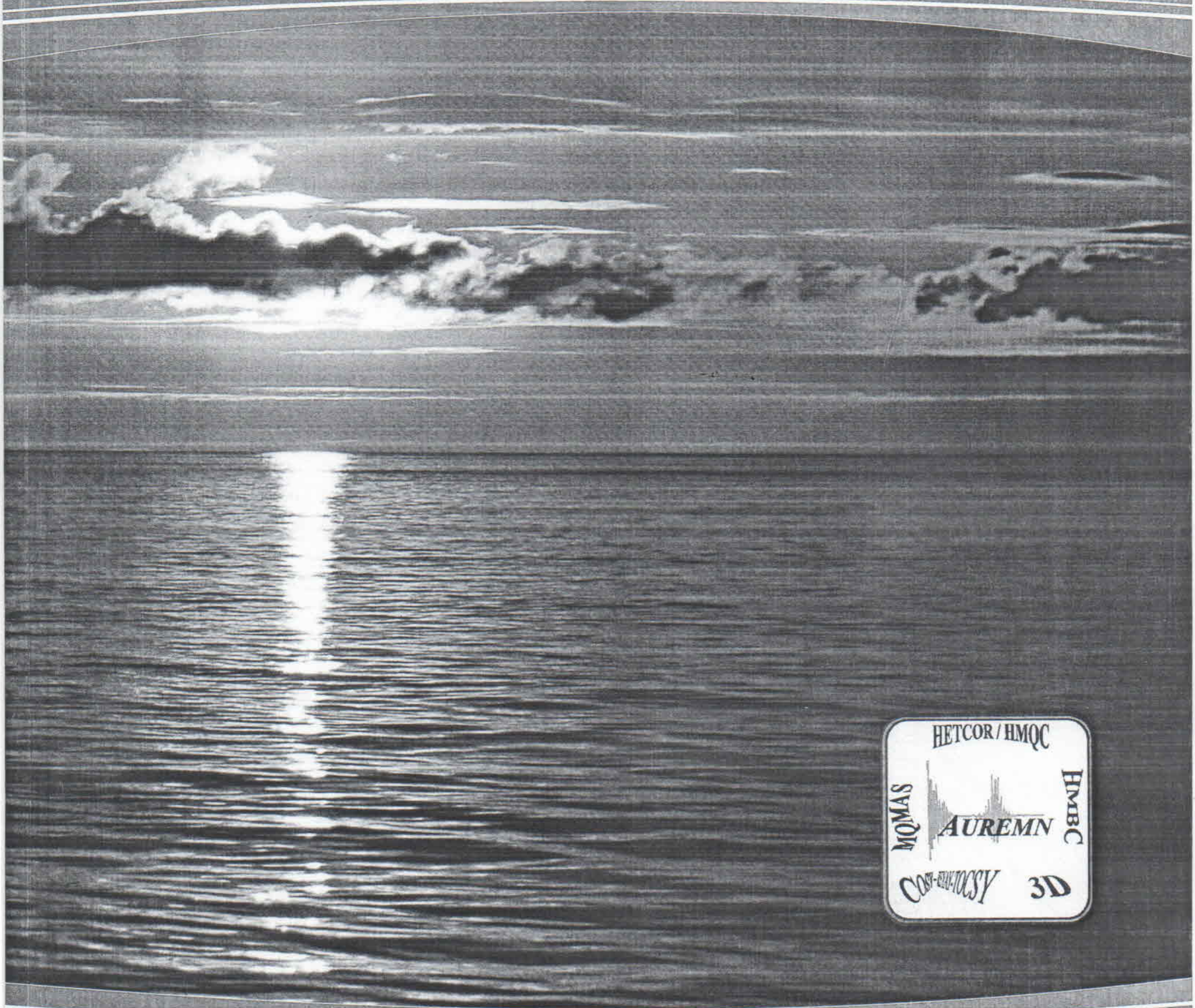
12th NUCLEAR MAGNETIC RESONANCE USERS MEETING

3rd IBEROAMERICAN NMR MEETING

MAY 4th - 08th, 2009 - HOTEL DO FRADE, ANGRA DOS REIS, RJ, BRAZIL



EXTENDED ABSTRACTS BOOK

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CWFP AS A TOOL FOR MONITORING THE CURE OF A COMMERCIAL EPOXY RESIN IN LOW FIELD NMR

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The cure of resins is an important reaction for material sciences, being a critical stage in some specific cases, such as resins for dentistry, where it is important to obtain an adherent and resistant material in a fast reaction. However, it is not so trivial to monitor so fast reactions like these ones, being necessary to use fast techniques. Low field NMR has already been used successfully to monitor the cure of epoxy resins, by using CPMG [1] and CWFP [2] techniques. Continuous Wave Free Precession (CWFP) was developed from the Steady State Free Precession (SSFP), and it is a fast and sensitive technique with several applications [3]. It was also demonstrated that CWFP technique can be used to determine T_1 and T_2 relaxation times in a fast and simultaneous simple way [4]. CWFP consists in a train of $\pi/2$ pulses with same phase, intensity and duration, separated by a time interval T_p. T_1 and T_2 relaxation times could be used to evaluate molecular dynamics, as in a polymerization reaction such as described here. The changes in the amplitude of the signal could also be used to study the kinetics of reaction. The purpose of this work is to use CWFP technique to monitor an epoxy reaction, taking account the dynamics and kinetics involved.

