

High-Resolution Carbon-13 Nuclear Magnetic Resonance Study of Natural Resins

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ABSTRACT: Developing a methodology of analysis for the identification of the components presented in natural resins without a previous isolation or treatment, we first chose to use liquid nuclear magnetic resonance (NMR) to assign the main components. However, solid-state NMR techniques give much more information about the chemical components presents in the resins than solution NMR, so we

changed the methodology. The first approach must be the application of solid-state NMR techniques and continuation of the identification process by analysis of the data obtained. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1848–1854, 2002

Key words: NMR; natural resins; characterization

INTRODUCTION

Natural resins use is increasing because they come from a renewable source. Generally, most natural resins are multiphase systems with high chemical complexity.¹ The study of their molecular dynamic behavior under natural conditions requires the use of a large set of complementary analytical methods.

High-resolution solid-state nuclear magnetic resonance (NMR) experiments can be used to characterize them in the solid phase by using the following methods: ¹³C magic-angle spinning (MAS); cross-polarization with magic-angle spinning (CPMAS); and cross-polarization/magic-angle spinning with dipolar dephasing (CPMASDD) spectroscopy.^{2–7} The application of faster MAS with short delay time permits detection of high-speed molecular motions of individual components. The use of CPMAS allows characterization of the total solid phase present in the sample. The CPMASDD allows evaluation of part of the sample, like no protonated carbons, but some very mobile carbons are also detected.^{5–7} NMR relaxation studies have been widely used to probe molecular dynamics.^{2–5} Normally, the approach is to measure one or more relaxation times and then attempt to interpret the data. The proton spin relaxation time in the rotating frame ($T_1^H\rho$) is an alternative method to obtain the response of the dynamic molecular of the role sample.^{1–7}

The purpose of this work is to establish an analytical methodology to study the chemical structure, composition, and molecular dynamics of the natural resins to use routinely and in a new application, focusing on the NMR results.

EXPERIMENTAL

The initial methodology chosen was as follows: (1) selection of natural resin (NR); (2) literature search for references about the NR; (3) botanic identification of NR; (4) solubility tests; (5) solution NMR to characterize the chemical structure; (6) crystallinity analysis; (7) solid-state NMR analysis to have response on chemical structure. To choose the NR it is important to know about its applicability. Therefore, popular information about the use of NRs is one of the important criteria to select the appropriate NR. Another important point is the focus of new application to be employed in polymeric blends and composites.

NMR measurements

Five NRs [*Schinus terebinthifolius* (ST), *Hura crepitans* (HCr), *cedrela fissilis* (CF), *Hymenaea courbaril* (HC), and *Peltophorum dubium* (PD)] were analyzed by ¹³C solution and solid-state NMR.

The solubility tests showed the suitable solvents to be used in NMR solution. Only the HC resin was soluble in CDCl₃, so D₂O was chosen as a solvent.

The solution was analyzed by NMR with a VARIAN MERCURY 300, operating at 75.4 MHz for car-

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TABLE I
Carbon-13 Chemical Shift Values Obtained by Solution
NMR for Natural Resins

| δ (ppm) | NR | | | | PD |
|----------------|----|-----|----|----|----|
| | ST | HCr | CF | HC | |
| 179.6 | | | | — | |
| 175.7 | | | | — | |
| 173.2 | | — | | — | |
| 171.6 | | | | — | |
| 164.5 | | | | — | |
| 145.2 | — | | | | |
| 144.1 | | | | — | |
| 130.0 | — | | | | |
| 120.2 | | | | — | |
| 114–112 | | | | — | |
| 107.2 | — | — | | | |
| 103.7 | | | | | |
| 86.3 | — | | | — | |
| 82.8 | | — | | | |
| 76.6 | — | | | — | |
| 76.0 | | — | | | |
| 57.5 | | — | — | | — |
| 55.3 | | | | — | |
| 48.6 | | | | — | |
| 41–30 | | | | — | |
| 29–24 | | | | — | |
| 21–18 | | — | | — | |
| 17–15 | | | — | — | — |
| 14.3 | | | | — | |

bon-13. The solution was prepared in D₂O and chloroform-*d* depending on the resin.

