Nucleation Mechanism of Polyhydroxybutyrate and Poly(hydroxybutyrate-*co*-hydroxyhexanoate) Crystallized by Orotic Acid as a Nucleating Agent

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ABSTRACT: The mechanism involved in the crystallization of bacterial polyhydroxybutyrate (PHB) and poly(hydroxybutyrate-*co*-hydroxyhexanoate) P(HB-*co*-HH) induced by orotic acid as a nucleant was investigated by using differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR). GPC measurements both carried on solvent cast and hot pressed samples did not show any significant drop of the molecular weight caused by the addition of the nucleant, indicating that no chemical reaction happened during the nucleation process. This result was confirmed by ^{1}H-NMR analysis of oligohydroxybutyrate (OHB) treated with an excess amount of orotic acid. The possibility of epitaxial growth of the polymer crystal on the surface of the nucleant crystal was then investigated. It was found that there is an outstanding crystalline lattice matching between the plane (100) of the PHB crystal and the plane (001) of the orotic acid crystal. In comparison, the matching obtained with conventional nucleating agents, such as boron nitride and talc, was worse. Moreover, some regular hydrogen bonds between the polyester and orotic acid could stabilize the physical process. According to these results, the physical mechanism involving the epitaxial matching between orotic acid and PHB appears to be the most probable nucleation mechanism. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 709–715, 2010

Key words: mechanism; nucleation; orotic acid; polyhydroxybutyrate; poly(hydroxybutyrate-*co*-hydroxyhexanoate)

INTRODUCTION

Nowadays, polymer materials have a wide range of applications, but most of these petrochemical plastics are used during short periods. According to the increasing of both plastic wastes and oil prices, the production of biodegradable polymers produced from renewable resources is a promising replacement solution. On that purpose several polyesters, such as bacterial poly(3-hydroxyalkanoates), have been intensively studied theses last decades. Unfortunately, the most common of these polymers, poly(3-hydroxybutyrate) (PHB), is very brittle, and is thermally unstable around its melting temperature.[1]

After several years of investigation it was found that the introduction of 3-hydroxyhexanoate (HH) monomer units (see chemical structure in Fig. 1) clearly improved the mechanical properties of PHB. Doi et al.[2] have reported an increase of the elongation at break from 5 to 850% as the HH unit content increased from 0 to 17%. Unfortunately, the crystallization of P(HB-*co*-HH)s containing high HH contents (>10%) is very slow, which make them difficult to use in industry. Moreover, it has been shown that the induction of the enzymatic degradation of such polyesters requires the presence of a crystalline phase or a rigid phase.[3] Therefore its biodegradability will be affected by the crystallinity, the spherulite morphology and the glass transition.[3,4]

It is well known in polymer crystallization science that additions of some fine solid particles induce rapid crystallization of semicrystalline polymers such as polyolefins, polyamides or polyesters. These chemicals, when they are added to the polymer, act as nucleating agents (or nucleants). As a result, the crystallization time is reduced, the degree of crystallinity is increased and a uniform crystalline morphology is obtained.

Our previous work[5] showed that orotic acid, a green chemical (See chemical structure in Fig. 1), was an outstanding nucleating agent for PHB and even for P(HB-*co*-HH) with high HH monomer

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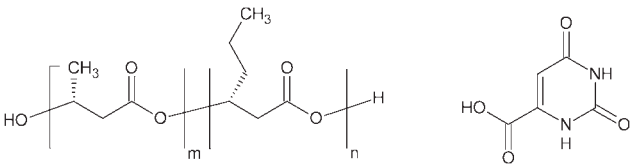


Figure 1 Chemical structure of P(HB-*co*-HH) and Orotic acid.

content (18%). Similar studies showed that nucleation efficiency of boron nitride (BN), a more commonly used nucleating agent for many kinds of polymers, was strictly decreasing with the increasing of the HH monomer content of P(HB-*co*-HH).[5] For further understanding why orotic acid shows this outstanding nucleating ability, its nucleation mechanism on PHB and P(HB-*co*-HH) was investigated in this study.

