Proceedings of the 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13–17, 2016

Dynamics of ^{1}H-^{13}C Cross Polarization in Nuclear Magnetic Resonance of Poly(3-hydroxybutyrate)

M. Koval'aková*, O. Fričová, M. Hutníková, V. Hronský and D. Olčák
Department of Physics, Faculty of Electrical Engineering and Informatics, Technical University of Košice, Park Komenského 2, 042 00 Košice, Slovakia

Poly(3-hydroxybutyrate) (PHB) is a semicrystalline biodegradable polymer with chains consisting of methyl (CH_3), methylene (CH_2), methine (CH) and carbonyl (CO) groups. The ^{1}H–^{13}C cross polarization NMR measurements were performed on an as-supplied powder PHB sample at a magic-angle spinning rate of 10 kHz. The measured cross polarization build-up curves and their analysis provided information on the dynamics of ^{1}H–^{13}C NMR cross polarization in functional groups with directly bonded hydrogens. The measurements required setting up the Hartmann–Hahn condition, which was inferred from the Hartmann–Hahn matching profiles measured for each functional group. The cross polarization build-up curves displayed an oscillatory course, which indicates the presence of rigid ^{1}H–^{13}C spin pairs isolated from the lattice. The frequency of the observed oscillations is directly proportional to the ^{1}H–^{13}C dipolar coupling constant, which is related to the C–H distance and its value also reflects the mobility of particular functional groups. The values of dipolar coupling constants were derived from splittings in the Fourier transforms of cross polarization build-up curves. The mobility of particular groups was assessed with the order parameter $\langle S \rangle$ calculated using experimental and rigid lattice values of dipolar coupling constants.

DOI: 10.12693/APhysPolA.131.1162
PACS/topics: 74.25.nj, 79.60.Fr, 61.05.Qr

1. Introduction

Polarization transfer in ^{1}H-^{13}C cross polarization NMR experiments performed on static samples occurs 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]. The effect on polarization transfer of sample spinning at the magic angle (MAS technique) is negligible for MAS frequencies smaller than homonuclear and heteronuclear dipolar interaction frequencies. However, when the MAS rate is comparable or higher than the frequencies of dipolar interactions, the HH condition splits into side-band match conditions known as the HH matching profile $\omega_{1,I} = \omega_{1,S} + n\omega_r$, where $n = \pm 1, \pm 2, \ldots, \omega_r$ is MAS angular frequency [2], at MAS rates considerably higher than dipolar interaction frequencies only four side-bands in the HH profile are observed [3] and polarization transfer at the exact HH condition is not expected [4].

In general, signal intensities in ^{1}H–^{13}C CP NMR spectra depend on the contact time during which the polarization transfers from ^{1}H to ^{13}C nuclei, the number of protons in the vicinity of particular ^{13}C nuclei, and the mobility of groups involved in the CP process. If there is a dominant dipolar interaction the polarization transfer shows oscillatory behaviour [5] and the CP build-up curve of a powder obeys a function combining the oscillatory term expressed using the Bessel functions and the term related to spin diffusion from remote spins [4, 6].

*corresponding author; e-mail: maria.kovalakova@tuke.sk

The dipolar coupling constant between ^{1}H and ^{13}C nuclei depends on their gyromagnetic ratios γ_H, γ_C and the internuclear distance r [4], and for the C–H bond it is 24.7 kHz. This value is considered as a rigid-lattice value D_{rigid}. The experimental values D_{exp} are lower since they are reduced by fast molecular processes. Hence the order parameter $\langle S \rangle = D_{\text{exp}}/D_{\text{rigid}}$ provides information on group mobility [7]. The frequency of transient oscillations f_{osc} is directly proportional to the dipolar coupling constant D_{exp} and when the value of f_{osc} is obtained from CP MAS experiments performed under the HH condition $\omega_{1,I} = \omega_{1,S} \pm \omega_r$, it can be calculated as $D_{\text{exp}} = 2f_{\text{osc}}$ [8].

