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Temperature influence on changes of parameters of the unit cell of biopolymer PHB

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The changes of parameters of the unit cell of biopolymer poly(β-hydroxybutyrate) (PHB) during heating from room temperature to the melting temperature are measured and results are presented here. The considerable increase of value of parameter a with increase of temperature is noticed with coefficient of thermal expansion of ($\approx 1.4 \pm 0.3) \times 10^{-4}\,{}^{\circ}\mathrm{C}^{-1}$. In the same time the changes of parameters b and c are negligible. On the basis of wide-angle X-ray scattering diffractograms the coefficient k is determined to be 1.06 ± 0.08 (Hermans–Weidinger method).

(Keywords: PHB; X-ray diffraction; unit cell)

Introduction

Poly(β-hydroxybutyrate) (PHB) is a natural polyester. It is one in the sequence of poly(β-hydroxyalkanoate)-type biopolymers. PHB is a thermoplastic ($T_m \approx 175^{\circ}$C) and belongs to the class of crystalline polymers with a high degree of crystallinity. Its physical and mechanical properties are close to those of isotactic polypropylene (IPP). Within the crystalline domains, PHB macromolecules accept the regular helicoidal conformation with two antiparallel chains (along the c-axis) in the rhombic unit cell ($P2_12_12_1$). Cell parameters[1] are $a = 5.76$, $b = 13.20$ and $c = 5.96$ Å. It was shown[2] that, during heating, at temperatures below T_m there arise visible changes in the degree of crystallinity and the size of crystalline domains in PHB.

Bluhm and collaborators[3] have shown that unit cell size increases with the increase of HV monomer content in the copolymer PHB/HV. In this paper we show that the unit cell parameter a of the PHB homopolymer changes linearly with temperature change. Besides that, using high-temperature wide-angle X-ray scattering (WAXS) diffractograms we have determined k, the coefficient in the expression for the quantitative estimate of the crystallinity degree of PHB following the Hermans–Weidinger method[4].

Experimental

PHB powder samples were provided by ICI Biological Products Division (Billingham, UK). WAXS diffractograms of PHB were obtained on a powder diffractometer (Philips, model PW 1050) using the module for the controlled sample heating (Anton Paar, model HTK 10). The PHB sample was submitted to a temperature change in two ways. In the first approach, the sample was heated from 30°C up to T_m. WAXS diffractograms were recorded at temperatures of 30, 80, 120, 160 and 180°C, after isothermal crystallization at each of these temperatures for 1 h. This time turned out to be sufficient for establishing thermal equilibrium and obtaining reproducible WAXS diffractograms. The same sample was then cooled from T_m through temperatures 160, 140, 120, 100, 80, 60 and 30°C. WAXS diffractograms were recorded again after isothermal crystallization for 1 h. The diffractograms obtained in this way were used for the determination of unit cell parameters and the calculation of the calibration constant for the determination of the degree of crystallinity of PHB.

Results and discussion

Unit cell change with temperature. Unit cell parameters were calculated on the basis of the positions (2Θ) of well separated diffraction maxima (020), (110) and (101) using the quadratic form for the rhombic cell. Characteristic WAXS diffractograms of PHB samples at 30 and 160°C, with indiced diffraction maxima, are given in *Figures 1* and *2*.

The change of PHB unit cell parameters with temperature is shown in *Figures 3*, *4* and *5*. Parameter a changes linearly with temperature in both directions, during heating as well as during cooling of the sample. At temperatures directly below T_m the value of parameter a (5.90 Å) becomes close to the value of parameter c (5.96 Å). Parameters b and c remain mostly unchanged in the whole temperature range. This could be expected for parameter c, since the bonds along the macromolecular chain (direction of the c axis) are the strongest and the change of parameter c would demand much higher energy. The stability of the parameter c with respect to temperature changes is a property characteristic of other crystal polymers (for example IPP).

Using the least-squares method we have fitted the experimental results to the function $y = y_0(1 + \lambda T)$, where y_0 is the value of the unit cell parameter at 0°C, and λ the thermal expansion coefficient of the corresponding parameter. Results are given in *Table 1*.

