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Polymer 43 (2002) 2095–2099

polymer

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Solid-state NMR study on the structure and mobility of the noncrystalline region of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)

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Received 16 July 2001; received in revised form 6 November 2001; accepted 11 November 2001

Abstract

The noncrystalline structures of poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) copolymers were studied by variable temperature solid-state wide-line ^{1}H NMR and solid-state high-resolution ^{13}C NMR spectroscopy. It is found that at room temperature there exists a rich and rigid component in the noncrystalline region of PHB and PHBV. The content of this component decreases with the increase in 3-hydroxyvalerate content in PHBV and with the increase in temperature. The brittleness of PHB may be partly attributed to the rigidness of the noncrystalline region at room temperature, while the improvement of the properties of PHBV may come from the enhanced mobility of the noncrystalline region.

Keywords: Poly(3-hydroxybutyrate); Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); Solid-state NMR

1. Introduction

As a bacterially synthesized semicrystalline polymer, poly(3-hydroxybutyrate) (PHB) has attracted much research interests for its biodegradability and biocompatibility [1]. However, its industrial application is quite limited, owing to its intrinsic brittleness and narrow processing window. Properties are greatly enhanced in the poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) copolymers [1–4]. Compared with PHB, PHBV exhibits decreased melting point, reduced brittleness and enhanced flexibility and has been used as a biodegradable substitute of polyolefin thermoplastics. Different mechanisms have been suggested to explain the high brittleness of PHB and the property improvement of PHBV over PHB [1,5–7]. Some early works by density measurement [3,8] reported that there is a dramatic decrease in the degree of crystallinity of PHBV with increasing hydroxyvalerate (HV) contents, so it is quite natural to attribute the brittleness of PHB to its high degree of crystallinity [5,6]. However, studies by X-ray, solid-state NMR and IR demonstrated that when the mole content of HV is less than 0.2, the degree of crystallinity barely changes with the variation of comonomer composition [9–12]. Meanwhile, the properties of the samples change considerably. Such a result implies that the brittleness of PHB and the property improvement of PHBV may also be associated with the noncrystalline region of the samples. Recently, Koning et al. [13] attributed the brittleness of PHB to the constraint imposed on the amorphous chains by the amorphous–crystalline interface.

In this work, we present a study on the packing structures and mobility of the noncrystalline region of PHB and PHBV by variable temperature solid-state wide-line ^{1}H NMR spectroscopy and solid-state high-resolution ^{13}C NMR spectroscopy. The aim of the work is to further reveal the phase structure and mobility changes induced by copolymerization and their relation to the properties of PHB and PHBV.

2. Experimental

Samples. PHB and PHBV copolymer samples were purchased from Aldrich Chemical Co. HV comonomer contents in three PHBV samples are 4.33 mol% (PHBV-4.33), 6.96 mol% (PHBV-6.96) and 10.50 mol% (PHBV-10.50), respectively.

The samples were cast from chloroform solution and the

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0032-3861/02/$ - see front matter
PII: S0032-3861(01)00792-3

obtained films were dried under vacuum to constant weight before measurement.

NMR experiments. Solid-state NMR experiments were carried out on a Bruker DSX-300 spectrometer with ^{1}H resonance frequency of 300.13 MHz and ^{13}C of 75.47 MHz. In solid-state wide-line ^{1}H NMR experiments, the ^{1}H 90° pulse width is 2 μs and the number of scans is 64. In solid-state high resolution ^{13}C NMR experiments, the ^{1}H and ^{13}C 90° pulse widths are 3.2 and 3.6 μs, respectively; the contact time for cross-polarization (CP) is 2 ms, the spin rate of the 4 mm rotor is 5 kHz and number of scans is 512–1024. Signal deconvolution was carried out by using a Bruker-made software named 'Winfit'.