All solid NMR spectra were determined on a VARIAN INOVA 300, operating at 75.4 MHz for carbon-13. The NMR experiments were conducted at ambient probe temperature and were performed using gated high-power decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the NMR spectra at

rates of 6 kHz. The ¹³C NMR spectra were determined in the cross-polarization mode with magic-angle spinning. For the variable contact time, a range of contact times was established from 50 to 8000 μ s. The CPMAS ¹³C NMR spectra with dipolar dephasing were recorded with a dephasing time, τ , of 40 μ s. Proton $T_{1\rho}$ values were determined from the intensity decay of ¹³C peaks with increasing contact times and also from the delayed contact time experiment, with a spin-locking range varied from 200 to 8000 μ s.

RESULTS AND DISCUSSION

All resins seem to be soluble, but the spectra did not show good resolution. The ¹³C NMR solution spectra did not tell us much about the chemical structure or even components present in the resins. The carbon-13 chemical shifts detected for all of NR is listed in Table I.

Although ST was soluble in water at room temperature, the ¹³C NMR spectrum was very difficult to obtain. After several trials, a spectrum that presents some signals was obtained at 80 °C (Figure 1). Even under this condition, the signals detected were wide and a very poor signal-to-noise ratio was obtained.

The HC resin presented good solubility, and a nice ¹³C NMR spectrum was obtained. However, the complexity of this resin did not allow us to get more than qualitative information on the components presented in the sample.

The ¹³C solution spectra of CF and PB in water were interesting. Both spectra have only two signals (Figure 2), one located at \sim 57 ppm (referred to as CH₂-O) and the other one at \sim 16 ppm (referred to as CH₃; see Table I).

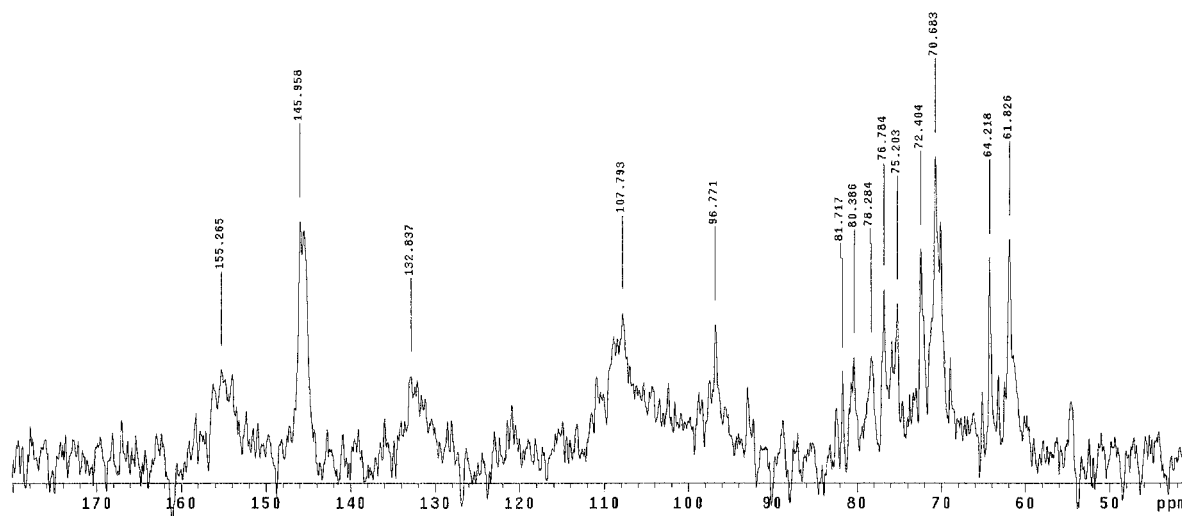


Figure 1 ¹³C NMR solution spectrum of ST obtained at 80 °C.

