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Stereochemical Control in the Anionic Polymerization of β-Butyrolactone Initiated with Alkali-Metal Alkoxides

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ABSTRACT: The anionic polymerization of (*R*)-β-butyrolactone initiated with either 18-crown-6 complexes of a potassium alkoxide or a simple carboxylate (reference initiator) proceeded with inversion of configuration. As a result (*R*)-β-butyrolactone formed an isotactic poly((*S*)-β-hydroxybutyrate) with these initiators at room temperature. Polymerization of (*R*,*S*)-β-butyrolactone under the same conditions gave an atactic polymer, but at lower temperatures the predominantly syndiotactic form of poly((*R*,*S*)-β-hydroxybutyrate) was produced from the racemic monomer.

Introduction

Poly(β-hydroxyalkanoates), such as poly(β-hydroxybutyrate), PHB, are produced in bacteria and mammalian organisms,[1,2] and these polymers play an important role in many biochemical processes.[3] It is believed that PHB in living cell membranes forms channels responsible for metal ions transportation.[4] Natural PHB contains repeating units with only the *R* configuration at the β-position, and an equivalent isotactic PHB can be prepared chemically by the controlled ring-opening polymerization of optically pure β-butyrolactone (β-BL) using various types of coordinative catalysts.[5−8] However, the polymerization of β-butyrolactone (β-BL) by coordinative catalysts at higher temperatures (50−100 °C) yields PHB with a broad molecular weight distribution. Syndiotactic poly(β-hydroxybutyrate), the polymer containing the alternating sequences of (*R*)- and (*S*)-β-hydroxybutyrate repeating units, was also synthesized recently using aluminum and tin-based catalysts.[6,7,9−15] This polymer is of interest for comparison with isotactic PHB in studies of the stereochemical and morphological effects on thermal properties and biodegradability.[16,17]

Anionic polymerization of β-BL using alkali-metal alkoxide/crown ether initiator[18] was recently found to be an effective method for PHB synthesis, yielding at room temperature polymers possessing number average molecular weights, M_n, as high as 40 000 and narrow molecular weight distributions. The polymerization reaction proceeds slowly, and stereocontrol in this process has not been studied in detail. In this report we demonstrate that PHB possessing various tacticities can be obtained by the anionic polymerization of β-butyrolactone with potassium alkoxide/18-crown-6 complexes as catalysts.

Experimental Part

Materials. (*R*,*S*)-β-Butyrolactone (from Fluka, bp 47 °C (5 mmHg)) and (*R*)-β-butyrolactone[11] were purified as described previously.[19] 18-Crown-6 (from Fluka) was purified according to ref 20. Potassium methoxide was obtained by reacting dry methanol with a potassium mirror. The excess methanol was then removed by evaporation. Potassium *tert*-butoxide (from Aldrich) was used as received. Potassium acetate (Aldrich) was dried for 60 h at 40 °C under vacuum. THF (tetrahydrofuran) was purified as described in ref 21 and then distilled over a sodium−potassium alloy in an atmosphere of dry argon.

Measurements. The NMR spectra were recorded using a Varian VXR-300 multinuclear spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were run in $CDCl_3$ by using TMS as an internal standard. GPC experiments were conducted in THF solution at 35 °C, at a flow rate 1 mL/min using a Spectra-Physics 8800 solvent delivery system with two Mixed C "Styragel" columns in series and a Shodex SE 61 refractive index detector. Polystyrene standards having a low polydispersity (PL Lab.) were used to generate a calibration curve. A volume of 10 μL of sample solutions in $CHCl_3$ (concentration 2% w/v) was injected. DSC measurements were performed using a DSC DuPont 1090B thermal analyzer apparatus at a heating rate of 20 °C/min. Optical rotation measurements were conducted in $CHCl_3$ using a Perkin-Elmer 141 polarimeter. FTIR spectra were recorded with a FTS 40A Bio-Rad spectrometer at room temperature.

Polymerization of (*R*)-β-Butyrolactone. (*R*)-β-BL (90% (*R*) + 10% (*S*)) was used for the polymerization reactions, which were conducted at a temperature of 20 °C in THF solution as described in ref 22. The monomer concentration was 1.0 mol/L in each experiment. The concentration of potassium methoxide/18-crown-6 and potassium acetate/18-crown-6 varied from 0.1 to 0.01 mol/L, respectively. The polymers were precipitated in hexane, washed with hexane, and dried in vacuum.