3. Results and discussion

The degrees of crystallinity of four samples were determined by measuring ^{13}C DD/MAS spectra with a 25 s relaxation delay time. Fig. 1 shows ^{13}C DD/MAS spectra of four samples. Peak assignment was made according to previous reports [14,15] and is shown in the figure. From the spectra, it is obvious that the methyl signal of 3-hydroxybutyrate (HB) unit consists of two overlapped peaks, a broader peak at higher field and a narrower one at lower field. These two peaks correspond to methyl groups in the noncrystalline and crystalline region, respectively. The relative intensities of these two peaks can be obtained by carrying out deconvolution on the signal. In order to get relative intensities of the methyl signals of both HB and

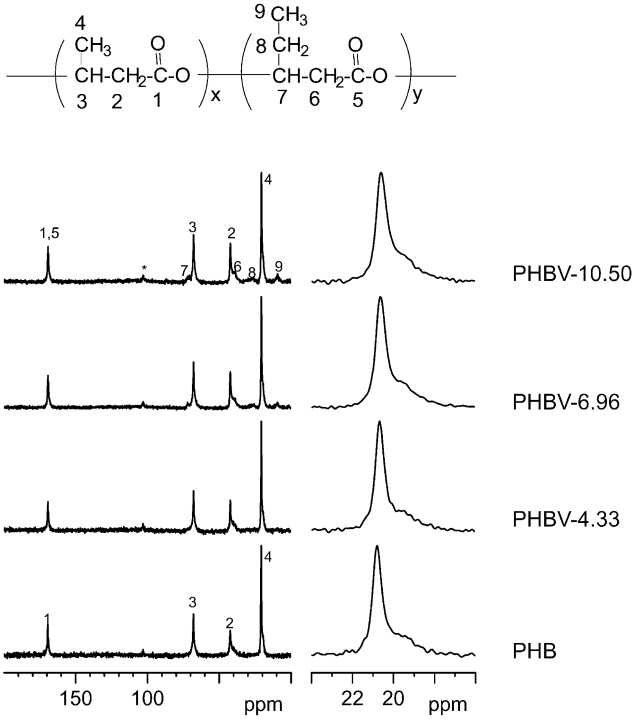

Fig. 1. ^{13}C DD/MAS spectra of PHB and PHBVs, where * denotes spinning sideband. On the right are the expanded spectra of the methyl group.

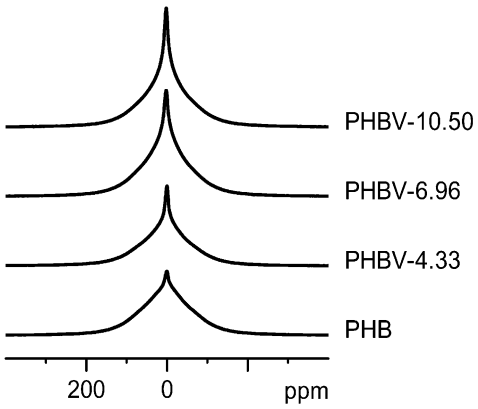

Fig. 2. Solid-state wide-line ^{1}H NMR spectra of PHB and PHBVs at room temperature.

HV units quantitatively, the relaxation delay time was set to be more than five times longer than the spin–lattice relaxation times (T_1) of the methyl groups. For the purpose of verification, a ^{13}C DD/MAS spectrum of PHB with a 100 s relaxation delay time was also acquired. The lineshape of methyl signal is almost the same as that appeared in the bottom trace in Fig. 1, indicating the quantitative nature of the methyl signals. According to previous reports [10,14,16], HV units are mostly excluded from the crystalline region if HV mol content in PHBV is lower than about 20%. Since HV mol contents of three PHBV samples studied in this work are much lower than that value, we roughly consider that all HV units exist in the noncrystalline region. Then, the degrees of crystallinity of four samples can be estimated from the relative intensities of the methyl peaks, i.e. the crystalline and noncrystalline methyl peaks of HB and the methyl peak of HV [14]. The degrees of crystallinity obtained for PHB, PHBV-4.33, PHBV-6.96 and PHBV-10.50 are 0.60, 0.60, 0.58 and 0.56, respectively, revealing that the degree of crystallinity changes little with HV content. Such a result agrees well with the previous studies [9–12].