EXPERIMENTAL SECTION

Materials and sample preparation

Bacterial PHB homopolymer sample ($M_w = 41.8 \times 10^4$ Da, $M_w/M_n = 3.0$) was purchased from Sigma-Aldrich Chemie GmbH (Germany) and the bacterial P(HB-*co*-10 mol %HH) copolymer ($M_w = 22.2 \times 10^4$ Da, $M_w/M_n = 2.6$) was supplied by Kaneka Corporation, Osaka, (Japan).

All polymer samples were purified by dissolution in hot chloroform and precipitated in cold ethanol before use.[6] Orotic acid monohydrate and talc were, respectively, purchased from the Tokyo Chemical Industry Co. (Japan) and Kanto Kagaku Company (Japan). Potassium bromide and BN were both provided by Nacalai Tesque (Kyoto, Japan).

The polymer films were prepared via a solvent casting method: the polymer was first dissolved in chloroform at 60°C under vigorous stirring during 3 hours and was cast on Teflon Petri dishes. Then, the solvent was evaporated during 1 day at room temperature. For the nucleated samples, the fine powders of nucleating agents were dispersed by ultrasonication in chloroform and the purified polymer was added to this solution (the amount of nucleating agent used for the two polymers samples was 1 wt %). To create a homogenous material, the shift of nucleating agents during the film casting was reduced by using high polymer concentrations (100 g/L). Moreover, chloroform has been selected by solvent screening for P(HB-*co*-HH) copolymers,[7] to have a good solvent, which could be easily removed by evaporation.

Differential scanning calorimetry (DSC)

Nonisothermal melt crystallization behaviour was investigated with a Pyris Diamond DSC (Perkin-Elmer Japan Co., Yokohama, Japan) under a nitrogen atmosphere. The polymer samples of 6–8 mg were first melted at 190°C for 2 minutes to erase thermal history and then cooled to −50°C at the cooling rate of 10°C/min.

Proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy

The ^{1}H-NMR spectra were recorded at room temperature with a 6H Brucker 600 MHz spectrometer (acquisition parameters: 45° pulse, 5 s pulse repetition time, 2500 Hz spectral width and 64 FID accumulations). All studied samples were solved in $CDCl_3$ before testing.

Gel permeation chromatography (GPC)

Molecular weight measurements were accomplished by using a Tosoh HLX-820 GPC system (Tosoh Corp., Tokyo, Japan), equipped with a refractive index detector and TSK gel G2000HXL columns. Polymer samples, with an average concentration of 1.5 mg mL^{-1}, were eluted with chloroform at a rate of 1 mL min^{-1}. The molecular weight and weight average molecular weight were obtained on Omni-Sec 4.2 software. The calibration of the apparatus was made with low polydispersity polystyrene standards.

RESULTS AND DISCUSSION

Nucleation efficiency of BN, Talc, KBr, and Orotic acid

From our recent studies,[5] it has been shown that orotic acid has a very good ability to induce the crystallization of PHB. Moreover, this nucleating agent is also able to nucleate P(HB-*co*-HH) copolymers containing up to 18%HH monomeric units. In

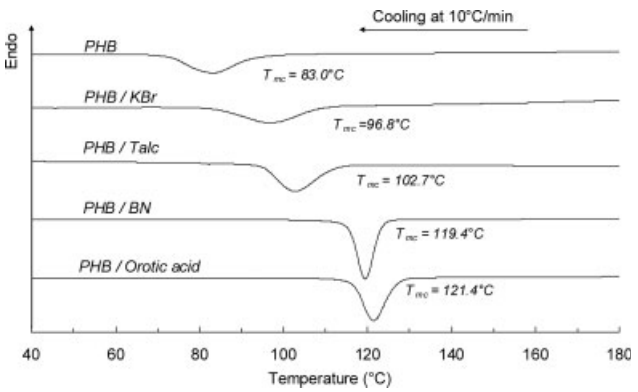


Figure 2 DSC curves recorded during nonisothermal melt crystallization at 10°C/min of PHB and their blends with potassium bromide (KBr, 1 wt %), talc (1 wt %), boron nitride (BN, 1 wt %), and orotic acid (1 wt %).