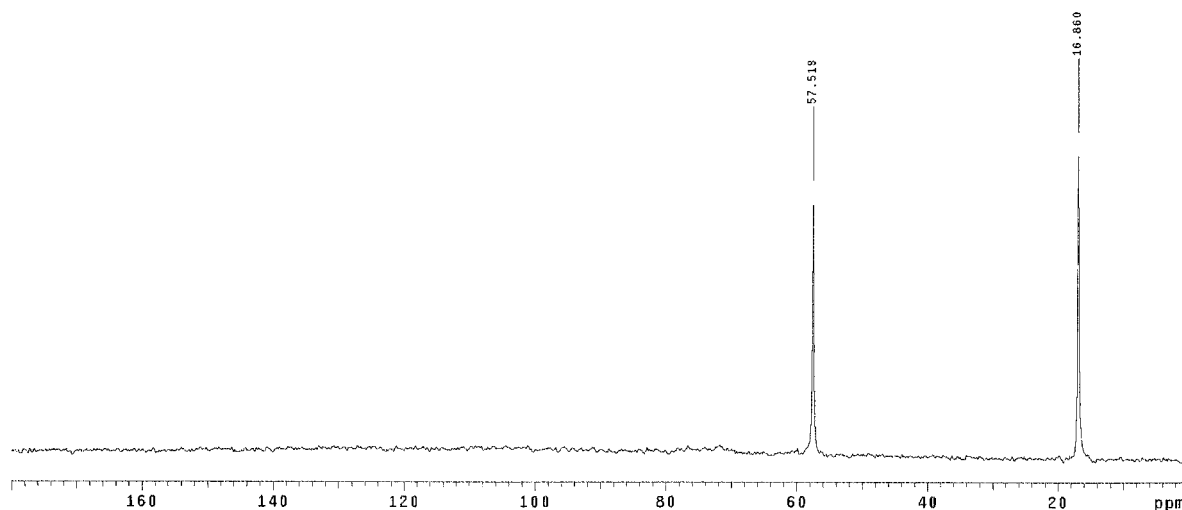


Figure 2 ^{13}C NMR solution spectra of CF and PD in water and at room temperature.

The ^{13}C solution NMR spectrum of HCr in water shows a good spectrum (Figure 3) with few resonance lines that can be attributed to an ester and a polysaccharide.

The ^{13}C NMR solution did not give the chemical structure or the type of components present in the NR. The solid-state measurements showed more information on those resins, indicating that a change in the methodology proceedings is necessary.

From the ^{13}C solid-state NMR spectra of all resins, several useful information has been extracted. The ST resin presented a poor CPMAS ^{13}C spectrum (Figure 4). However, signals from polysaccharide and ester were detected. The cross polarization with variable contact time was carried out from short contact time (μs) to long contact times (ms). As was expected, the efficiency was not good; that is, only wide signals located at short contact times were detected. From these responses we can suppose that this resin is

amorphous and rigid. This rigidity is related to the sample spatial conformation and may present a metal in its structure, which contributes to the difficulties of the polarization transfer, making the signals wider. The assumption of the metal in this structure can be supported by the fact that the ^{13}C MAS spectrum with short delay time did not present signals because this sample does not have a domain in this time scale, probably because it is a rigid amorphous polysaccharide complexes with a metal. The $T_{1\rho}^{\text{H}}$ values determined for the resolved carbons are shorter than the values determined for the other resins, due to the rigidity of the sample.

The HCr resin CPMAS ^{13}C showed signals from the polysaccharide and from oil, probably a triacylglycerol. The signals from polysaccharide reveal that these resins present a crystalline and an amorphous polysaccharide (Figure 5) and other signals come from an ester.

