KINETICS OF ^{1}H-^{13}C NMR CROSS POLARIZATION IN RIGID POLYMERS

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1. Introduction

The ^{1}H-^{13}C cross polarization (CP) NMR technique makes it possible to enhance the signal of diluted ^{13}C nuclei through polarization transfer from abundant ^{1}H nuclei when the radiofrequency fields applied to ^{1}H (*I*) and ^{13}C (*S*) nuclei fulfil the Hartmann-Hahn (HH) condition $\omega_{1,I} = \omega_{1,S}$[1]. Signal intensities in ^{1}H-^{13}C CP MAS NMR spectra depend on the contact time τduring which the polarization is transferred from protons to carbon nuclei, moreover on the number of protons in the vicinity of particular carbon nuclei, and the mobility of groups involved in the CP process, which is characterized by the T_{CH} cross polarization constant (*I-S* model). If spin diffusion is fast and both systems are in contact with the lattice, the relaxation process is governed by relaxation times in the rotating frame $T_{1\mathrm{\rho}}^{\mathrm{H}}andT_{1\mathrm{\rho}}^{\mathrm{C}}$[2]. The polarization intensity $I_{\mathrm{C}}(\tau)$in the CP spectrum, on condition that $\frac{T_{\mathrm{CH}}}{T_{1\mathrm{\rho}}^{\mathrm{C}}} \approx 0$, can then be expressed as

$$I_{\mathrm{C}}(\tau) = I_{0\mathrm{C}}\left[exp\left(-\frac{\tau}{T_{1\rho}^{H}}\right) - exp\left(-\frac{\tau}{T_{CH}}\right)\right] \tag{1}$$

If the ^{1}H-^{13}C pair is rigid and isolated from the lattice, the polarization transfer proceeds through transient oscillations first observed in the spectrum of ferrocene crystal, where the frequency of oscillations is directly related to the C-H dipolar coupling constant D and depends on the orientation of the crystal in the magnetic field [3].
The dipolar coupling constant between ^{1}H and ^{13}C nuclei depends on their gyromagnetic ratios γ_H, γ_C and internuclear distance r [4]:

$$D = \frac{\mu_0 h \gamma_H \gamma_C}{16\pi^3}\frac{1}{r^3} \tag{2}$$

In a powder sample due to the averaging of crystallites orientation the transient oscillations are damped and the observed polarization intensity $I_{\mathrm{C}}(\tau)$can be described with the following expression [5]:

$$I_C(\tau) = I_{0H}\left(\frac{1}{2}\left(1 - exp(-k_1\tau)\, g_n(\tau)\right) - \left(\frac{I_{qeC}}{I_{0H}} - \frac{1}{2}\right)(1 - exp(-k_2\tau))\right) \tag{3}$$

where$g_n(\tau)(n = 0)$ is an oscillatory term expressed using Bessel functions, the frequency of which is directly proportional do the dipolar coupling constant D,I_{0H} is the polarization of ^{1}H nuclei, quasi-equilibrium polarization of ^{13}C is defined as $I_{qeC} = \frac{NI_{0H}}{(N+1)}$ where N is the number of bonded ^{1}H, $k_1$and k_2 are the first-order rate constants that describe the decay of transient oscillations and the spin diffusion with remote ^{1}H spins (*I-I*-S* model). In the case of an isolated spin pair (N = 1) the second term in the above expression describing spin diffusion vanishes.

The effect of spinning the sample at magic angle with respect to the direction of the external magnetic field (MAS technique) on the polarization transfer between abundant and dilute spins is negligible for small spinning frequencies [6,7] and the polarization transfer occurs when the HH condition $\omega_{1,I} = \omega_{1,S}$[1]is fulfilled. However, when MAS frequencies $\omega_r$exceed homonuclear and heteronuclear dipolar interaction frequencies(characterized by dipolar coupling constants) the HH condition splits into side-band match conditions$\omega_{1,I} = \omega_{1,S} + n\omega_r, n = \pm 1, \pm 2$.At fast spinning speeds the polarization transfer at exact HH condition is not expected, but it can be effective only due to heteronuclear scalar coupling and flip-flop processes among remote I spins [4]. When the CP experiment is performed on a sample spinning at magic angle with rate$\frac{\omega_\mathrm{r}}{2\pi} \gg D$, the observed magnetization $I_\mathrm{C}(\tau)$can be expressed using equation (3) in which $g_\mathrm{n}(\tau)$ terms (n=±1, ±2) take into account the averaging of dipolar coupling constant D and can also be expressed in terms of Bessel functions [5].