Polymerization of (*R*,*S*)-β-Butyrolactone. The polymerization experiments were conducted as described above at temperatures of 20 and −10 °C. After completion of polymerization, the polymers obtained were precipitated in hexane, washed with hexane, dried in vacuum, and characterized by GPC and NMR. The polymer so obtained was further fractionated by dissolving in warm methanol and placing the methanol solution in a freezer for several days. The methanol-

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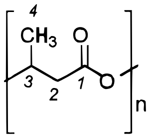
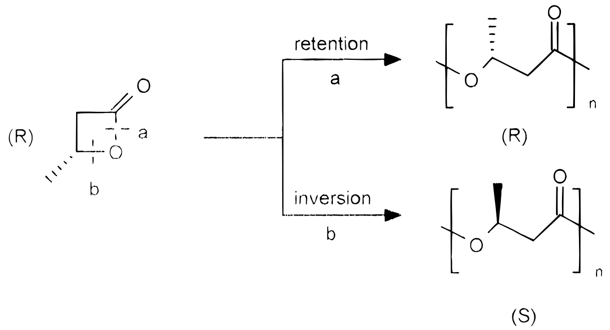
Table 1. Diad and Triad Stereosequence Distribution of Poly(β-hydroxybutyrate)s Obtained from (*R*)-β-Butyrolactone



		diads distribution, %									
		i_d			s_d			C² triads distribution,[a] %			
entry	catalyst	C*H*₃	C¹	C⁴	C*H*₃	C¹	C⁴	*I*	H_i	*S*	H_s
1.	MeOK/18-crown-6	83	83	83	17	17	17	72 (73)	9 (9)	10 (9)	9 (9)
2.	AcOK/18-crown-6	83	82	84	17	18	16	74 (73)	8 (9)	8 (9)	10 (9)

[a] The values given in parentheses were calculated according to the following formulas: $I = [R]^3 + [S]^3$; $S = H_s = H_i = [R]^2[S] + [S]^2[R]$ where [*R*] and [*S*] are the stereochemical contents of *R* and *S* enantiomeric units in polymers investigated, assuming total inversion of monomer containing [*R*]/[*S*] = 90/10.

Scheme 1



insoluble fraction formed was isolated by filtration at −15 °C, washed with cold methanol, and dried in vacuum for analysis.

Results and Discussion

Synthesis of Isotactic Poly(β-hydroxybutyrate) from (*R*)-β-Butyrolactone. Isotactic polymers may be formed from optically active β-lactone monomers by the use of polymerization in which either alkyl−oxygen or acyl−oxygen bond cleavages can occur exclusively to give either retention or inversion of the configuration at the β-position, respectively, as shown in Scheme 1.

The results obtained in the present study show that the potassium methoxide/18-crown-6 complex forms an active initiator for anionic polymerization of optically active (*R*)-β-butyrolactone with inversion, and isotactic polyester was produced. The precipitated polymer was highly crystalline with a melt transition, T_m, of 126 °C, as revealed by DSC measurements.

The stereoregularity of poly(β-hydroxybutyrate)s obtained from the (*R*)-β-butyrolactone (90% *R* + 10% *S*) was determined by proton and carbon NMR measurements. If only alkyl−oxygen bond cleavage occurred during the polymerization of (*R*)-β-BL with inversion of configuration (reaction b) to yield a statistical distribution of *S* and *R* stereosequences, using a monomer of 90% *R* configuration, in the polymer formed the isotactic (*i*) and syndiotactic (*s*) diad fractions, as calculated according to Doi,[23] should be as follows:

$$i_d = [R]^*[R] + [S]^*[S] = 0.82$$

$$s_d = [R]^*[S] + [S]^*[R] = 0.18$$

Using the chemical shift assignments reported previously for poly(β-butyrolactone),[24,25] the contents of isotactic diad fraction were determined by ¹H NMR from the integration of the **C**H₃ peaks for the iso and syndio diads and by ¹³C NMR from both methyl and carbonyl carbons peaks. The results for the polymer obtained using potassium methoxide/18-crown-6 complex as initiator are compared with those estimated for polymer formed with a carboxylate/crown ether complex initiator in Table 1. The results from the ¹H NMR measurements indicated that the calculated value ($i_d = 0.82$) was in good agreement with the observed diad fractions, for both types of the anionic initiators (alkoxide and carboxylate).

