# Nuclear Magnetic Resonance Study of Commercial Poly(vinyl acetate)

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**ABSTRACT:** The commercial poly(vinyl acetate) bulk was studied by nuclear magnetic resonance (NMR) at solution and solid state to understand much better the behavior of this polymer to obtain information on structure, sample molecular mobility, and heterogeneity. To analyze the behavior of this polymer, we have chosen NMR techniques, such as carbon-13 solution, magic angle spinning, cross-polarization/magic angle spinning, proton spin-relaxation time in the rotating frame parameter  $(T_1\rho)$ , and dipolar dephasing experiment. Therefore, from the NMR response, poly(vinyl acetate) presents a random monomer sequence distribution along the macromolecule chains, and this provides microdomains with different mobilities. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2457–2461, 1998

Key words: NMR; PVAc

## INTRODUCTION

Poly(vinyl acetate) (PVAc) varies with molecular weight from viscous to brittle polymeric materials.<sup>1,2</sup> Because this polymer presents a low softening temperature, it can be used to mold solidshaped articles. The great majority of PVAc applications are in compounding solutions, such as dispersions with plasticizers, inert fillers and pigments for paints, and binders and adhesives.<sup>3</sup> Besides these applications, the PVAc can be used in polymer blends with a particular objective.

The main purpose of this work is to obtain information on bulk PVAc before blending with other polymers to prepare a new product with good molding properties and specific application. To extract as much information as possible on PVAc structure<sup>4,5</sup> and its molecular dynamic,<sup>6–13</sup> we have chosen nuclear magnetic resonance (NMR) spectroscopy using both solution and solid-state experiments. From the carbon-13 solution, it is possible to identify the microstructure of polymer chains.<sup>5</sup> The comparison between magic angle spinning (MAS) (using special conditions to detect only the mobile regions) and cross-polarization (CP)/MAS is the first indication of molecular mobility and heterogeneity.<sup>9–13</sup> Through proton  $T_1\rho$ , we can detect the spin–spin communication; if it is not efficient, two or more domains can be detected as a consequence of sample heterogeneity.<sup>10–13</sup> The dipolar dephasing experiment can be used with a purpose to select the mobile region, using an appropriate dephasing time.

#### **EXPERIMENTAL**

The PVAc studied herein is a commercial product. The sample was run as a 20% solution in chloroform-d as the lock solvent. All NMR solution spectra were conducted on a VARIAN Gemini 300 spectrometer operating at 300.1 MHz and 75.4

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Figure 1 Solution carbon-13 NMR spectrum of bulk PVAc.

MHz for <sup>1</sup>H and <sup>13</sup>C, respectively. All experiments were performed at ambient probe temperature using a 90° pulse angle. The nuclear Overhause effect (NOE) was eliminated. All <sup>1</sup>H and <sup>13</sup>C shifts were referred to tetramethylsilane.

All NMR solid-state spectra were obtained on a VARIAN VXR 300 spectrometer operating at 299.9 MHz and 75.4 MHz for  $^{1}$ H and  $^{13}$ C, respec-

Table I	Chemical	Shifts	of	Carbon-13	Groups
of PVAc					

$\begin{array}{c} Chemical \ Shift \\ \delta \ (ppm) \end{array}$	Structure
169.9 169.8	С=0
67.5	$C_{\alpha}$ (mm)
66.5 66.3 65.9	$\mathrm{C}_{lpha}\left(\mathrm{mr} ight)$
65.5	$C_{\alpha}$ (rr)
39.5 39.1 38.8 38.3	$\mathrm{C}_{oldsymbol{eta}}$
20.7	$CH_3$

tively. The experiments were performed at ambient probe temperature and performed using gated high-power decoupling. Zirconium oxide rotor of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra at spinning rates of 5 kHz. Carbon-13 spectra are referred to the chemical shift of the methyl group carbons of hexamethyl benzene (17.3 ppm). The <sup>13</sup>C were conducted in the CP/MAS mode with a 90° pulse and a delay of 2 s; CP/MAS with time dipolar dephasing,  $\tau$ , and 400 and 800  $\mu$ s; and variation contact time and MAS. A range of contact time was established as 100–8,000  $\mu$ s. Proton  $T_1\rho$  were determined from the intensity attenuation of carbon-13 peaks with increasing contact times.

