

Solid State ^{13}C Nuclear Magnetic Resonance Study of Morphology and Molecular Mobility in Quenched Poly(3-hydroxybutyrate)

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Single pulse magic angle spinning ^{13}C NMR spectra and the carbon spin–lattice relaxation times $T_1(^{13}\text{C})$ were used for the study of morphology and molecular mobility in poly(3-hydroxybutyrate) quenched in cold water after melting in a twin-screw extruder. The crystallinity of the quenched sample was found to be comparable with that of virgin material, and the decrease in dimensions of the crystallites grown after quenching was deduced from the single pulse magic angle spinning ^{13}C NMR spectra. The spin–lattice relaxation curves for the carbons of the CO, CH, CH_2 and CH_3 groups were found to be bi-exponential, which enables the molecular mobility within crystalline and amorphous domains to be studied. The spin–lattice relaxation times $T_1(^{13}\text{C})$ estimated for the carbons of the CO, CH, CH_2 groups show the chain mobility enhancement within crystalline domains of the quenched sample, but the influence of the quenching on the CH_3 group rotation and on the main chain motion within amorphous regions was not observed.

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1. Introduction

Biodegradable polymers are currently attracting much interest from researchers because of their physical properties, which are similar to those of conventional thermoplastics such as polyethylene and polypropylene. One of these polymeric materials is poly(3-hydroxybutyrate) (PHB) which is a semi-crystalline polymer belonging to the class of polyhydroxyalkanoates. It is a fully biodegradable and biocompatible polymer produced from renewable resources. Such biodegradability and biocompatibility together with its renewable and environmentally-friendly nature make PHB particularly attractive for many applications in biomedicine, food packaging, or drug delivery systems [1].

The physical properties of polymers are strongly dependent on their structure and morphology, which can be influenced by changing the crystallization conditions and by quenching or annealing at different temperature. In this paper, the effect of quenching on morphology and molecular mobility of PHB was studied using solid-state NMR techniques.

2. Experimental

The virgin powdered PHB (PHB-v) supplied by Biomer, Germany and quenched PHB (PHB-q) prepared by melting PHB-v in a twin screw extruder at 190°C and subsequently quenching in cold water (approximately 15°C) at temperature which was above the glass transition temperature of PHB (5°C) were used for this study.

The high-resolution solid state ^{13}C NMR measurements were performed on a Varian 400 MHz NMR spectrometer (Palo Alto, CA, USA) at a resonance frequency of approximately 100 MHz, a magic angle spinning (MAS) rate of 10 kHz, and using a 4 mm zirconium oxide rotor. The temperature of the variator was set at the room temperature, but the temperature of the spinning sample was 31°C [2].

The single-pulse (SP) MAS ^{13}C NMR measurements were performed with the use of SPINAL pulse high-power proton decoupling of 90 kHz [3]. Recycle delay, spectral width, and acquisition time were 120 s, 50 kHz and 20 ms, respectively. The NMR spectrum was obtained using the Fourier transformation of the free induction delay (FID), which involved an average of 1400–1500 scans. The chemical shifts of all spectra were referenced to tetramethylsilane using adamantane as an external standard.

Spin–lattice relaxation times $T_1(^{13}\text{C})$ were measured using the cross polarization (CP) MAS NMR technique according to Torchia [4]. The Hartmann–Hahn condition was obtained with radio frequency field strength of 60 kHz, contact time of 2 ms, acquisition time of 20 ms and delay between two consecutive scans of 6 s. A pulse high-power proton decoupling field of 90 kHz was applied during the acquisition. The $T_1(^{13}\text{C})$ related to the respective resonance lines were found by fitting the intensities of the lines detected after the recovery time, which increased up to 300 s.

3. Results and discussion

3.1. Single-pulse MAS ^{13}C NMR spectra

The SP MAS ^{13}C NMR spectra for virgin and quenched PHB samples are shown in Fig. 1. In spite of the quenching the SP MAS ^{13}C NMR spectra for both samples are very similar and show four clearly resolved

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resonances at 169.8, 68.4, 42.8, and 21.4 ppm corresponding to carbonyl (CO), methine (CH), methylene (CH_2) and methyl (CH_3) groups, respectively. All resonance lines are composed of narrow and broad components arising from crystalline and amorphous domains respectively.