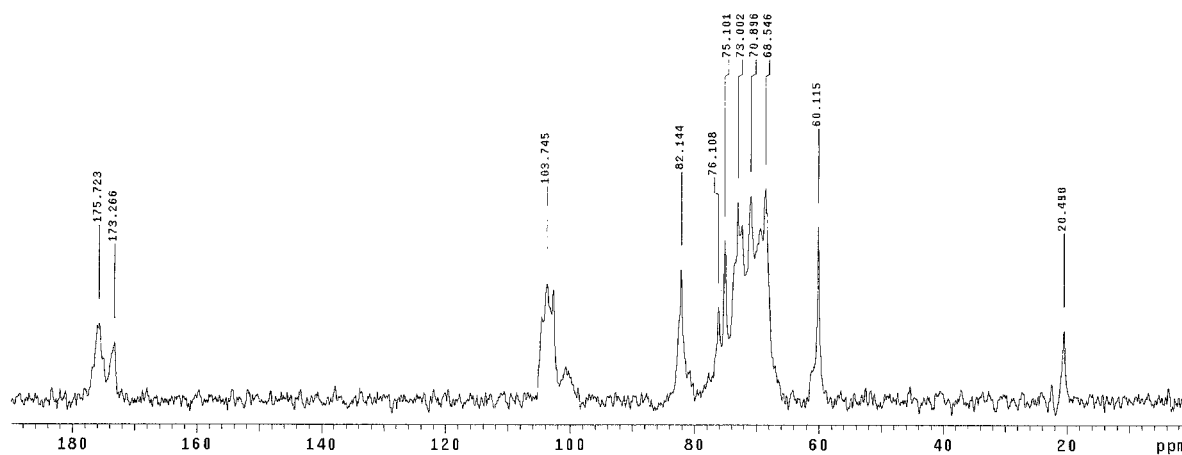


Figure 3 ^{13}C solution NMR spectrum of HCr in water and at room temperature.