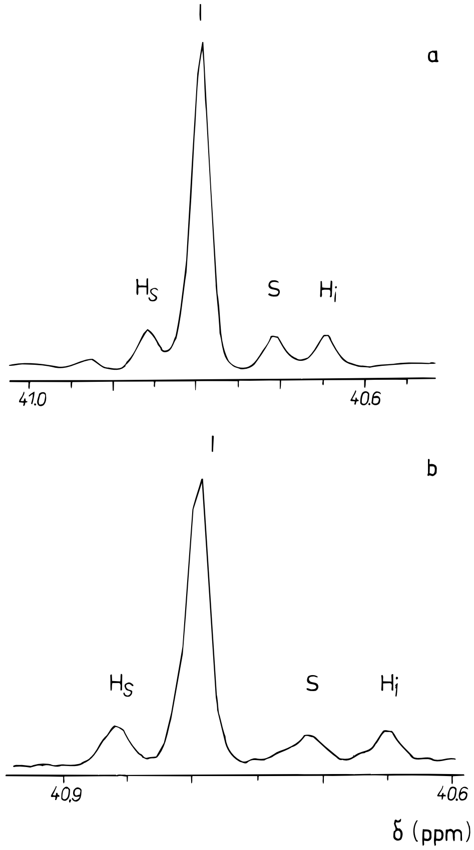


Figure 1. ¹³C NMR spectra (methylene carbon region) of poly(β-hydroxybutyrate)s obtained via polymerization of (*R*)-β-butyrolactone initiated with 18-crown-6 supramolecular complexes of: (a) potassium methoxide and (b) potassium acetate.

The ¹³C NMR spectra in the methylene carbon region shown in Figure 1 revealed the triad stereosequence distribution[12] for the polymers obtained with the results presented in Table 1. The triad stereosequence distribution observed was in good agreement with the calculated values for a random copolymer containing 90% *R*/10% *S* units. These results indicate that the anionic polymerization of (*R*)-β-BL with the supramolecular

Table 2. Specific Rotation Measurements of Synthesized from (*R*)-*β*-Butyrolactone (90% *R*/10% *S*) and Natural Origin PHB Samples in $CHCl_3$

entry	catalyst	M_n (GPC)	M_w/M_n	% iso[a]	$[\alpha]^{25}_{365}$[b]
1	MeOK/18-crown-6[c]	5 500	1.1	83	−9.0
2	AcOK/18-crown-6[d]	4 100	1.2	82	−6.9
3	Natural origin PHB	120 000	3.1	100	+11.5

[a] Isotactic diad content determined by ^{13}C NMR of the carbonyl carbon. [b] $c = 0.028$ g/cm^3. [c] Catalyst concentration $[I]_0 = 0.015$ mol/L, yield 96%. [d] $[I]_0 = 0.020$ mol/L, yield 93%.

complex of either potassium methoxide or a carboxylate anion, yielded isotactic polymers with nearly the same microstructure.

Optical rotation measurements demonstrated that the ring-opening polymerization reaction occurred with inversion of configuration as shown in Table 2. All polymers were found to possess the optical activity opposite to that of natural poly((*R*)-*β*-hydroxybutyrate).

The observed inversion of configuration in the case of alkali-metal alkoxide initiator can be explained on the basis of the recently published revised mechanism of *β*-lactones polymerization by alkali-metal alkoxides, valid for α-unsubstituted *β*-lactones.[22,26−28] According to this addition−elimination mechanism, polymers with either double bonds or hydroxyl end groups, instead of the group from the initiator, are produced. Due to nucleophilic attack of the alkoxide anion on the carbonyl carbon atom of the monomer, the selective cleavage of the *β*-lactone acyl-oxygen bond occurs with the formation of the *β*-hydroxycarboxylic acid ester alkoxide. In contrast to the previous proposals,[29] this alkoxide does not propagate polymerization but undergoes elimination and an alkali-metal hydroxide is formed, which attacks the carbonyl carbon atom of the next *β*-lactone molecule. However, elimination again occurs, and carboxylate active centers formed are responsible for further propagation occurring via alkyl−oxygen bond cleavage of a monomer.

The alkyl−oxygen bond cleavage with inversion of configuration also takes place in the polymerization with carboxylate salt as initiator[30] and from (*R*)-*β*-butyrolactone optically active *S* polymer is formed when supramolecular complex of simple carboxylate has been used as a reference initiator.