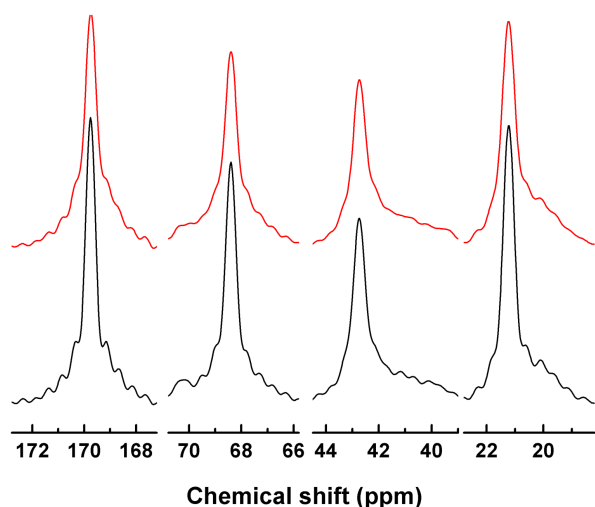


Fig. 1. SP MAS ^{13}C NMR spectra measured at 31°C for virgin PHB-v (bottom) and quenched PHB-q (top) samples.

The ratios of the integral intensities of carbon resonances assigned to CO, CH, CH_2 and CH_3 groups were found to be 0.66 : 0.81 : 0.62 : 1 and 0.71 : 0.87 : 0.70 : 1 for PHB-v and PHB-q, respectively, which differ from the ratios of the numbers of carbons within respective groups, 1:1:1:1. The integral line intensities of CO, CH, and CH_2 carbons were considerably reduced due to a not completely relaxed spin system during recycle delay, which was 120 s. Therefore, only CH_3 carbon resonances of the SP MAS ^{13}C NMR spectra were used for quantitative analysis [5].

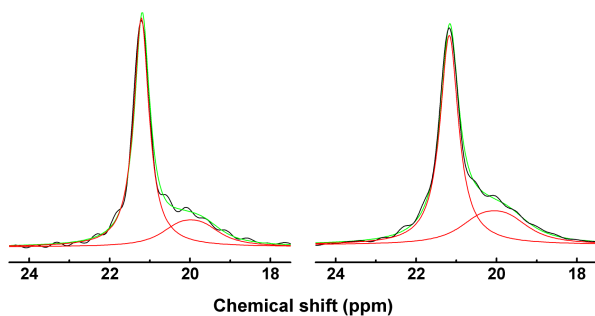


Fig. 2. Deconvolutions of the methyl resonances of the SP MAS ^{13}C NMR spectra measured for PHB-v (left) and PHB-q (right) into Lorentzian and Gaussian lines.

In order to find the effect of quenching on morphology of PHB, deconvolutions of the methyl resonances into Lorentzian (LL) and Gaussian (GL) lines related to the carbons within crystalline and amorphous regions respectively, were carried out. Deconvolutions of the lines are

shown in Fig. 2 and data resulting from deconvolutions are summarized in Table I. The crystallinities X_C were calculated as the ratio of the area below the lines associated with crystalline domains to the total area below resonance line, which is in accordance with two phase model of semi-crystalline polymer.

TABLE I

Widths of the CH_3 resonance lines associated with carbons within amorphous (GL) and crystalline domains (LL) and crystallinities of PHB-v and PHB-q samples.

	CH ₃ carbons		X_C [%]
	Width [Hz]		
	GL	LL	
PHB-v	152	46	75
PHB-q	178	55	69

The data in Table I show that quenching of PHB does not bring about a considerable decrease in the crystallinity as compared with the crystallinity of PHB-v. The increase in the widths of the components related to the crystalline and amorphous domains due to the quenching is evident. The broader lines for the PHB-q sample can be explained by the broader chain conformation distribution within amorphous and crystalline domains after quenching of the virgin PHB. The width of the Lorentzian line related to the crystalline regions depends on the regularity of the chains inside the crystal lattice and within the crystal lattice close to the lamellae surface [6]. Smaller crystallites have a larger relative number of nuclei in the surface layer, which have slightly distorted environment reflected in the Lorentzian line broadening.

3.2. Spin-lattice relaxation times $T_1(^{13}\text{C})$

The spin-lattice relaxation times $T_1(^{13}\text{C})$ for CO, CH, CH_2 and CH_3 carbons were estimated from the areas of the respective resonances of the measured array. The decrease in the intensity for each resonance shows bi-exponential behavior characterized by the $T_{1,l}$ and $T_{1,s}$ relaxation times associated with the long and short components of the relaxation curves. The spin-lattice relaxation curves for respective carbons of virgin PHB are shown in Fig. 3 and the fitted parameters are listed in Table II. It can be noticed from the data that the $T_{1,s}$ values are at least 7 times lower than corresponding $T_{1,l}$, which makes it possible to estimate reliably also the large $T_{1,l}$ values from the relaxation curves measured at recovery times up to 300 s. The relaxation times $T_{1,l}$ and $T_{1,s}$ can be associated with the crystalline and amorphous regions respectively [7]. The spectra of the arrays were detected using the CP technique, and for this reason the intensities in Table II cannot be referred to the amount of crystalline and amorphous domains.