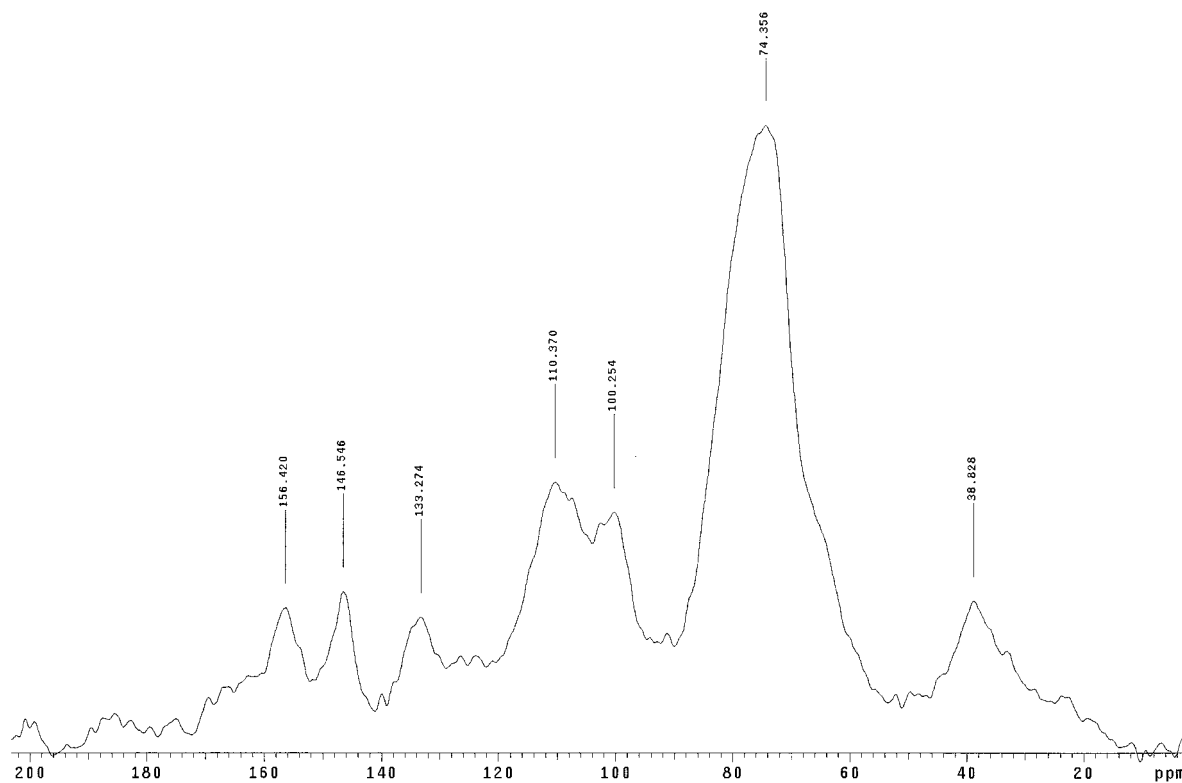


Figure 4 CPMAS ¹³C NMR spectrum of ST resin.

When the PD resin was analyzed by CPMAS ¹³C it showed signals from polysaccharide and an ester (Figure 6). The polysaccharide signals are not well re-

solved as was the case for the HCr resin. The two signals detected for an ester indicate that these came from acetate.

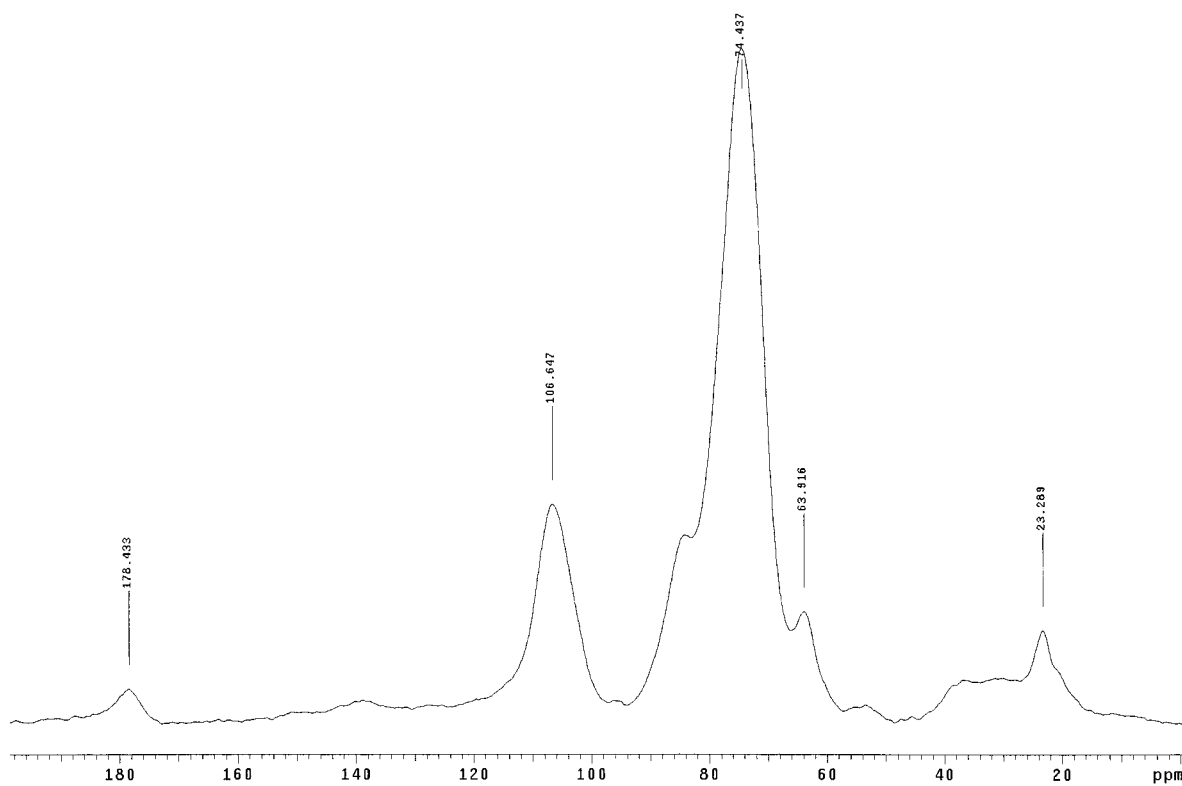


Figure 5 CPMAS ¹³C NMR spectrum of HCr.