Synthesis of Atactic versus Syndiotactic Poly(*β*-hydroxybutyrate) from (*R,S*)-*β*-Butyrolactone. The syndiotactic PHB from racemic *β*-butyrolactone has been obtained with the coordinative initiators including aluminoxanes and tin alkyl alkoxides.[6,7,9−15] Fractionation of crude polymers so obtained was used to separate the predominantly syndiotactic from the isotactic and atactic fractions.[9] Tin-based catalysts can also cause acyl−oxygen ring opening in the polymerization of *β*-BL,[6,13] and the formation of syndiotactic PHB by this initiator is influenced by the polymerization temperature.[6]

Previous studies on the anionic polymerization of (*R,S*)-*β*-BL indicated that for several different types of initiators (supramolecular complexes of alkali metals,[25] alkali-metal naphthalenides,[31] hydrides,[32] phosphonoacetate,[33] and alkoxides[26]), only an atactic poly(*β*-hydroxybutyrate) was produced at room temperature. However, in the presence of some additives, such as esters of tartaric acid a syndiotactic PHB fraction can be obtained by these anionic polymerization reactions at ambient temperature.[17]

In the present study the influence of the polymerization temperature on the microstructure of poly(*β*-hydroxybutyrate) obtained by the anionic polymerization of racemic *β*-BL initiated with 18-crown-6 complexes of potassium methoxide, *tert*-butoxide, and acetate was determined. Polymerization reactions were carried out at 20 and −10 °C, either with or without equimolar amounts of tartarate esters with respect to the initiator, and the results of these experiments are summarized in Table 3.

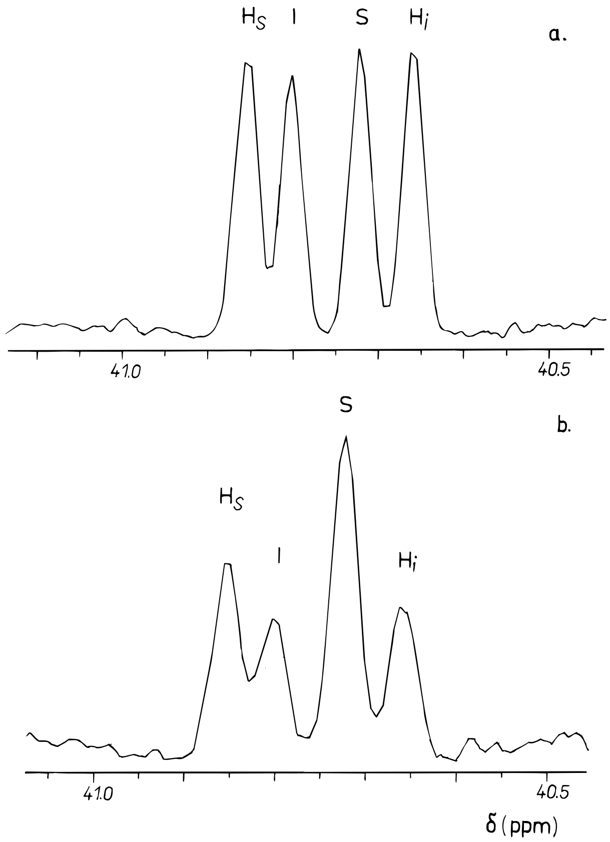


Figure 2. ^{13}C NMR spectra (methylene carbon region) of poly(*β*-hydroxybutyrate)s obtained by polymerization of (*R,S*)-*β*-butyrolactone initiated with 18-crown-6 supramolecular complexes of potassium methoxide: (a) at 20 °C; (b) at −10 °C (methanol-insoluble fraction).

The stereoregularity of poly(*β*-hydroxybutyrate) obtained from racemic *β*-BL was determined using both proton and carbon NMR. The ^{13}C NMR spectrum (methylene carbon region) depicted on Figure 2, revealed the triad stereosequence distribution for the polymers obtained in the presence of potassium methoxide/18-crown-6 complex at both room temperature (Figure 2a) and at −10 °C (Figure 2b). The results of diad and triad stereosequence distribution analysis, based on the assignment discussed above[12,24,25] are presented in Table 4. These results indicate that predominantly syndiotactic poly(*β*-hydroxybutyrate) was obtained at the low temperature as well as at room temperature in the presence of tartarate diesters. The influence of the polar additives on the kinetics of anionic polymerization of *β*-lactones has been reported by one of us previously,[34] but the combination of both these factors (polar additives and temperature) did not influence significantly the content of syndiotactic sequences in the polymers obtained (compare Table 3: entries 2, 3 and 11, 12).