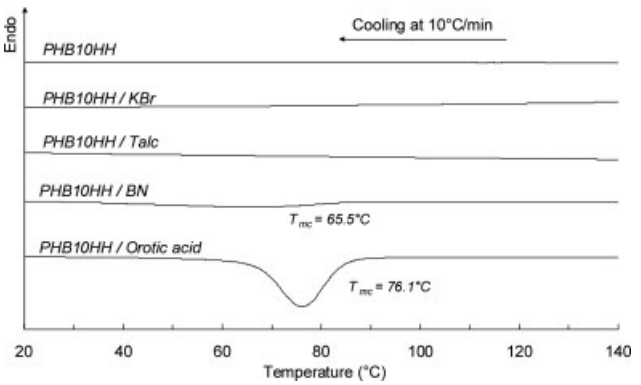


Figure 3 DSC curves recorded during nonisothermal melt crystallization at 10°C/min of P(HB-*co*-10%HH) (PHB10HH) and their blends with potassium bromide (KBr, 1 wt %), talc (1 wt %), boron nitride (BN, 1 wt %) and orotic acid (1 wt %).

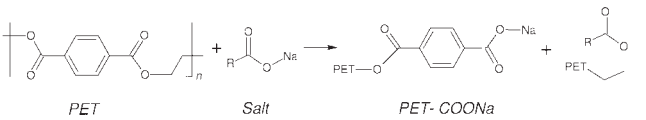
the following Figures are shown the melt crystallization of PHB and P(HB-*co*-10%HH) (PHB10HH) with various nucleating agents.

Judging from the melt crystallization temperatures obtained in Figure 2, the addition of orotic acid has led to a much faster crystallization. Moreover, only orotic acid showed a significant melt crystallization of P(HB-*co*-10%HH) (Fig. 3).

In the following parts, several possible nucleation mechanisms will be investigated to understand the molecular origin of the high efficiency of orotic acid as a nucleating agent for PHB and P(HB-*co*-HH).

Nucleation mechanisms

As fast crystallizing polymers are ideal candidates for injection modeling applications, polymers crystallization mechanisms and kinetics have been intensively studied.[8,9] The crystallization of the polymer consists of two major parts: the nucleation and the growth of the crystal. Contrary to the crystal growth mechanism which could be explained by well established theories, the nucleation phenomena still remains quite empirical.[8] Up to date, only four main mechanisms have been identified with precision: the homogenous nucleation, the self-nucleation, the chemical nucleation and the epitaxial nucleation. As homogenous and self-nucleation take place in pure materials, the discussion will focus on the two last mechanisms.



Scheme 1 Nucleation of PET by organic salt.

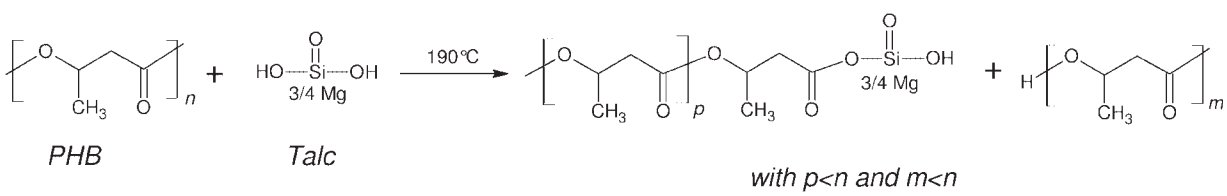
Chemical nucleation

During these last decades, it has been shown that some organic salts[10–17] have the ability to nucleate the crystallization of some polymers via a chemical mechanism. In that case, the nucleating agent added to the polymer does not act as an inert heterogeneous substrate, but is dissolved in the polymer melt. For these cases, it has been shown by IR analysis[17,18] that molten polymer chains reacted with the nucleant, inducing the random chain scission of polymers and the creation of new ionic chain ends. These ionic species will then form some organized ionic aggregates which will become the true nucleating species. The following scheme shows the chemical nucleation of polyethylene terephthalate (PET) by such organic salt[10,16,19] (Scheme 1).