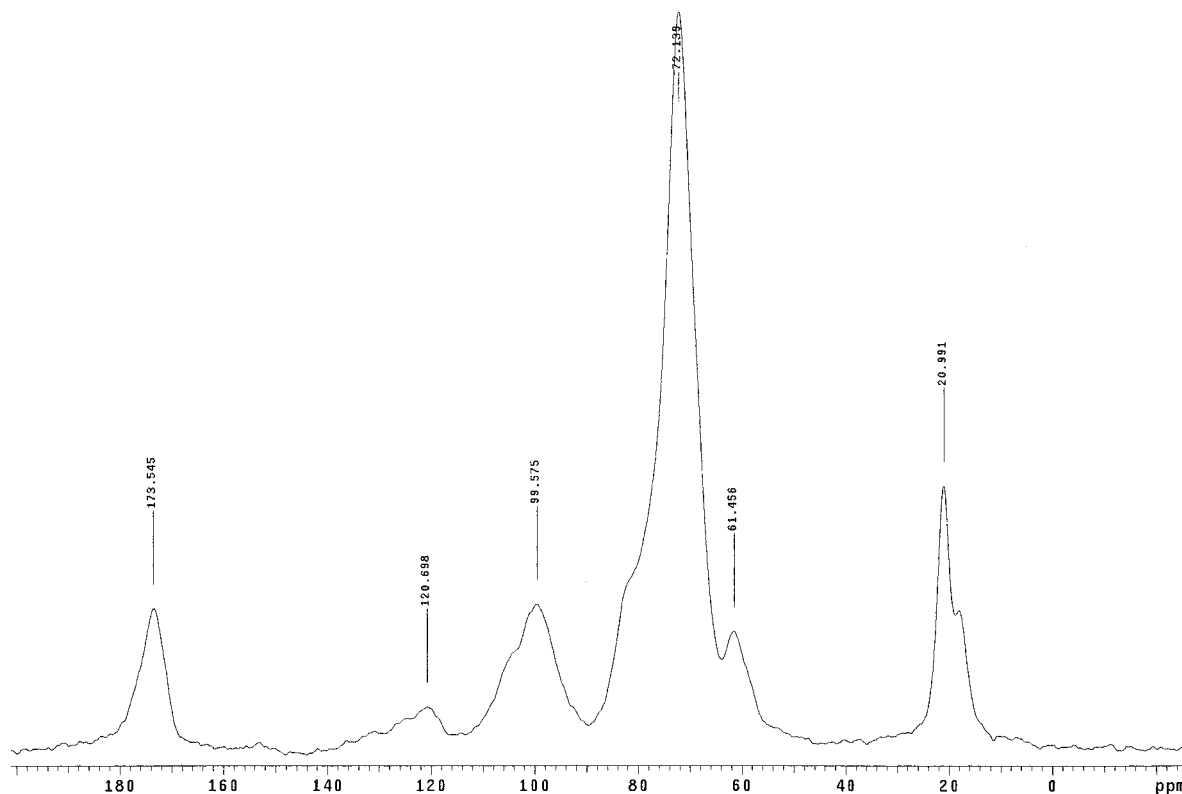


Figure 6 CPMAS ^{13}C spectrum of PD resin.

The CPMAS ^{13}C spectrum for the CF resin (Figure 7) showed the same signals found for PD resin. This result indicates that these two different type of resins may be comprised of the same or at least very similar components.

Comparing all distribution form of the CPMAS ^{13}C decays, during the variable contact time experiment (Figure 8), it is clear that the ST resin is very much more rigid than the other resins. The optimum contact

time was $\sim 100 \mu\text{s}$ and ST is also amorphous, therefore the NMR signals very wide. The CF resin is rigid and amorphous as well, and the signals were broad. The HCr and PD resins presented higher molecular mobility and the best contact time for the polarization transfer was $\sim 1000 \mu\text{s}$ for the BB and $600 \mu\text{s}$ for the HCr.