Poly(3-hydroxybutyrate) ([–CH(CH_3)–CH_2–CO–O–]$_n$) is a semicrystalline thermoplastic biodegradable and biocompatible material with great potential for replacing conventional plastics. Its physical and mechanical properties are comparable to those of isotactic polypropylene. The glass transition temperature of PHB is in the range of 5–15 °C and the melting temperature in the range of 168–182 °C. PHB crystallizes in an orthorhombic crystal structure with two antiparallel helical chains in a crystalline cell. Its crystallinity is 55–85% [9]. The crystalline structure is stabilized by hydrogen bonding between carbonyl (CO) and methyl (CH_3) groups of adjacent helices [10].

In a semicrystalline polymer the mobility of chain segments in amorphous domains markedly increases with temperature above the glass transition temperature, while chains in crystalline domains remain rigid. Molecular dynamics in amorphous and crystalline regions of PHB was studied using ^{13}C NMR [11–13] at room temperature and at elevated temperatures.

The main drawbacks of PHB are its brittleness, poor thermal stability, and degradation of its mechanical prop-

erties due to secondary crystallisation [9]. Elucidation of the structural and molecular dynamics of PHB plays the key role in governing its properties in the course of preparation and storage. The aim of this study was to assess the mobility of functional groups in PHB structure with the order parameter $\langle S \rangle$ calculated using experimental and rigid lattice values of dipolar coupling constants.

2. Experimental

Virgin powdered PHB (Biomer, Germany) was used for NMR measurements. The ^{1}H–^{13}C CP MAS NMR and ^{1}H NMR measurements were performed on a Varian 400 MHz solid-state NMR spectrometer (Palo Alto, CA, USA) with Varian Wide Bore Triple Resonance T3 MAS NMR Probe (setting in HX configuration). 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 10 kHz at room temperature. The spectra were recorded under CP conditions with 90° pulse of 3.6 μs, contact time of 0.02–20 ms and 0.01–2 ms, acquisition time of 40 ms, high power proton decoupling of 70 kHz, recycle delay of 10 s, and averaging over 128 scans. The transmitters were set on resonance for particular functional groups during measurements. The spectra were processed using MestReNova software. The Fourier transform of detailed CP build-up curves (integral intensities of the lines in NMR spectra plotted as a function of the contact time) were carried out after multiplying the data by –1, subtracting the final signal value and zero-filling in the Origin program.

3. Results and discussion

The Hartmann–Hahn matching profiles were measured for CH, CH_2 and CH_3 groups (Fig. 1) at contact times of 1 and 0.1 ms. Profiles measured at the contact time of 0.1 ms are characterized by a low signal at the exact HH condition and overlapping sidebands positioned symmetrically with respect to the exact HH condition at ±10 and ±20 kHz. The initial stage of the CP process is governed by heteronuclear dipolar interactions. In PHB structure the strength of these interactions must be larger than 10 kHz since this MAS rate cannot separate the pairs of spinning sidebands as it is below the fast MAS regime [3]. The HH profiles measured at contact time of 1 ms show that there is polarization transfer at the exact HH condition and six spinning sidebands are observed in the profiles of all three functional groups. Weaker dipolar coupling for CH_3 groups can be deduced from the sharp spinning sidebands observed in the HH matching profile (Fig. 1c).

The CP build-up curves for CH, CH_2, and CH_3 groups were then measured under CP condition $\omega_{1,I} = \omega_{1,S} + \omega_r$ and at contact times of 0.02–20 ms (insets in Fig. 2). Transient oscillations can be observed in the initial stages of the CP process for all functional groups and 10 kHz oscillations related to quasi-equilibria states [14]. In order to obtain more detailed data on transient oscillations the CP build-up curves were measured again at equidistant increments of contact time of 0.01 ms up to 2 ms