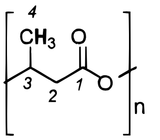
The predominantly syndiotactic polyesters obtained were found to be partially crystalline as revealed by DSC analysis (see Figure 3). Several melting transitions were observed over a broad temperature range

Table 3. Polymerization of (*R*,*S*)-*β*-Butyrolactone Initiated by Potassium Alkoxide and Acetate Complexes with 18-Crown-6 in THF

entry	initiator	$[M]_0/[I]_0$[a]	additive[b]	temp [°C]	time [h]	yield[c] [%]	M_n GPC[d]	M_w/M_n[e]	% syn[f]
1.	MeOK	225		20	120	95 (0)	18100	1.05	50
2.	MeOK	105		−10	200	96 (28)	8600 (8900)	1.10 (1.10)	52 (58)
3.	MeOK	55	(−)-DMT	−10	150	97 (30)	4900 (5100)	1.11 (1.09)	55 (64)
4.	*t*-BuOK	55		20	24	98 (0)	4800	1.05	50
5.	*t*-BuOK	55		−10	130	95 (32)	4900 (6600)	1.10 (1.10)	53 (62)
6.	AcOK	55		20	48	98 (0)	4500	1.21	50
7.	AcOK	55		−10	150	96 (29)	3300 (3400)	1.18 (1.15)	52 (58)
8.	AcOK	55	(−)-DMT	20	72	94 (25)	4200 (4300)	1.20 (1.11)	52 (57)
9.	AcOK	55	(+)-DMT	20	75	95 (23)	3400 (3700)	1.18 (1.15)	53 (58)
10.	AcOK	55	(±)-DMT	20	76	93 (22)	3200 (3400)	1.23 (1.15)	53 (59)
11.	AcOK	55	*mezo*-DBT	20	80	94 (23)	3300 (3400)	1.18 (1.15)	54 (63)
12.	AcOK	55	*mezo*-DBT	−10	150	90 (25)	3000 (3300)	1.24 (1.16)	54 (62)

[a] Monomer concentration 10 mol/L. [b] DMT, dimethyl tartarate; DBT, dibutyl tartarate. [c] Yield of methanol-insoluble polymer fraction has been given in parentheses. [d] M_n of methanol-insoluble polymer fraction has been given in parentheses. [e] Polydispersiy of methanol-insoluble polymer fraction has been given in parentheses. [f] Determined by ^{1}H NMR of the CH_3 protons (see Tables 1 and 4), syndiotactic diad content of methanol-insoluble polymer fraction has been given in parentheses.

Table 4. Diad and Triad Stereosequence Distribution of Poly(*β*-hydroxybutyrate)s, Obtained by Anionic Polymerization of (*R*,*S*)-*β*-Butyrolactone, Estimated from ^{1}H and ^{13}C NMR



	tacticity, %									
	diads									
	s_d			i_d			C^2 triads			
entry[a]	CH_3	C^1	C^4	CH_3	C^1	C^4	*S*	H_s	H_i	*I*
2	58	59	58	42	41	42	37	22	21	20
3	64	63	64	36	37	36	41	23	20	16
5	62	63	63	38	37	37	40	23	20	17
12	62	63	62	38	37	38	40	22	21	17

[a] Entry numbers corresponding to those in Table 3.

(≈40 °C) for the samples prepared at room temperature in the presence of tartarate diesters (Figure 3a,b). Heat of fusion was similar as reported previously by the DSC studies of predominantly syndiotactic PHB prepared using tin-based catalysts.[12,13,16] It was claimed in those reports that syndiotactic sequences were somewhat blocky in nature and the blocky syndiotactic chain segments formed crystalline regions with different thermodynamic stability.[13,16] However, for the predominantly syndiotactic polymers obtained at lower temperature (−10 °C), sharper melting transitions were observed (Figure 3c,d), which indicate the formation of more uniform crystalline ordering in the solid state which may indicate the formation of a lower dispersity of chain stereosequences.

