Overhauser effect to small changes in mobility permits to monitor spatial inhomogeneity in the very early stages of the gelling process.

Keywords: calcium alginate; MRI; Overhauser Imaging

INTRODUCTION

The use of polysaccharides for gel entrapment or encapsulation has developed considerably in recent years [1-4]. The most interesting applications appear to be the immobilization of cells or enzymes as well as the use of these systems as implantation materials [5]. Sodium alginate is particularly attractive for its ability to form, with divalent ions such as Ca^{2+}, a lattice of cross-linked chains that provides a

relatively mild environment for immobilizing living cells within gel droplets of controllable size [3].

The gellification process of sodium alginate by Ca^{2+} ions has been studied by several methods. Various parameters are known to affect the rigidity and the homogeneity of the resulting gel. The role of factors such as the average size of mannuronic (M) blocks and guluronic (G) blocks, appears to be presently well understood. Also the role of anti-gelling ions such as sodium and the ideal conditions for chemical stability have been clarified.

Gel inhomogeneity is a particularly important aspect from a practical point of view. It has been carefully studied, in the case of calcium alginate, by conventional magnetic resonance imaging in high magnetic field [6] as well as by more direct methods [7]. In most cases the inhomogeneity of the final gel, governed by the amount of calcium alginate at various distances from the alginate-$CaCl_2$ interface, has deserved special attention. In at least two cases however, the dynamics of the process has also been considered by inspecting the position of the "gelling front" as a function of time [7,8].

In this paper we present a new method of monitoring the dynamics of the gelling process and its spatial variation employing Overhauser magnetic resonance imaging in ultralow magnetic fields [9-11]. This method is very sensitive to small changes in local water mobility and furnishes a different view of the early stages of gelling. The technique is also attractive because the instrumentation can be made relatively simple through the use of a very low magnetic field.

EXPERIMENTAL METHOD AND SAMPLE PREPARATION

Overhauser imaging was performed in a magnetic field of only 16 mT corresponding to a proton Larmor frequency of 680 kHz. Magnetization transfer from the electron spins of the nitroxide free radical TEMPO [10,11] to the protons was achieved by irradiation of one of the three hyperfine electron spin resonance transitions of the radical, at a frequency of 403 MHz. Following an irradiation period of 500 msec, the NMR signal was acquired in a normal spin-echo imaging mode with echo time TE = 30 msec and repetition rate TR = 1 sec. Typical imaging time was 9 minutes.

Sodium alginate, prepared from macrosystis pyrifera (Sigma) in 1% aqueous solution, was employed to obtain the gels. To that end, the sodium alginate solution was dialyzed against a 0.06 M aqueous solution of $CaCl_2$ and Overhauser images were recorded at various times.

The experimental arrangement consisted of a cylindrical reservoir 2.8 cm in diameter and 2.5 cm height, with an approximately concentric dialysis membrane 1.6 cm in diameter. The $CaCl_2$ solution was placed in the space between the two cylinders and the sodium alginate, containing a 5mM concentration of TEMPO, was placed in the inner cylinder. Arrangements with different initial conditions were also employed and gave compatible results. A bird-cage coil, tuned and matched to the electron spin Larmor frequency was inductively coupled to an amplifier producing 10 watts of power at 403 MHz. A head coil [10,11] was employed as a receiver coil for the proton NMR signal.

RESULTS

Typical radial one-dimensional profiles obtained from two-dimensional Overhauser images are shown in Figure1 and Figure 2. Figure1 shows a series of profiles at time intervals of approximately 12 minutes, where the dominant process appears to be the diffusion of the free radical TEMPO through the membrane.

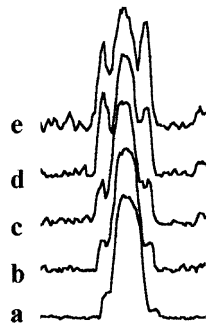

FIGURE 1 One-dimensional profiles during the free radical diffusion process. (a) t = 35 min; (b) t = 47 min; (c) t = 61 min; (d) t = 72 min; (e) t = 84 min.

Figure 2a suggests that the radical has reached an approximately homogeneous distribution inside the membrane and in the external cylindrical region but water mobility near the alginate-$CaCl_2$ interface is reduced relative to the center, due to the progress of the gelling process In Figure 2b to Figure 2e, water mobility is further reduced as a whole causing a drop in the overall signal amplitude, but still showing some inhomogeneity. Complete gellification is only achieved many hours after Figure 2e, when the Overhauser signal amplitude is severely reduced.

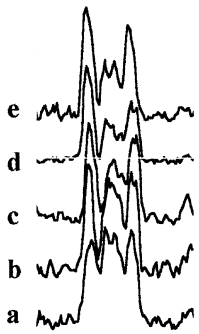

FIGURE 2 One-dimensional profiles during the gelling process of calcium alginate. (a) t = 95 min; (b) t = 107 min; (c) t = 119 min (d) t = 133 min; (e) t = 146 min.

CONCLUSIONS

We conclude that, in spite of the weak magnetic field that permits a much-simplified instrumentation, Overhauser imaging can be effective in monitoring the very early stages of alginate gel formation and its spatial inhomogeneity. Effects due to anti-gelling ions, alginate/$CaCl_2$ ratio and polymer chemical composition can be followed, in the initial stages of gellification, as a function of time. As in the case of conventional NMR imaging of gel formation, where contrast is caused spin-spin relaxation (T_2) differences [6,8], a calibration procedure is also necessary in the present case if a quantitative determination of calcium concentration profiles becomes necessary.

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