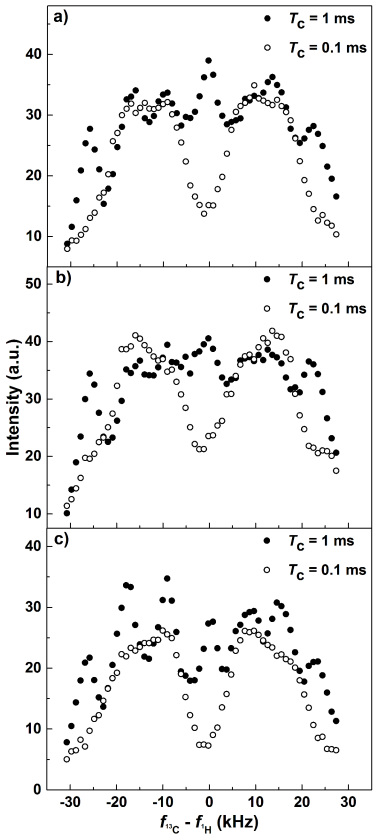

Fig. 1. Hartmann–Hahn matching profiles measured for (a) CH, (b) CH_2, and (c) CH_3 groups in PHB at contact times of 1 and 0.1 ms.

(Fig. 2). As mentioned above, the frequency of transient oscillations was directly related to the dipolar coupling constant. Its value can be derived from the dipolar spectrum obtained by the Fourier transforms of the CP build-up curve [8], since the splitting in this spectrum can be used for calculation of the dipolar coupling constant value. The Fourier transforms can be seen in Fig. 3 and dipolar coupling constant values calculated using expression $D_{\mathrm{exp}} = 2\sqrt{2} f_{\mathrm{osc}}$ are listed in Table I.

Our measurements were performed at room temperature, which is above the glass transition temperature of PHB and for this reason increased mobility can be expected in its amorphous phase. The presence of crystalline and amorphous phases in the studied sample was inferred from the shape of the measured ^{13}C NMR spectra (not shown). However, the differences in mobility of backbone CH and CH_2 groups in crystalline and amorphous domains of PHB are probably too small to be reflected in $\langle S \rangle$ values (Table I) due to the proximity of room temperature to the glass transition temperature. The values of $\langle S \rangle$ parameter indicate that these groups are rather rigid in both crystalline and amorphous phases. The situation is different for mobile side-chain CH_3 groups with threefold axis of symmetry performing rotational motion. Their $\langle S \rangle$ values are distinctly lower. The largest $\langle S \rangle$ value of 0.43 could be related to CH_3 groups in crystalline domains which are stabilized

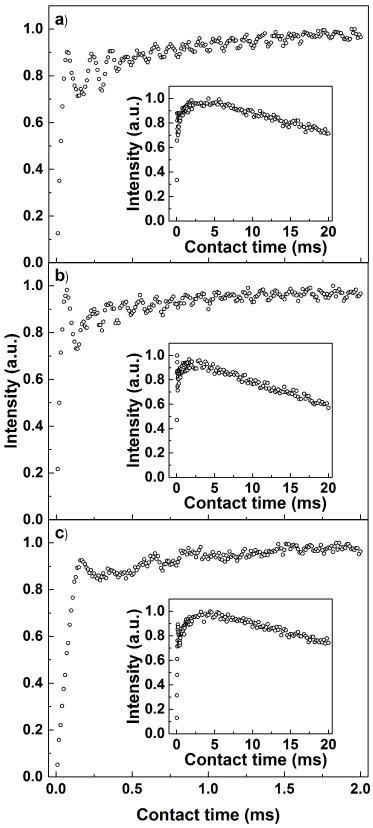

Fig. 2. Detailed CP build-up curves for (a) CH, (b) CH_2, and (c) CH_3 groups in PHB measured up to contact time of 2 ms and overall CP build-up curves measured up to 20 ms (insets).