The FTIR spectra of poly(*β*-hydroxybutyrate)s with various tacticity, obtained in the anionic polymerization reactions with alkali-metal alkoxide/18-crown-6 complexes, are compared with that of natural PHB (Figure 4). For predominantly syndiotactic polymer (Figure 4a) the appearance of the band at 1206 cm^{-1} with a decrease of the intensity at 1185 cm^{-1} together with the increase of the intensity of the band at 1103 cm^{-1} has been observed as compared with that of atactic one (Figure 4b). The absence of the band at 1279 cm^{-1}, characteristic for the isotactic synthetic and natural PHB (Figure 4c,d), is also observed. The FTIR spectra of the samples studied are similar to those reported previously for PHB prepared using tin-based catalyst.[12]

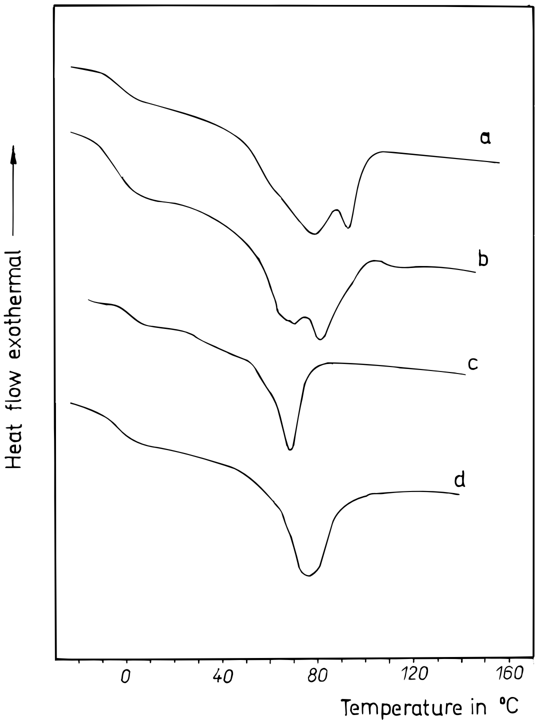


Figure 3. DSC traces of precipitated from solution samples of predominantly syndiotactic poly(*β*-hydroxybutyrate)s obtained via polymerization of (*R*,*S*)-*β*-butyrolactone initiated with (a) AcOK/18-crown-6 in the presence of (*mezo*) DBT at 20 °C; (b) AcOK/18-crown-6 in the presence of (±)-DMT at 20 °C; (c) MeOK/18-crown-6 at −10 °C; (d) AcOK/18-crown-6 in the presence of *mezo*-DBT at −10 °C.

Conclusions

It was shown that inversion of configuration occurred in the polymerization of optically active *β*-butyrolactone monomer carried out in the presence of alkali-metal alkoxide/18-crown-6 complexes. Use of the racemic monomer under the same conditions yielded atactic poly(*β*-hydroxybutyrate), but at low temperature or in the presence of tartarate ester additives, predominantly syndiotactic polymers were formed. These results demonstrate the high versatility of the anionic initiators studied and the stereochemical control that can be achieved in the anionic polymerization of *β*-butyrolactone initiated with alkali-metal alkoxides to either isotactic, syndiotactic, or atactic polymers under selected reaction conditions.

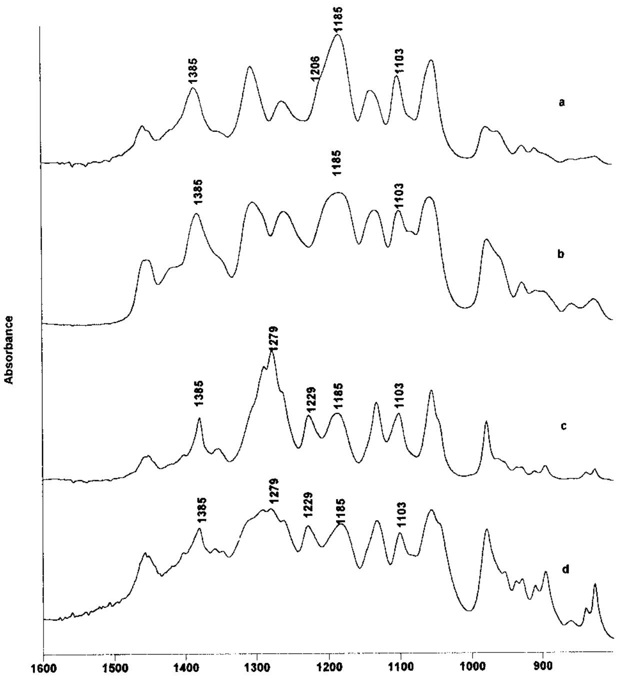


Figure 4. FTIR spectra of poly(β-hydroxybutyrate)s (KBr pellets): (a) predominantly syndiotactic (62% syndio diads, Table 3, entry 5); (b) atactic (Table 3, entry 1); (c) predominantly isotactic (83% *iso* diads, $M_n = 5500$); (d) natural PHB.

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