From all the results, the following suitable methodology was chosen: (1) selection of NR; (2) literature search about and botanic identification of NR; (3) solid-

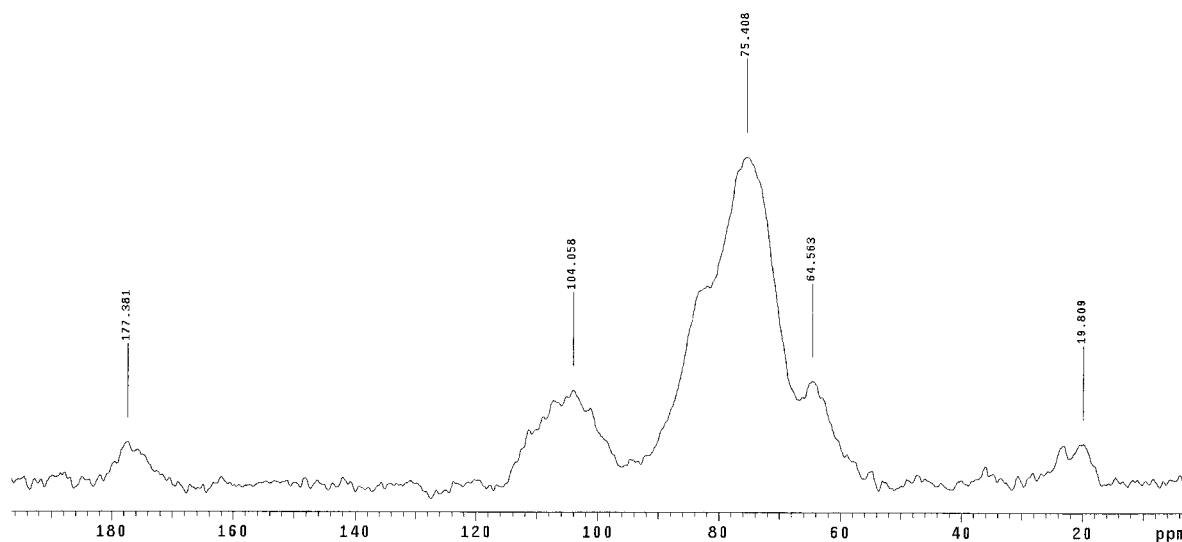


Figure 7 CPMAS ^{13}C spectrum of CF resin.