For these experiments was chosen a fast curing commercial epoxy resin, consisting in a mixture of epoxy resin and hardener 1:1. This mixture was homogenized for approximately 2 minutes and then it was inserted in a plastic tube (1 cm diameter) to perform the measurements. The zero time reaction was assumed since the components were mixed. The reactions was monitored in three different experiments by using CPMG pulse sequence with 300μs echo time for T_2 measurements; null point inversion-recovery for T_1 determination, and finally CWFP for T_1, T_2 and kinetics evaluation, by using 300μs of T_p. The measurements were acquired with 10s interval. The equipment employed is composed of a 2T Oxford magnet with a 30cm bore and electronic based on an Apollo-Tecmag spectrometer, a power amplifier AMT 2035 and a pre amplifier Miteq 1054. It was also employed a 1cm diameter home-made solenoidal coil, covered with an epoxy resin to keep it rigid. Neither plastic tube nor epoxy resin exhibit NMR signal in such conditions.

As could be observed in fig 1(a) with the progress of reaction the CWFP signal amplitude decreases. A first order kinetic treatment of this data results in a curve like shown in fig 1(b), where it could be seen that the total reaction proceeds mainly in two stages. According to literature [1] the first one is related to epoxide ring opening with rate constant of 3.43×10^{-3} s^{-1}, followed by an intermediate stage, probably referred to a phase transition and the last one is related to a reticule formation, by chain intercrossing, with rate constant of 2.24×10^{-2} s^{-1}. The reticulation can be confirmed by analyzing the change in T_1 and T_2 relaxation times. As the reticulation occurs, the chain mobility starts to be decreased and this stage is characterized by a drastic shortening of T_1 and T_2 relaxation times, as could be seen in the figs 2(a) e (b). By comparing CWFP results (fig 2a) with those ones obtained by inversion recovery and CPMG methods (fig 2b) it can be verified a good agreement despite some deviations in the T_1 obtained by null point inversion recovery, which is not an accurate way to be done.

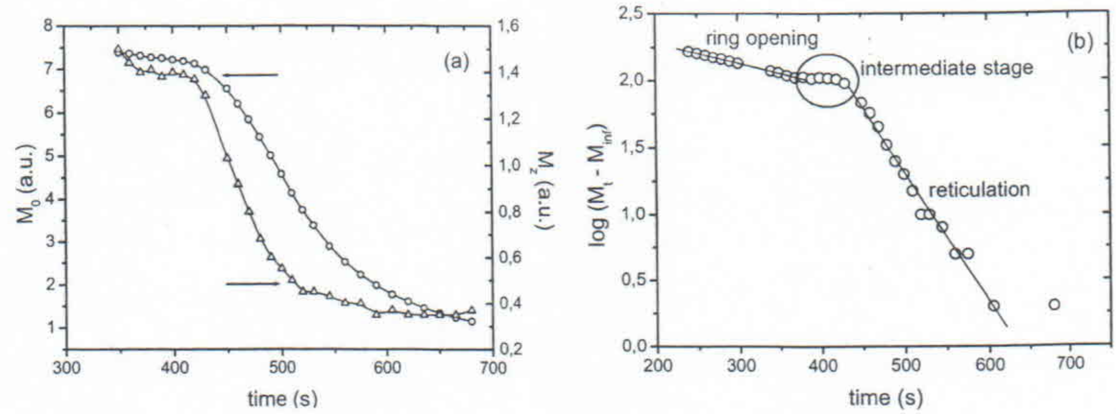

Figure 1: (a) CWFP signal amplitude at zero time (M_0, o) and at truly stationary state (M_z, Δ); **(b)** by applying a kinetic first order law equation to CWFP signal amplitude.

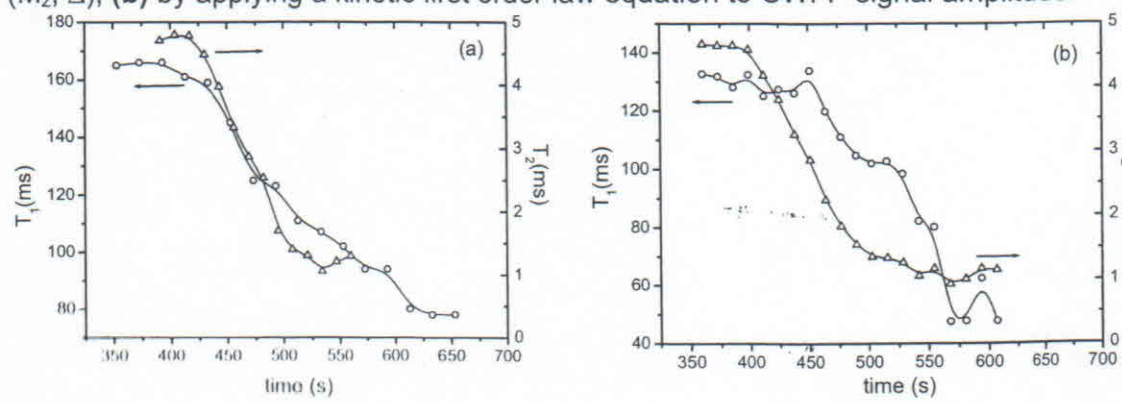

Figure 2: (a) time dependent T_1 (o) and T_2 (Δ) determined by null point inversion recovery and CPMG respectively; **(b)** time dependent T_1 (o) and T_2 (Δ) by CWFP.

The advantage of CWFP method is that with only one experiment is possible to determine the kinetic of the reaction, through the measurement of signal amplitude; and also the dynamic of molecules with the progress of the reaction, through T_1 and T_2. To determine T_1 and T_2 changes by conventional methods is necessary to perform two experiments, which could not be done in the same conditions. The information about T_1 changes can be obtained by CWFP in a more accurate way compared to null point inversion recovery method.

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