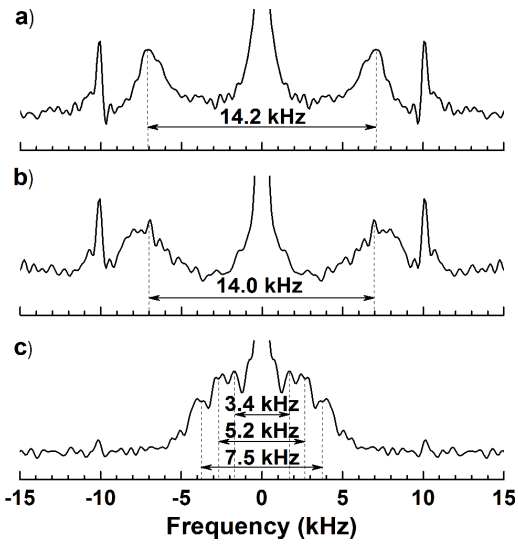

Fig. 3. Fourier transform of CP build-up curves for (a) CH, (b) CH_2, and (c) CH_3 groups in PHB.

by hydrogen bonds. The more mobile CH_3 groups with $\langle S \rangle$ values of 0.30–0.19 could be located in amorphous domains in which less mobile groups can be involved in chain entanglements and hydrogen bonds which restrict their mobility.

TABLE I

The values of dipolar coupling constant $D^*_{\rm exp}$ and order parameter $\langle S \rangle$ for CH, CH_2 and CH_3 groups in PHB.

Group	CH	CH_2	CH_3	
$D_{\rm exp}$ [kHz]	20.1	19.8	10.6	7.4–4.8
$\langle S \rangle$	0.81	0.80	0.43	0.30–0.19

* the estimated error is ±0.3 kHz.

4. Conclusions

The dipolar coupling constants and the values of order parameter for CH, CH_2, and CH_3 groups derived from the analysis of CP build-up curves revealed that at room temperature the mobility of backbone chain groups (CH and CH_2) does not differ distinctly in crystalline and amorphous domains. In contrast, the side-chain CH_3 groups are sensitive to space restrictions and their mobility is different in the rigid crystalline phase and the amorphous phase, in which slow segmental motion creates more favourable conditions for CH_3 rotational motion.

Acknowledgments

This research was supported by the project "Centre of Excellence for Integrated Research & Exploitation of Advanced Materials and Technologies in Automotive Electronics" ITMS 26220120055.

References

[1] S.R. Hartmann, E.L. Hahn, *Phys. Rev.* **128**, 2042 (1962).

[2] E.O. Stejskal, J. Schaefer, J.S. Waugh, *J. Magn. Reson.* **28**, 105 (1977).

[3] S. Hediger, B.H. Meier, R.R. Ernst, *Chem. Phys. Lett.* **213**, 627 (1993).

[4] C.A. Fyfe, A.R. Lewis, J.-M. Chézeau, *Can. J. Chem.* **77**, 1984 (1999).

[5] L. Müller, A. Kumar, T. Baumann, R.R. Ernst, *Phys. Rev. Lett.* **32**, 1402 (1974).

[6] S. Hediger, Ph.D. Thesis, Eidgenössische Technische Hochschule, Zürich 1997.

[7] E.R. Andrew, R.G. Eades, *Proc. R. Soc. Lond. A* **216**, 398 (1953).

[8] S.A. Reinsberg, Ph.D. Thesis, Durham University, 1998.

[9] I. Chodák, in: *Monomers, Polymers and Composites from Renewable Resources*, Eds. N.M. Belgacem, A. Gandini, Elsevier, 2008, p. 451.

[10] H. Hoshina, Y. Morisawa, H. Sato, A. Kamiya, I. Noda, Y. Ozaki, Ch. Otani, *Appl. Phys. Lett.* **96**, 101904 (2010).

[11] L. Zhang, H. Tang, G. Hou, Y. Shen, F. Deng, *Polymer* **48**, 2928 (2007).

[12] F. Nozirov, Z. Fojud, J. Klinowski, S. Jurga, *Solid State Nucl. Magn. Reson.* **21**, 197 (2002).

[13] Y. Chen, G. Yang, Q. Chen, *Polymer* **43**, 2095 (2002).

[14] D. Sakellariou, P. Hodgkinson, S. Hediger, L. Emsley, *Chem. Phys. Lett.* **308**, 381 (1999).