The aim of the presented research is to show that information on the C-H dipolar coupling constants whose values reflect molecular dynamics of particular groups in rigid polymers can also be obtained from the ^{1}H-^{13}C CP MAS NMR spectra. The NMR measurements were performed on polylactic acid (PLA),whose structure contains rigid CH groups, mobile CH_3 groups and CO groups with no directly-bonded protons.

2. Experimental

NMR measurements were performed on an amorphous PLA sample prepared from virgin pelletized PLA 4042D, Nature Works, LLC, USA, quenched in cold water after melting in a twin-screw extruder at 190 °C.

The ^{1}H-^{13}C CP MAS NMR and ^{1}H NMR measurements were performed on a Varian 400 MHz NMR spectrometer (Palo Alto, CA, USA). The high-resolution ^{13}C NMR spectra were recorded at a resonance frequency of approximately 100 MHz with the use of 4 mm ZrO_2 rotors and MAS frequency of 4 and 10 kHz at room temperature. ^{13}C NMR spectra were recorded under cross-polarization (CP) condition with 90° pulse of 6 μs, contact time of 0.1-15ms, acquisition time of 20ms, high power proton decoupling of 67.6kHz, recycle delay of 6 s, and averaging over 256scans. The spectra were processed using MestReNova software. The fitting procedure of the obtained integral intensities of the lines in NMR spectra plotted as a function of the contact time was carried out using the SciDavis programme.

3. Results and Discussion

The ^{13}C MAS NMR spectrum of amorphous PLA displays three broad lines at 169.9, 69.5 and 16.9 ppm, which are assigned to CO, CH and CH_3 groups respectively. As mentioned above the measurements of ^{1}H- ^{13}C CP MAS NMR spectra require setting the HH condition. This can be done by measuring the HH matching profile, i.e. recording NMR spectra at a constant ^{1}H r.f. field while changing the ^{13}C r.f. field. The HH matching profiles for a CH group measured at 4 and 10 kHz (Fig. 1) at contact time of 1 ms show that MAS rate of 4 kHz has a negligible effect on the polarization transfer between ^{1}H and ^{13}C nuclei, since the shape of the profile at this MAS rate is similar to that of static samples[5]. The MAS rate of 10 kHz resulting in partial splitting of the HH profile into sidebands obviously does not exceed homonuclear and heteronuclear interaction frequencies. For this reason the ^{1}H- ^{13}C CP MAS NMR spectra at increasing constant contact times were measured at MAS rate of 4 kHz under exact HH condition.

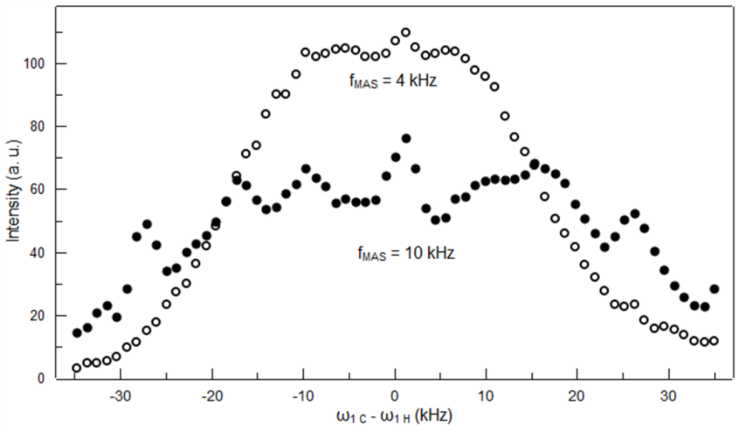

Fig.1:*Hartmann-Hahn matching profiles for CH group measured at MAS rates of 4 kHz and 10 kHz and contact time of 1 ms.*

The normalized integral intensities of the CH line in ^{1}H- ^{13}C CP MAS NMR spectra were plotted against contact time (Fig. 2). The fitting of the CP curve required the combination of two functions (1) with two different $\boldsymbol{I_{0C}}$ fractions ($\boldsymbol{I_1}$, $\boldsymbol{I_2}$) and $\boldsymbol{T_{CH}}$ values (insert in Fig. 2, Tab. 1), while $\boldsymbol{T_{1\rho}^{H}}$ was determined from other CP measurements. In spite of the fact that the PLA sample is amorphous and CH carbons produce only one broad peak in the NMR spectrum, two carbon relaxation times were observed for these carbons [8]. The shorter and longer $\boldsymbol{T_{CH}}$times can then be related to carbons with different mobility.