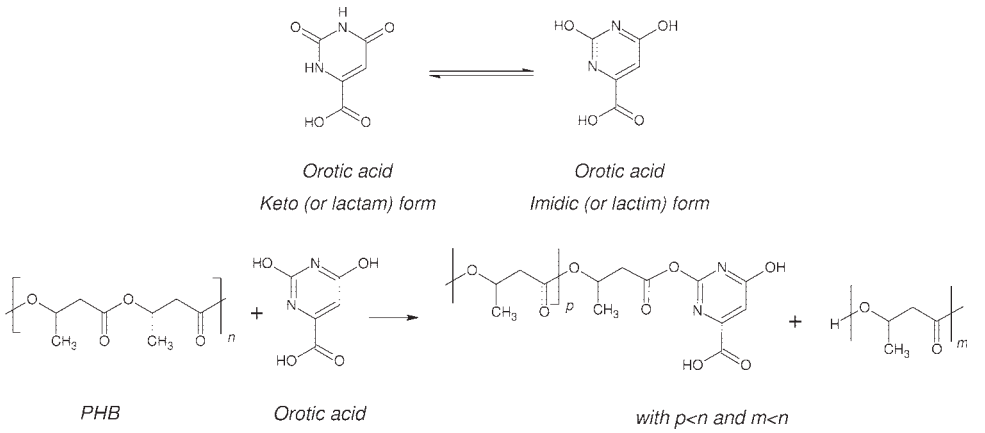
More recently, this nucleation mechanism has been proposed for the nucleation of some polyesters (PET and PHB[20]) by talc. In this case, the strong interaction between talc hydroxyl groups and polyester carbonyl groups was said to lead to the dissolution of talc crystals in the molten polymer. Polyester should then react with talc hydroxyl groups via the same trans-esterification process as described before (Scheme 2).

Thus, the possibility of such a chemical mechanism has been studied for a system containing orotic acid and PHB. As described in Scheme 3, it involves the reaction of orotic acid imidic form with PHB molecules. Of course, the second hydroxyl function of orotic acid could also react via the same scheme, and consequently fix a second polymer chain.

According to our POM (Polarized Optical Microscopy) observations reported in a previous work,[5] orotic acid is not dissolve in PHB and PHB10HH melts during the preparation of the sample (2 min at 190°C), nevertheless unnoticeable dissolution could happened on the nucleating agent crystal surface and lead to a chemical nucleation via the process described in Scheme 3. To identify this chemical mechanism, and to see if this mechanism is



Scheme 2 Nucleation of PHB by talc.



Scheme 3 Suggested chemical nucleation mechanism of PHB by orotic acid.

promoted by a thermal treatment, gel permeation chromatography (GPC) tests were carried out on both solvent cast and hot pressed sample.

Results (Table I) did not show any significant decrease in the molecular weight due to the introduction of the nucleating agent. Of course it could be noticed that both number and weight average molecular weight (M_n and M_w) strongly decreased due to the thermal treatment in the hot press. In the case of the hot pressed samples, the small difference of M_n between the nucleated and the neat PHB could be explained by the fact that the acidity of the nucleating agent could promote polymer chain scission.

^{1}H-NMR measurements performed on both nucleated PHB and OHB (Oligo-3-hydroxybutyrate) confirm the previous results. In Figure 4 are shown the spectra of neat PHB and of nucleated OHB (NA: OHB ratio 4 : 1 (w/w) heated during 1 h at 190°C).

On both spectra could be observed the three characteristic signals of the HB monomers[21]: a doublet at $\delta = 1.29$ ppm (CH_3 group coupled to one proton), a doublet of quadruplet around $\delta = 2.55$ ppm (CH_2 group adjacent to the asymmetric carbon), and a multiplet at $\delta = 5.25$ ppm (hydrogen atom fixed to the asymmetric carbon). In addition, spectrum (b) shows some evidence of cis-elimination or Mac Lafferty rearrangement ($\delta = 5.80$ ppm and 6.95 ppm) caused by the thermal treatment (see Scheme 4).[22–32]

Then, by comparing the spectrum (b) with the peaks of orotic acid ($\delta = 6.04$, 6.90, 10.84, and 11.32 ppm), no evidence of a possible chemical reaction between the nucleant and the polymer backbone was found, suggesting that PHB nucleation should not be induced by a chemical process. Similar NMR results (not shown in this article) have been obtained for P(HB-*co*-HH) nucleated with orotic acid.