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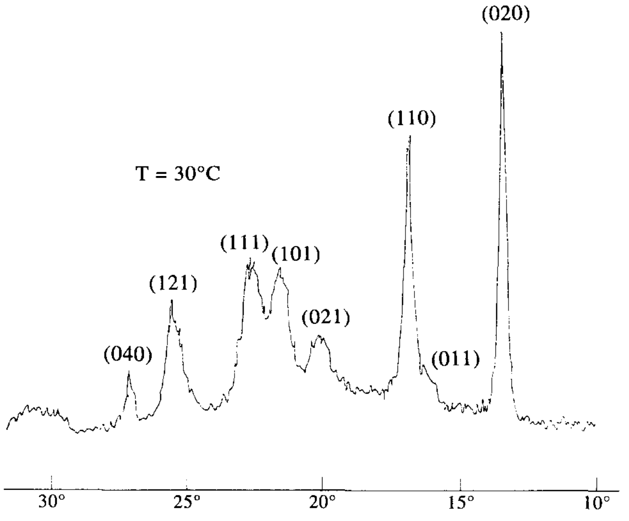

Figure 1 WAXS diffractogram of PHB biopolymer at 30°C

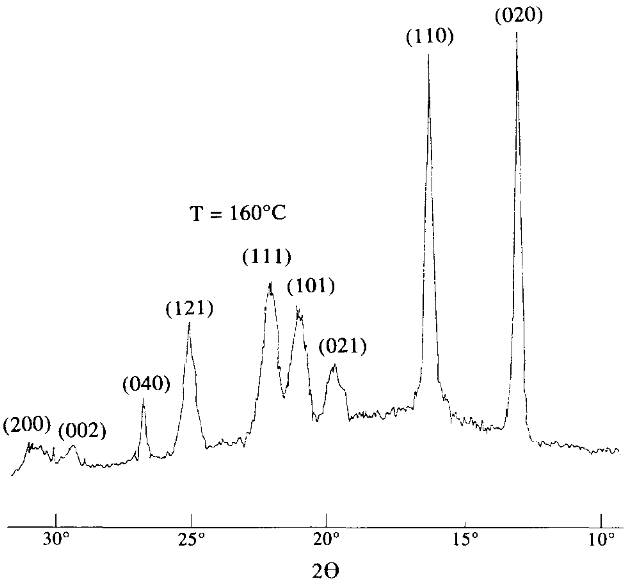

Figure 2 WAXS diffractogram of PHB biopolymer at 160°C

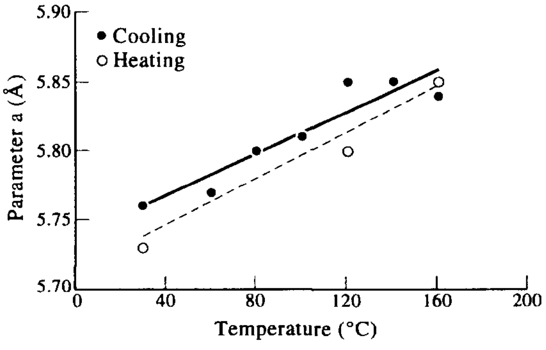

Figure 3 Temperature dependence of PHB unit cell parameter *a*

Correlation coefficients show that only for parameter *a* does there appear an expressed linear dependence on temperature, while for parameters *b* and *c* there is an evident substantial value spreading. Thermal expansion coefficient λ_a shows no significant difference in the case of sample heating and cooling and it is an order of magnitude higher than the values of λ_b and λ_c.

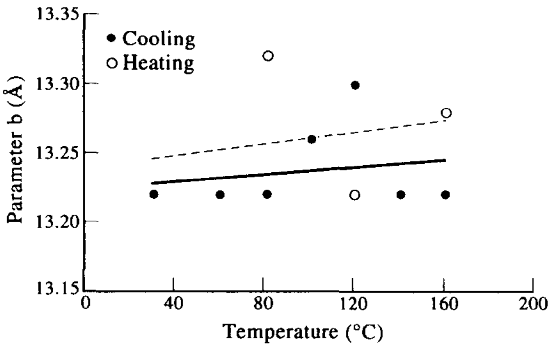

Figure 4 Temperature dependence of PHB unit cell parameter *b*

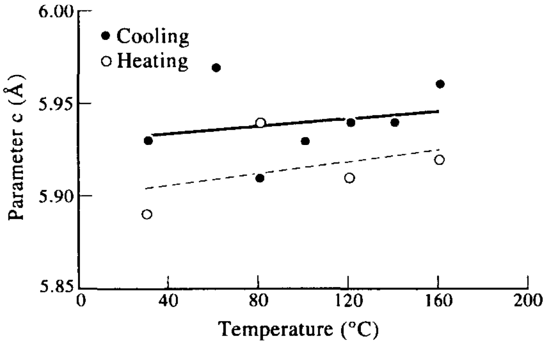

Figure 5 Temperature dependence of PHB unit cell parameter *c*

Table 1 Values of the unit cell parameters and thermal expansion coefficients λ of PHB (experimental data)