In the initial stage of CP transfer, transient oscillations were observed(Fig. 2) and the expression (3) for $\boldsymbol{n = 0}$ was fitted to the CP curve. The dipolar coupling constant $\boldsymbol{D}$ is directly proportional to the frequency of transient oscillations. The C-H distance in PLA is 0.107 nm, which results in dipolar coupling constant $\boldsymbol{D = 24.7}$ **kHz** (2). This value can be considered as the rigid-limit value [9]. Lower values of $\boldsymbol{D}$ constants result in a larger C-H distance, which can be considered as an “effective distance” enlarged due to the motion. Since there are two kinds of carbons with different mobility, two values of dipolar coupling constant can be expected and for this reason a combination of two functions (2) with different $\boldsymbol{I_{0H}}$fractions ($\boldsymbol{I_1}$, $\boldsymbol{I_2}$) and $\boldsymbol{D}$ values was fitted to the CP curve (Fig. 2, Tab. 1).

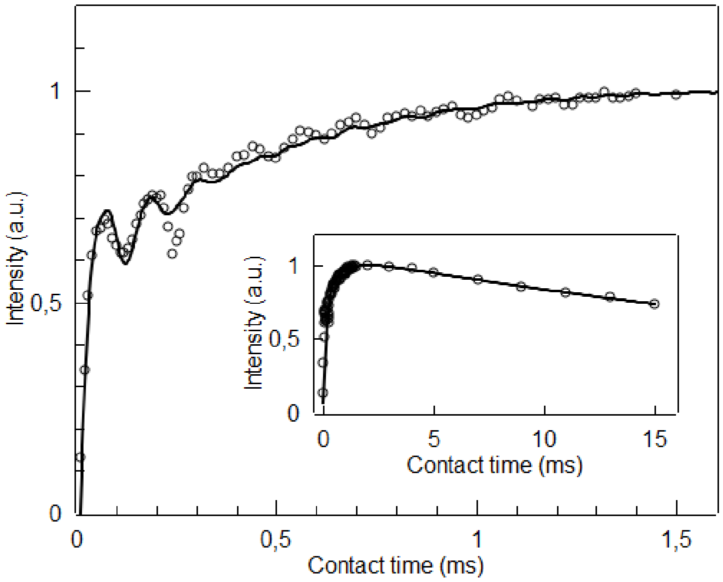

Fig.2: *Transient oscillations in ^{1}H-^{13}C cross polarization of CH group*

Tab. 1.*The intensity fractions and dipolar coupling constants obtained from the fitting procedure of the functions (1) and (3) for I-Sand I-I*-S cross polarization models respectively.*

CP	*I-S*				*I-I*-S*			
Group	I_1	I_2	T_{CH1} (ms)	T_{CH2} (ms)	I_1	I_2	D_1 (kHz)	D_2 (kHz)
CH	0.68	0,32	0,12	0,73	0,71	0,29	18,3	16,4
CH_3	0,57	0,43	0,62	0,05	0,67	0,33	8,8	7,8

The results obtained from the fitting procedure of the measured CP curves confirmed the presence of two kinds of CH and CH_3 carbons with different mobility. For CH carbons very close values of intensity fractions for more rigid CH carbons (0.68 and 0.71) were obtained from both CP models. TheCH_3intensity fractions for more rigid carbons (0.43 and 0.67) differ, which can be caused by lower values of the dipolar coupling constant and hence higher uncertainty in estimation of the frequency of transient oscillations.

4. Conclusion

The parameters of ^1H-^{13}C CP NMR kinetics provide information on the mobility of carbon species in rigid polymers. In spite of the amorphous character of the studied PLA sample, the presence of two kinds of CH and CH_3carbons with different mobility can be deduced from the fitting parameters of the CP curves measured for both carbon groups.

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