Epitaxial mechanism

Contrary to the previous mechanism, the epitaxial nucleation is only created by physical interactions between the nucleant and the polymer. This mechanism consists in the epitaxial growth of polymer crystals on the surface of the nucleating agent. The epitaxial phenomenon has been shown to follow quite well the rules postulated by Louis Royer (1928).[33] In these rules,[34] the growing of one crystal on another is governed by the possible matching of the two lattices planes in contact. The misfit, expressed as the deviation percentage for one

TABLE I
Molecular Weights of Cast and Hot Pressed Samples Obtained from GPC

	Original cast samples			Hot pressed samples[a]		
System	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n
PHB	14.1	41.8	3.0	7.9	18.9	2.4
PHB-OA[b]	13.2	40.3	3.1	5.2	17.2	3.3
PHB10HH	8.7	22.2	2.6	3.9	11.0	2.8
PHB10HH-OA[b]	8.3	22.9	2.8	3.6	11.2	3.1

[a] Original samples after thermal treatment in hot pressed at 190°C during 3 min.
[b] PHB-OA and PHB10HH-OA respectively correspond to PHB and PHB10HH samples containing 1 wt % orotic acid.

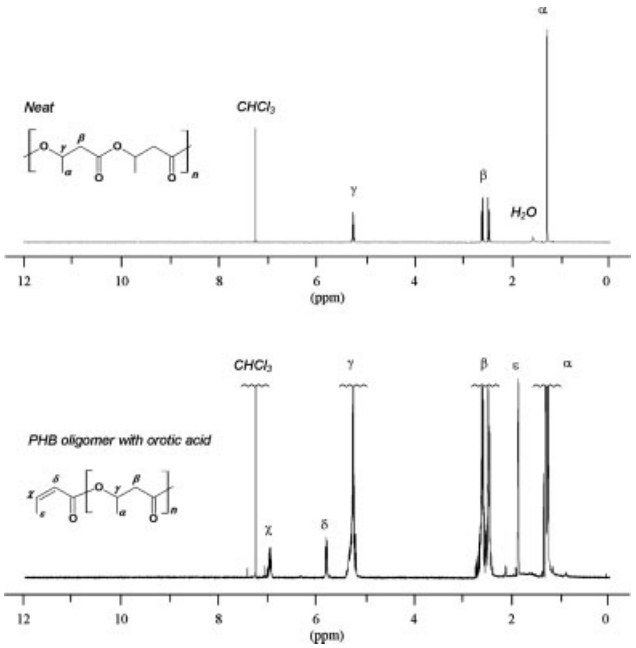


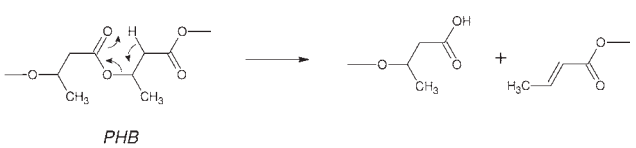
Figure 4 ^{1}H-NMR spectra of neat PHB and of nucleated OHB (NA: OHB ratio 4 : 1 (w/w) heated during 1 h at 190°C). For more clarity the peak intensity of the second spectrum has been increased.

period, could be accommodated by the polymer elasticity up to 15%.[35]

After studying the nucleation of PHB, Barham and coworkers[36] have suggested that the nucleating effect of saccharin, ammonium chloride and BN were following this last mechanism. The efficiency of these nucleants was explained by a good lattice matching between the nucleating crystal and the *b* spacing of the polymer. In their previous work,[37] they also showed that the polymer crystal growth of PHB occurs along the *a*-axis (Fig. 5).

This means that the nucleating agent should be in contact with the plane (100) of the polymer. To understand the efficiency of different nucleating agents, PHB *b* and *c* spacing have been compared to the lattice parameters of the studied nucleants. Some possible lattice matching following the Royer rules[34] are proposed in Figure 6. The crystal parameters involved in these models are given in Table II.

According to these results, the best lattice matching is obtained with orotic acid between the planes $(100)_{PHB}//(001)_{OA}$. In this case, even though the angles in contact are not the same ($\alpha_{PHB} = 90°$ and



Scheme 4 Degradation of PHB by cis-elimination.