			Correlation coefficient	
	Heating	Cooling	Heating	Cooling
a_0 (Å)	5.72 ± 0.02	5.74 ± 0.01	0.96	0.93
b_0 (Å)	13.24 ± 1.60	13.22 ± 2.00	0.27	0.49
c_0 (Å)	5.90 ± 0.02	5.93 ± 0.02	0.45	0.24
λ_a (°C^{-1})	$(1.4 \pm 0.3) \times 10^{-4}$	$(1.3 \pm 0.3) \times 10^{-4}$		
λ_b (°C^{-1})	$(2 \pm 4) \times 10^{-5}$	$(1 \pm 1) \times 10^{-5}$		
λ_c (°C^{-1})	$(3 \pm 4) \times 10^{-5}$	$(2 \pm 3) \times 10^{-5}$		

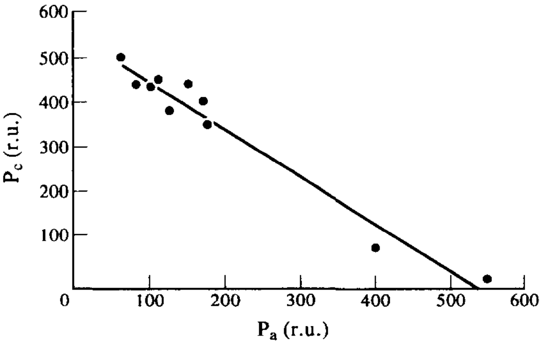

Figure 6 P_c value (scattering from crystalline regions) vs. P_a (scattering from amorphous regions) for PHB biopolymer

Bluhm *et al.*[3] and Mitomo *et al.*[6] have shown the expansion of the unit cell of the copolymer PHB/HV

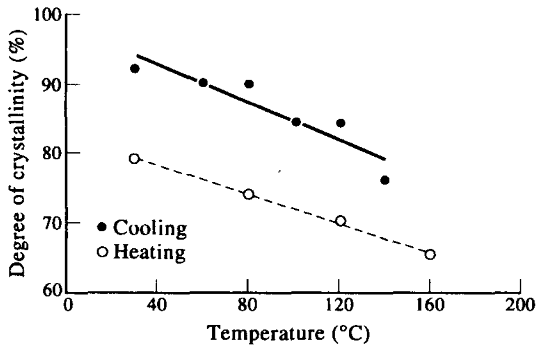

Figure 7 Dependence of crystallinity degree x_c on temperature for biopolymer PHB

with an increase of HV monomer contents. PHB/HV unit cell parameter a increases linearly from 5.76 Å (for 0 mol% HV) up to about 5.80 Å (for 30 mol% HV). In this range HV monomer concentration in the crystal lattice corresponds to PHB unit cell. At HV contents above 30 mol%, copolymer crystallizes with the unit cell typical for PHV.

Our studies show that thermally produced unit cell expansion of PHB is equivalent to the expansion caused by the increase of HV monomer concentration. In the range from room temperature up to T_m there arises a linear increase of parameter a for approximately the same value as with the increase of HV monomer in the structure of PHB/HV. In both cases these small changes of unit cell dimensions are not followed by any significant change of the crystal lattice of PHB or PHB/HV.

The change of the degree of crystallinity with temperature. WAXS diffractograms of PHB at various temperatures are suitable for the determination of the coefficient k in the expression for the calculation of the degree of crystallinity x_c (ref. 4)

$$x_c = \frac{1}{1 + k\frac{P_a}{P_c}}$$

where P_a is the surface under the amorphous background at the diffractogram, which corresponds to the X-ray scattering from the amorphous region, and P_c is the surface of diffraction maxima corresponding to scattering from the crystalline regions. Determining the function $P_c = f(P_a)$ (*Figure 6*), the coefficient k was determined to be 1.06 ± 0.08. The degree of crystallinity x_c of the powder sample of PHB as a function of temperature (isothermal crystallization) is shown in *Figure 7*. The degree of crystallinity changes linearly with temperature, both during heating and cooling of the sample. One can notice the increase of the values of x_c during cooling with respect to the values determined during heating. One of the possible causes for this could be the partial thermal degradation (chain shortening) due to the biopolymer's high sensitivity to temperature increase[7].

Conclusion

On the basis of WAXS powder diffractograms obtained at various temperatures, it was shown that PHB unit cell parameter a changes linearly with temperature. Parameters b and c remain approximately constant with an evident spread of measured values. Thermal expansion coefficient $\lambda_a \approx (1.4 \pm 0.3) \times 10^{-4}\,°C^{-1}$. The increase of parameter a, approximately to the value of parameter c (close to T_m), is equivalent to the increase of the value of parameter a caused by an increase of HV monomer content at PHB/HV copolymer, at lower HV concentrations (<30 mol%).

Using WAXS diffractograms, the value of the coefficient $k = 1.06 \pm 0.08$ in the expression for the calculation of crystallinity degree of PHB biopolymer after the Hermans–Weidinger method was determined. A linear change of the degree of crystallinity as a function of crystallization temperature was detected, with x_c values obtained during heating lower than those obtained during the cooling process.

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