The rate of the spin-lattice relaxation, which is inversely proportional to the relaxation time, depends predominantly on the ^1H - ^{13}C dipolar interactions with directly bonded protons and on fluctuations of the local

magnetic fields produced by protons. The strength of the dipolar interactions is dependent on the distance between the ^{13}C and ^1H nuclei and the fluctuations of the magnetic fields are determined by molecular motion. In general, relaxation rates for the carbons within amorphous regions are higher than for those within crystalline regions due to higher mobility of the chains within amorphous regions.

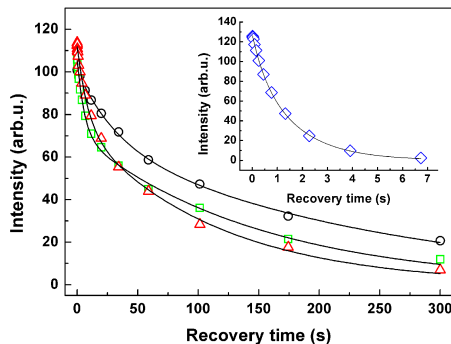


Fig. 3. Decrease in intensities for CO (\circ), CH (Δ) and CH_2 (\square) carbon resonances in dependence on recovery time in the spin-lattice relaxation time measurements for virgin PHB. The inset shows this dependence for the CH_3 (\diamond) resonance.

The relaxation rate of the carbonyl carbons is determined only by the weak dipolar interactions between ^{13}C nuclei and non-bonded intra and inter-chain ^1H nuclei, and it follows from the data in Table I that it is the lowest compared to those of CH, CH_2 , and CH_3 carbons. The relaxation rates of CH, CH_2 , and CH_3 carbons are predominantly determined by fluctuations of local magnetic fields produced by directly bonded protons. The relaxation times estimated for CH_3 carbons are one or two orders lower than those for CO, CH, and CH_2 carbons, which indicates fast relaxation process due to the rotation of methyl carbons.

TABLE II

The relaxation times $T_{1,l}$, $T_{1,s}$ [s] and intensities (given in parentheses) associated with the long and short components of the spin-lattice relaxation curve.

		PHB-v	PHB-q
CO	$T_{1,l}$	240 \pm 18 (0.69)	193.9 \pm 7.3 (0.71)
	$T_{1,s}$	31.3 \pm 4.7 (0.31)	26.4 \pm 1.9 (0.29)
CH	$T_{1,l}$	112.6 \pm 7.4 (0.67)	90.8 \pm 4.8 (0.77)
	$T_{1,s}$	8.9 \pm 1.3 (0.33)	7.98 \pm 0.85 (0.23)
CH_2	$T_{1,l}$ [s]	149.4 \pm 7.2 (0.67)	129.1 \pm 7.1 (0.62)
	$T_{1,s}$	5.66 \pm 0.58 (0.33)	5.51 \pm 0.54 (0.38)
CH_3	$T_{1,l}$	1.67 \pm 0.11 (0.78)	1.60 \pm 0.03 (0.77)
	$T_{1,s}$	0.50 \pm 0.12 (0.22)	0.43 \pm 0.03 (0.23)

It is noteworthy that the relaxation times $T_{1,l}$ for the CH and CH_2 groups do not correspond to the number of directly-bonded hydrogen nuclei, which is in agreement with line intensities obtained from SP MAS ^{13}C NMR

spectra of both samples. Due to the longer relaxation time $T_{1,l}$ for the CH_2 carbons, lower intensity is observed for CH_2 carbons than for CH carbons. The higher relaxation rate of CH carbons than that of CH_2 carbons could be explained by the relatively strong interactions of the CH carbons with ^1H nuclei in the crystal lattice mainly hydrogens of the CH_3 group.

The spin-lattice relaxation times $T_{1,l}$ estimated for CO, CH and CH_2 carbons in quenched PHB are lower than corresponding relaxation times estimated for the virgin sample. On the other hand, the decrease in the $T_{1,s}$ relaxation times due to quenching is observed only within the limits of errors. Furthermore, the data in Table II show that the quenching does not influence the methyl group rotation either within crystalline or amorphous regions.

The decrease of the $T_{1,l}$ values related to the respective main chain carbons within crystalline domains in the quenched sample indicates some chain mobility enhancement. The crystalline chains close to the surfaces of smaller crystals compared with those of the virgin PHB could be the reason for the chain mobility enhancement.

4. Conclusions

The effect of quenching poly(3-hydroxybutyrate) at a temperature just above its glass transition on the morphology and molecular mobility was investigated. Decrease in the dimensions of the crystallites and the mobility enhancement within crystalline domains due to the quenching were concluded from the analysis of SP MAS ^{13}C NMR spectra and the carbon spin-lattice relaxation times $T_{1,l}$ (^{13}C). The influence of the bonded and non-bonded protons on the spin-lattice relaxations of CH and CH_2 groups was also discussed.

Acknowledgments

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