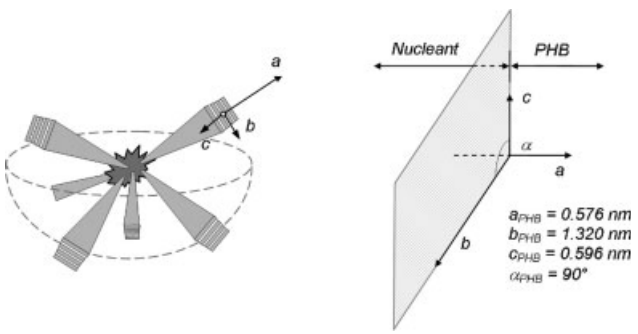


Figure 5 Diagram showing the orientation of the crystal axes in PHB spherulites.[36,37]

$\gamma_{OA} = 68.4°$), every PHB motif could be matched by one motif of the orotic acid crystal. Moreover, as shown in Figure 7, there is a good molecular fitting

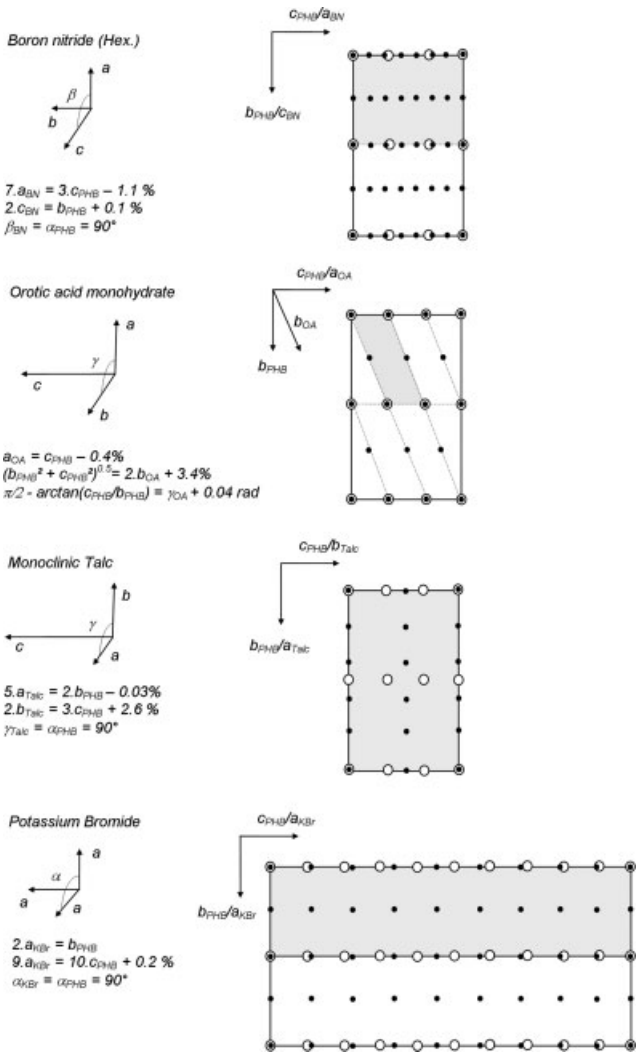


Figure 6 Suggested epitaxial nucleation scheme of various nucleating agents with PHB. This diagrams show the superposition of the PHB (100) plane with planes of various nucleating agents (PHB/NA). PHB and nucleating agents motifs are respectively represented by ○ and ●. The shaded regions represent the smallest area delimited by four motif matches.

TABLE II
Crystal Parameters of PHB and of the Different Nucleating Agent Studied

	System	a (nm)	b (nm)	c (nm)	α (°)	β (°)	γ (°)
PHB[38]	Orthorombic	0.572	1.318	0.592	90.0	90.0	90.0
Boron nitride[39]	Hexagonal	0.251	0.251	0.660	90.0	90.0	120.0
Talc[40]	Monoclinic	0.526	0.91	1.881	90.0	100.0	90.0
Potassium bromide[41]	Cubic	6.59	6.59	6.59	90.0	90.0	90.0
Orotic acid monohydrate[42a]	Triclinic	0.590	0.693	0.959	74.7	72.3	68.4

[a] As the orotic acid parameters found by Takusagawa and Shimada (1973)[43] were recently redetermined by Portalone (2008)[42], the following work will be based on the new parameters.

between orotic acid crystal layers[42] and PHB helices.[37]

Judging from this model, some regular hydrogen bonds between the hydrogens (OH, COOH or NH) of orotic acid and the ester functions of PHB could stabilize the nucleation.