Fig. 2 shows the solid-state wide-line ^{1}H spectra of PHB and PHBV at room temperature. The lineshape changes dramatically with the change of the HV content. Each spectrum can be decomposed to three components with different lineshape and linewidth. These three components are designated as C1, C2 and C3, respectively. The decomposed solid-state wide-line ^{1}H spectrum of PHB at room temperature is shown in Fig. 3 as an example. The relative content of each component corresponds to the number of protons of the

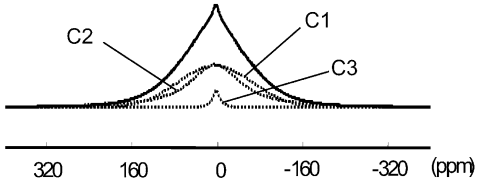

Fig. 3. The decomposed solid-state wide-line ^{1}H NMR spectrum of PHB at room temperature.

Table 1
Fitting results of variable temperature solid-state wide-line ^{1}H NMR spectra of four samples

T (K)	Relative contents of different components (%)											
	PHB			PHBV-4.33			PHBV-6.96			PHBV-10.50		
	C1	C2	C3	C1	C2	C3	C1	C2	C3	C1	C2	C3
298	49.2	48.4	2.4	55.4	39.3	5.3	48.9	46.0	5.2	49.5	40.4	10.0
308	49.1	47.5	3.4	57.6	35.5	6.8	49.9	39.9	10.1	51.1	32.9	16.0
318	49.2	45.4	5.4	56.6	32.1	11.4	49.5	30.9	19.7	52.7	19.9	27.4
328	47.2	44.0	8.8	55.5	23.1	21.4	49.0	28.5	22.5	49.8	12.7	37.5
338	47.5	37.0	15.5	54.1	17.4	28.5	48.2	16.3	35.5	49.9	5.0	45.1
348	48.7	30.5	20.9	54.4	9.2	36.4	53.1	4.1	42.8	50.3	0	49.7
358	48.4	26.7	25.0	54.9	0	45.1	53.9	0	46.1	49.3	0	50.7

component relative to the total number of protons in the sample and is very close to the weight fraction of each component in our case. Table 1 shows the results of the computer fitting. The Gaussian component with the largest linewidth, C1, is easily attributed to the crystalline region. Its relative content, which is about 50%, is in good conformance with the crystallinity estimated from DD/MAS spectra. While both the Lorentzian components C2 and C3 can only come from the noncrystalline region, they are quite different in relative contents and linewidth. The content and the linewidth of C2 are much larger than those of C3, indicating that at room temperature there exists a rich and rigid component in the noncrystalline region of the four samples. From Table 1, it is clearly seen that the content of C2 component decreases with the increase of HV content in PHBV. This means the noncrystalline region of the sample becomes softer with the increase in HV content.

^{1}H spin–spin relaxation times (T_2) of the four samples were indirectly measured by acquiring ^{13}C spectra. Fig. 4 shows the pulse sequence used in this experiment. After a 90° pulse, ^{1}H magnetization is allowed to relax with T_2 in VD, then after CP, partially relaxed ^{13}C spectrum is acquired, in which the peak intensities reflect the ^{1}H spin–spin relaxation. By fitting the methyl signal of HB in each spectrum, we obtained the variation curves of intensities of crystalline peak and noncrystalline peak of methyl group with time. Then, ^{1}H T_2 of crystalline and noncrystalline regions were determined by fitting the curves. Table 2 shows the fitting results. The ^{1}H T_2 values of the crystalline and noncrystalline regions of PHB were calculated to be 10 and 19 μs by this means. This result indicates that the noncrystalline region of PHB is mainly composed of a quite rigid component, i.e. the C2 component. The soft component (C3) in wide-line ^{1}H spectra was not observed in the measurement, owing to the low efficiency of CP incurred by its high mobility. Similar ^{1}H T_2 values are also obtained for three PHBV samples. Such a result supports our assignment and analysis of wide-line ^{1}H spectra.