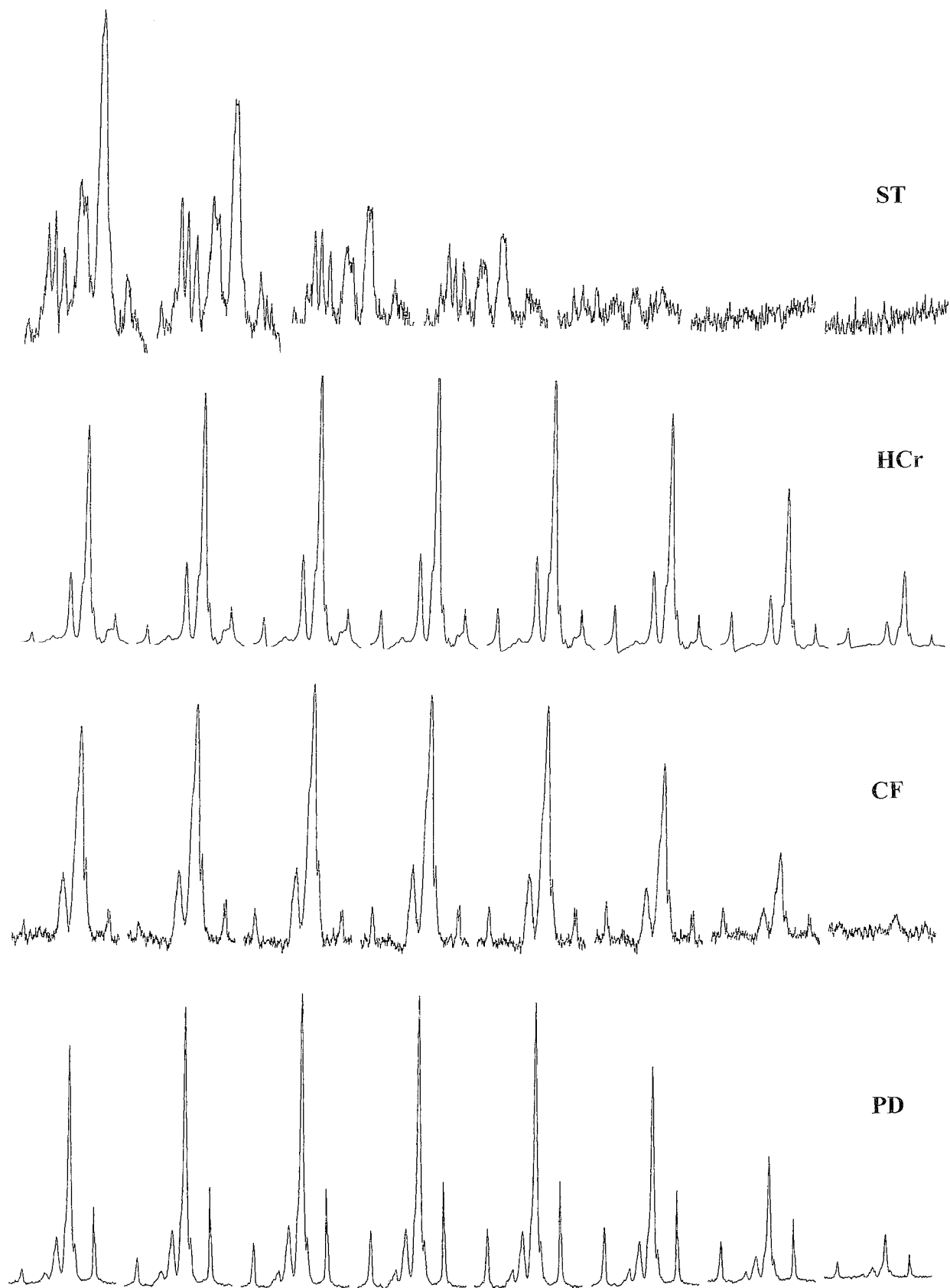


Figure 8 Distribution form of the CPMAS ¹³C decays during the variable contact time experiment for all NRs.

state NMR; (4) solubility tests and crystallinity analysis; (5) solution NMR to characterize the chemical structure.

CONCLUSION

In this work we first chose to use liquid NMR to identify the components in the NRs. However, the solid-state NMR techniques gave much more information about the resins than solution NMR. So, the first approach must to be the application of solid-state NMR techniques to continue the identification process. The ^{13}C signals were much better detected and additional information on the NR was also obtained.

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References

1. Silva, E.O.; Bathista, A.L.B.S.; Tavares, M.I.B., Nogueira, J.S. III Encontro Regional de Polímeros, Rio de Janeiro, 22 de Novembro de 2000.
2. Costa, D.A.; Oliveira, C.M.F.; Tavares, M.I.B. *J Appl Polym Sci* 1998, 69, 129.
3. Souza, C.M.G.; Tavares, M.I.B. *J Appl Polym Sci* 1998, 70, 2457.
4. Silva, N.M.; Tavares, M.I.B.; Stejskal, E.O. *Macromolecules* 2000, 33, 115.
5. Harris, R.K. In *Proceedings of the Fifth International Conference on Applications of Magnetic Resonance in Food Science*; University of Aveiro, Portugal, 2000; pp.18–20.
6. Mothé, C.G.; Tavares, M.I.B. In *Proceedings of the Fifth International Conference on Applications of Magnetic Resonance in Food Science*; University of Aveiro, Portugal, 2000; Vol. I, p. 140.
7. Harris, R.K. In *Polymer Spectroscopy*; Fawcett, A.H., Ed.; John Wiley & Sons: England, 1996.