Table II	Chemical	Shifts	of H	ydrogen	of	<b>PVAc</b>
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Chemical Shift δ (ppm)	Hydrogen Type
4.74	СН—О
1.92 1.90 1.87	${f CH}_3$ Isotactic CH $_3$ Atactic Syndiotactic
1.71 1.64	$\overset{\mathbf{CH}_2}{\mathbf{CH}_2}$



Figure 2 Carbon-13 CP/MAS NMR spectra of three different contact times of bulk PVAc. \*ssb—spinning side bands

## **RESULTS AND DISCUSSION**

From the carbon-13 NMR solution spectrum (Fig. 1), it can be seen that PVAc is a amorphous polymer, and it presents a random distribution of configurational sequences. The assignments of the carbon-13 as namely in Structure 1 are listed in Table I.



Structure 1

From Table I, it can be seen that the multiplicity of the  $C_{\alpha}$  signals is due to the isotactic (mm), heterotactic (mr), and syndiotactic (rr) triads. The value of each microstructure sequence was obtained from the integration of carbon-13 signals that are: isotactic, 21.2%; heterotactic, 71.2%; and syndiotactic, 7.6%.

The hydrogen NMR solution spectrum was also registered, and the presence of distinct sequences distribution were confirmed from the triads assignments (Table II). The solid-state behavior of an amorphous polymer can be initially analyzed by a comparison between MAS and CP/MAS spectra.<sup>12,15,16</sup>



**Figure 3** Logarithmic plots of intensity decay *vs.* contact time (milliseconds) of bulk PVAc.

The MAS carbon-13 NMR spectrum of PVAc did not present a significant change in both chemical shifts and lines formed in comparison with CP/MAS spectrum. Three CP/MAS carbon-13 NMR spectra at different contact times (short contact time, 100  $\mu$ s; intermediate contact time, 800  $\mu$ s; and long contact time, 2,000  $\mu$ s) (Fig. 2) show the same NMR lines as the MAS spectrum, which can be a first indication that the sample is homogeneous and confirms that PVAc is completely amorphous.

The proton spin-lattice relaxation times in the rotating frame  $(T_1^H \rho)$  were measured from the carbon-13 intensity decay for all types of all resolved carbon-13 in the macromolecular chains. Figure 3 shows the plot of carbon-13 intensity decay *versus* contact time, and the values of  $T_1^H \rho$  parameter are listed in the Table III.

Only one value of  $T_1^H \rho$  was found for all types of resolved carbons, which confirms the homogeneity of the homopolymer.

The carbon-13 CP/MAS spectrum with dipolar dephasing using a dephasing time of 400  $\mu$ s was recorded. Four signals were detected: one at 168.7 ppm referred to a C=O of carboxyl group; a second one at 40.2 ppm, which was attributed to CH<sub>2</sub> group, but the signal was inverted as a consequence of no complete dephasing; and the last one at 19.6

**Table III**  $T_1^H \rho$  Values of PVAc

	Proton $T_1\rho$ (ms)			
Sample $\delta(^{13}C)$	170.7	67.3	40.2	21.5
PVAc	3.6	3.1	3.3	1.7



**Figure 4** Carbon-13 CP/MAS/DD NMR spectra: (a) dephasing time, 400  $\mu$ s; (b) dephasing time, 800  $\mu$ s. SSB—spinning side bands

ppm was attributed to methyl group, which possibly comes from the syndiotactic sequence [Fig. 4(a)]. When the dephasing time was 800  $\mu$ s, only two signals were observed: the C=O of carboxyl and methyl groups that presented the same chemical shifts in relation to the spectrum obtained at 400  $\mu$ s [Fig. 4(b)]. From this technique, it was possible to observe some microstructure differences in NMR solid state. In this experiment, the <sup>1</sup>H decoupler was turned off for 400  $\mu$ s before data acquisition started, a treatment that typically quenches signals due to solid phase. This occurred because of strong dipolar interactions with linked protons. Although carbons-13, which have rapid rotation even in solid attenuates, <sup>13</sup>C-<sup>1</sup>H dipolar interactions, as well as nonprotonated carbons, are expected to be observed. The methyl and CH—O groups have high mobility and normally are detected if the dipolar dephasing time is equal to 400  $\mu$ s. The resonance lines detected by CP/MAS/dipolar dephasing at the two different dephasing times confirm the presence of a domain that presents high mobility, which was not able to be detected by normal CP/MAS. They were assigned as different monomer sequence arrangement and confirm the presence of microstructure in this polymer.

#### CONCLUSIONS

The NMR response from the solid-state relaxation parameter—MAS and CP/MAS, as well as CP/MAS/dipolar dephasing—was permitted to analyze the behavior of this polymer in relation to the molecular mobility. It was also possible to understand better the chains conformation and molecular heterogeneity due to the small domains created by the microstructures, which was pointed out by the dipolar dephasing technique.

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