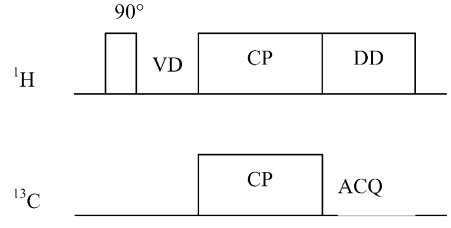

Fig. 4. The pulse sequence for measuring ^{1}H T_2 of PHB and PHBVs.

To further prove the above conclusion, variable temperature solid-state wide-line ^{1}H NMR experiments were carried out over a temperature range of 298–358 K for all the four samples. Fig. 5 shows the acquired spectra of PHB. From the spectra, it can be clearly seen that the lineshape changes obviously with the temperature. Computer fitting is then applied to all the spectra and each spectrum was decomposed into three components using the mentioned method. The obtained results are also listed in Table 1. The fitting results indicate that the content of C1 keeps constant during the heating process. This proves again that C1 corresponds to the crystalline region, since the experimental temperature range is well below the melting point of PHB and the content of C1 is supposed to be unchanged with temperature. On the other hand, the relative contents of C2 and C3 change markedly with increasing temperature. The relative content of C2 decreases with the increase in temperature. Similar phenomena were observed for PHBV samples. The variation of contents of C2 and C3 of four samples with temperature were presented in Figs. 6 and 7, respectively. It can be seen that when the temperature rises to about

Table 2
T_2 values of CH_3 ^{1}H in crystalline and noncrystalline regions of PHB and PHBV

Sample	T_2 of CH_3 ^{1}H (μs)	
	Crystalline region	Noncrystalline region
PHB	10.3	19.0
PHBV-4.33	10.4	19.5
PHBV-6.96	10.4	19.4
PHBV-10.50	10.2	22.9

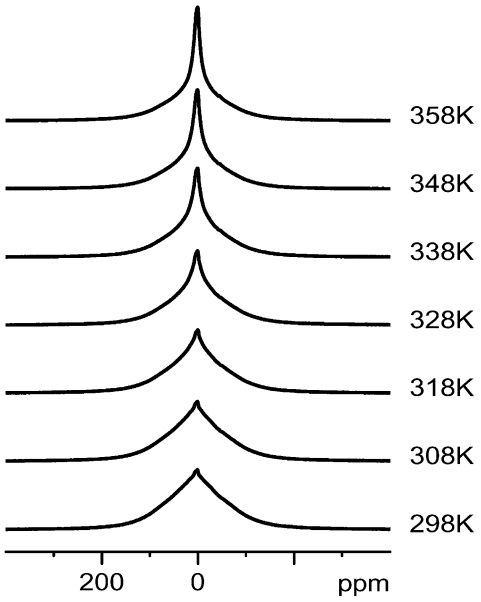

Fig. 5. Variable temperature solid-state wide-line ^{1}H NMR spectra of PHB.

358 K, C2 of three PHBV copolymers completely disappear. This indicates the noncrystalline region becomes fully soft and has good mobility at such a temperature. However, for PHB homopolymer, C2 does not disappear over the whole temperature range. This conforms to the research work of Morin and Marchessault [17], in which static ^{13}C solid-state NMR spectra of the amorphous component of a PHB and a PHBV sample with 21 mol% content of HV were acquired at 20 and 68 °C by single pulse excitation and low power proton decoupling. Signals are only observed in the spectrum of the PHBV sample at 68 °C, revealing the difference of mobility between the amorphous regions of PHB and PHBV.

