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DEGRADABILITY OF POLY(β-HYDROXYBUTYRATE)S. CORRELATION WITH CHEMICAL MICROSTRUCTURE

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ABSTRACT

Poly(β-hydroxybutyrate)s (PHB) of different microstructures were synthesized via anionic polymerization of β-butyrolactone initiated by two initiators: 1) supramolecular complexes of alkali metals with asymmetric induction agents, and 2) alkali metal alkoxides. The relationships between chemical microstructure and hydrolytic as well as thermal degradation properties of synthetic and natural PHB are discussed.

INTRODUCTION

Ring-opening polymerization of β-butyrolactone leads to poly(β-hydroxybutyrate)s of different tacticities which mimic those found in nature [1, 2]. Supramolecular complexes of alkali metals, alkali metal naphthalenides, and alkoxides are effective initiators for the anionic polymerization of racemic β-butyrolactone, yielding biodegradable amorphous polyesters [3–5]. Such polymers can be applied as biodegradable plasticizers [6] and for chemical modification of polymers via block and graft copolymerization [7, 8]. It has also been recently demonstrated that polymerization of racemic (*R,S*) β-butyrolactone initiated with potassium/18-crown-6 supramolecular complex and carried out in the presence of (+) dimethyl tartarate leads to polymer containing predominantly syndiotactic sequences [9].

In this work we report on the relationships between chemical microstructure and hydrolytic as well as thermal degradation properties of synthetic and natural PHB.

RESULTS AND DISCUSSION

Polymer Synthesis and Microstructure

Chemically synthesized poly(β-hydroxybutyrate)s were obtained by ring-opening anionic polymerization of β-butyrolactone. The polymerization of racemic (*R,S*) β-butyrolactone (β-BL) with potassium *tert*-butoxide/18-crown-6 complex leads to amorphous polymer. On the other hand, semicrystalline polymer was obtained via polymerization of racemic β-BL initiated with potassium metal/18-crown-6 complexes in the presence of (+) dimethyl tartarate (DMT). The polymerizations were carried out in THF or in bulk.

The molecular weight, polydispersity index, and thermal properties of the chemically synthesized poly(β-hydroxybutyrate)s and that of microbial PHB studied are summarized in Table 1.

The stereoregularity of the investigated polymers was determined by ^{13}C NMR. The results of diad and triad stereosequence distribution analysis, based on the intensity of the split signals of carbonyl carbon C^1 (diad effect [10]) and methylene carbon C^2 (triad effect [1]) depicted in Fig. 1, are summarized in Table 2.

The atactic structure was demonstrated for PHB obtained in the presence of potassium *tert*-butoxide/18-crown-6 complex (Sample 1). The predominantly syndiotactic structure was revealed for polymer synthesized using potassium/18-crown-6 supramolecular complex in the presence of (+) dimethyl tartarate (Sample 2), while that of microbial PHB is completely isotactic (Sample 3).

TABLE 1. Properties of Poly(β-Hydroxybutyrate) Samples Used for Degradation

Sample[a]	M_n	M_w/M_n	T_g,[b] in °C	T_m,[b] in °C	T_d,[c] in °C
1	20,300	1.15	1	–	255
2	10,600	1.08	3	76	255
3	10,500	2.90	4	178	260

[a] Sample 1 was obtained via anionic polymerization initiated with potassium *tert*-butoxide/18-crown-6. Sample 2 was obtained via polymerization initiated with potassium supramolecular complex with 18-crown-6 in the presence of DMT. Sample 3 is natural origin PHB.

[b] Scan rate 20°/min.

[c] Maximum decomposition temperature.

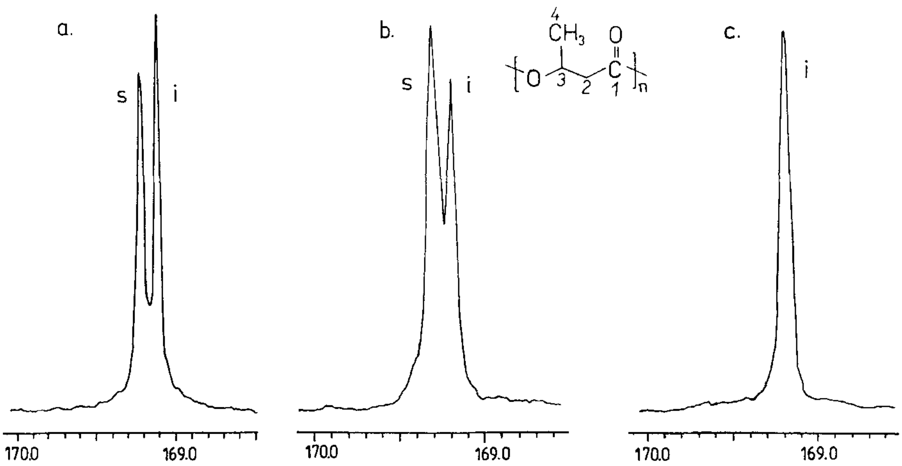

FIG. 1. ^{13}C-NMR spectra (carbonyl region) of (a) atactic PHB, (b) predominantly syndiotactic PHB, and (c) isotactic (natural) PHB.