BN and talc also show quite good lattice matches with their respective planes [(010) for BN and (001) for talc]. In the case of potassium bromide, which has been presented as a promising nucleating candidate due to its perfect matching with the PHB *b* spacing,[36] the low compatibility could be explained by the bad matching between a_{KBr} and c_{PHB}. It is important to notice that all these results predicted theoretically are in accordance with those obtained experimentally from the DSC melt crystallization (Figs 2 and 3).

Nucleation of P(HB-*co*-HH) copolymers

In our recent studies,[44] it has been shown that PHBHH could be successfully nucleated by using ternary blends of the following composition: PHB (10 wt %), P(HB-*co*-21%HH) (88 wt %) and BN (2 wt %). In that case, it is believed that during the cooling process, BN particles induce a fast and selective crystallization of PHB, which will promote the fast crystallization of the P(HB-*co*-HH) copolymer. According to the fact that BN has a selective nucleating effect for P(HB-*co*-HH) with very low HH content, it was believed that orotic acid would act via a different mechanism (such as by chemical nucleation) or could adapt better than BN to the lattice change caused by the introduction of the HH monomer. The fact that PHB and PHB-*co*-HH (<12 mol %HH) have the same lattice parameters[45] exclude this last hypothesis.

It is reasonable to think that orotic acid could establish some interactions (hydrogen bonds) with the polymer, and thus be less affected by the increasing of the HH unit content than BN. As it was found in our previous study for BN,[44] ternary blends containing PHB and orotic acid could also be an effective way to nucleate P(HB-*co*-HH) copolymers with high HH contents.

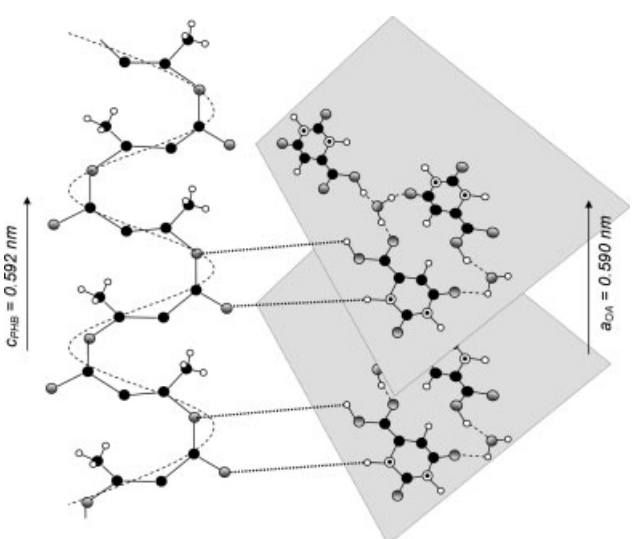


Figure 7 Molecular fitting and hydrogen bonds at the interface between orotic acid and PHB. (●: carbon; ○: hydrogen; ◍: oxygen; ⊙: nitrogen).

CONCLUSION

Mechanisms which could be involved in the nucleation of PHB and P(HB-*co*-HH) by orotic acid were studied. GPC measurements both carried out on solvent cast and thermally processed samples did not show any significant drop of the molecular weight caused by the addition of the nucleant, indicating that no chain scission happened during the nucleation process. Moreover the ^{1}H-NMR analysis of oligohydroxybutyrate (OHB) treated with orotic acid (1 : 4 wt) did not show any evidence of a chemical reaction between the nucleating agent and the polymer backbone. On the other hand, it was found that there is an outstanding crystalline lattice matching between the plane (100) of PHB and the plane (001) of orotic acid. Moreover, some regular hydrogen bonding between PHB and orotic acid could stabilize the physical process, thus explaining the good nucleating efficiency of orotic acid with P(HB-*co*-HH) copolymers.

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