Concerning with the nature of the C2 component, we believe that it is not reasonable to simply assign the

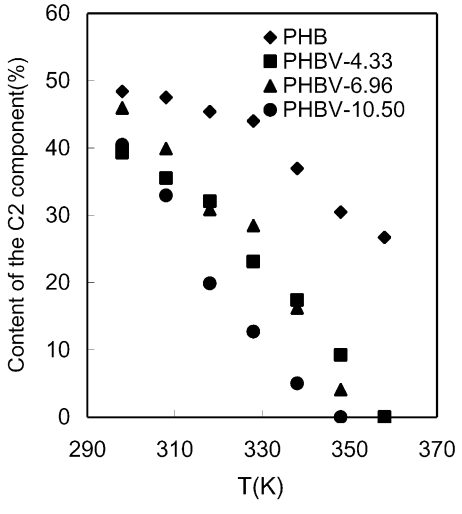

Fig. 6. Contents of C2 of four samples versus temperature.

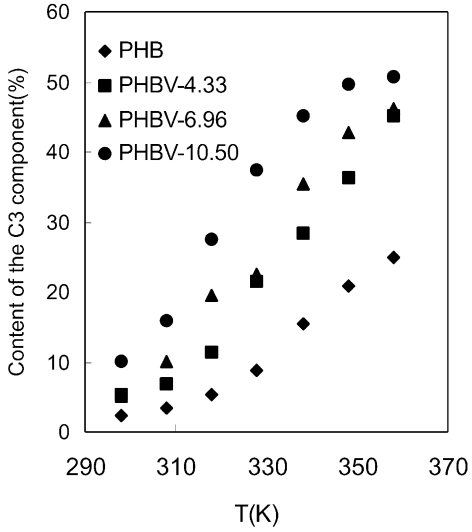

Fig. 7. Contents of C3 of four samples versus temperature.

component to the interface between crystalline and amorphous regions because of its high content at room temperature and the feature that its content steadily decreases with the increase in temperature. It is preferable to assume that the C2 component is mainly corresponding to a relatively tightly packed structure compared with the real amorphous component C3 in the noncrystalline region of PHB and PHBV. On the other hand, relative to the crystalline region, the structure of C2 component should be less regularly packed as revealed by the larger linewidth of the noncrystalline methyl peak of HB unit compared with that of the crystalline methyl peak in ^{13}C DD/MAS spectrum. Based on such an assumption, we can understand the following experimental results easily: (1) the decrease in the content of the C2 component with increasing temperatures is due to that these relatively tightly packed structures are gradually destroyed with the increase in temperature; and (2) as mentioned earlier, within the content range of PHBV samples studied in this work, HV units are mostly excluded from the crystalline region. Therefore, with the increase in HV content, the regularity of the chain structure of the noncrystalline region will decrease, leading to the decrease in the possibility of forming relatively tightly packed structures. This is the reason, we believe, that the content of C2 component decreases with increasing HV contents.

As shown above, the noncrystalline region of PHB is quite rigid at room temperature due to the existence of the C2 component. The noncrystalline region of PHBV becomes softer with the decrease in the content of the C2 component. From this result, it is rational to conclude that the rigidness of the noncrystalline region is one of the important factors that lead to the high brittleness of PHB at room temperature. Meanwhile, the property improvement of PHBV over PHB can be partly attributed to the fact that the noncrystalline is softer compared with that of PHB.

Therefore, to change the packing structures of the noncrystalline region consciously might be one of the possible ways of improving the properties of PHB.

4. Conclusions

From the above experimental results and discussion, the following conclusions can be drawn: (1) there exists a rich and rigid component in the noncrystalline region of PHB and PHBV at room temperature. The content of the component decreases with increasing temperatures and HV contents. Such a component is possibly corresponding to the relatively tightly packed structures existing in the noncrystalline region; and (2) the brittleness of PHB can be partly attributed to the rigid noncrystalline region at room temperature, while the improvement of the properties of PHBV can be attributed to the enhanced mobility of the noncrystalline region.

Acknowledgements

This work was supported by the Teaching and Researching Award Fund for outstanding Young Teachers in Higher Education Institutions and BOSHIDIAN foundation of MOE, PRC and by the foundations of the Committee of Science and Technology of Shanghai Municipality.

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