Hydrolytic Degradation

The hydrolytic degradation of polyesters studied has been carried out in a phosphate buffer (pH 7.4) at a temperature of 70°C. The value of M_w/M_n of the samples studied was observed to broaden slightly during hydrolytic degradation. The molecular weight (M_n) changes are presented in Fig. 2.

It has been revealed that the simple hydrolysis of the polyesters investigated proceeds regardless of their microstructure, similarly to what was described previously by Doi for isotactic PHB and its copolymers of natural origin [11]. Two stages of degradation were observed: the first related to the random hydrolytic chain scission of the ester groups, and then (after a 50% loss of the initial M_n) the onset of molecular weight loss was observed. However, the influence of the sample's crystallinity on the rate of hydrolytic degradation was observed. The sample of atactic PHB degrades faster than the semicrystalline ones.

TABLE 2. Results of Diad and Triad Stereosequence Distribution Analysis of PHB

	Tacticity					
	C^1		C^2			
Sample[a]	s_d	i_d	S	H_s	H_i	I
1	50	50	25	24	26	25
2	64	36	41	20	21	18
3	0	100	0	0	0	100

[a]See Footnote [a] in Table 1.

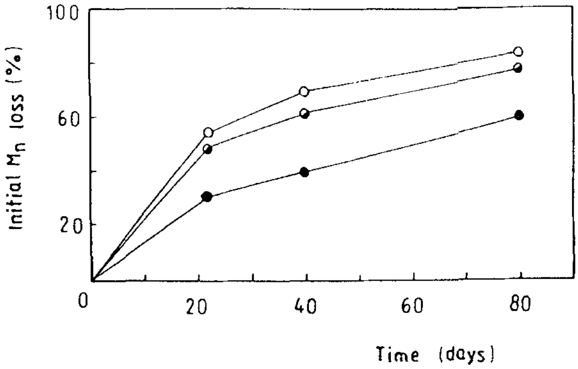

FIG. 2. Molecular weight (M_n) loss of PHB samples of various tacticities (○) atactic (M_n = 20,300), (◑) predominantly syndiotactic (M_n = 10,600), and (●) isotactic (M_n = 10,500).

Thermal Degradation

The thermal decomposition temperature of the polyesters studied was found to be in the 255 to 260°C region (Table 1). The structure of the products formed during the thermal decomposition of the chemically synthesized polymers has been studied by direct pyrolysis mass spectrometry (DPMS) [12] using a Finnigan MAT SSQ 700 spectrometer. CI-MS analysis of the oligomers formed during pyrolysis conducted on the MS spectrometer solid probe revealed the formation of oligomers with crotonate and carboxylic end groups regardless of PHB tacticity (Fig. 3).

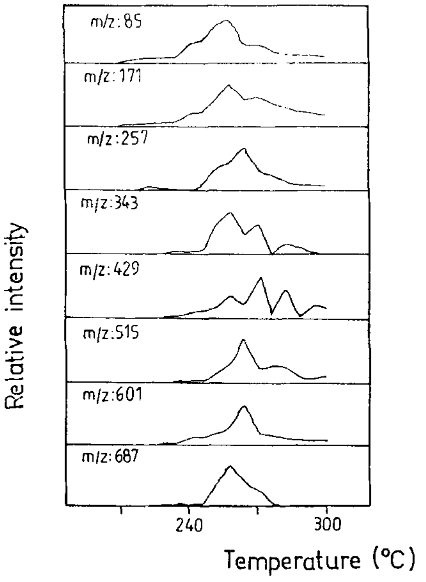

FIG. 3. Negative ion CI-MS SIC curves of the direct pyrolysis products of atactic PHB.

Similar oligomers were detected recently by Montaudo et al. during pyrolysis of isotactic PHB using the FAB MS technique [13]. These results indicate that regardless of the tacticity of the polyesters studied, the thermal decomposition of poly(β-hydroxybutyrate) proceeds via random scission of polymer chains as proposed previously for natural PHB [14].

CONCLUSIONS

It has been revealed that the chemical microstructure has no substantial influence on the mechanism of both hydrolytic and thermal degradation of atactic, predominantly syndiotactic, and isotactic poly(β-hydroxybutyrate)s. The hydrolytic and thermal degradation proceeds, regardless of the microstructure of the polymers studied, via random scission of the polyester chain. However, the degree of crystallinity of the PHB influences the rate of its hydrolytic degradation.

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