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Heat capacity of poly(3-hydroxybutyrate)

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Dedicated to the memory of the late
Professor Manuel Ribeiro da Silva

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ABSTRACT

The heat capacity of poly(3-hydroxybutyrate) (P3HB) has been measured using a quantum design Physical Property Measurement System (PPMS), differential scanning calorimetry (DSC), and temperature-modulated differential scanning calorimetry (TMDSC) over the temperature range of (1.9 to 460) K. The results within the range of (1.9 to 250) K were obtained using the quantum design PPMS, and established the baseline of the solid heat capacity. This experimental low-temperature heat capacity was linked to the vibrational molecular motion of P3HB. The solid heat capacity of P3HB was computed based approximately on groups of vibration and skeletal vibration spectra. The skeletal vibration heat capacity contribution was estimated by a general Tarasov equation with three Debye characteristic temperatures $\Theta_1 = 549.1$ K and $\Theta_2 = \Theta_3 = 71.8$ K, and ten skeletal modes, $N_{\text{skeletal}} = 10$. The experimental and calculated solid heat capacities agree with an error of ±0.2% over the temperature range from (5 to 250) K. The vibrational, solid heat capacity was extended to higher temperatures to judge additional contributions to the experimental heat capacity from other large-amplitude motion or latent heat during the quantitative thermal analysis of semi-crystalline P3HB. The liquid heat capacity of semi-crystalline P3HB above its melting temperature and of fully amorphous P3HB above the glass transition temperature was approximated by a linear regression and expressed as $C_p^{liquid}(\text{exp}) = 0.1791\ T + 94.722$ in units of $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The calculated solid and liquid heat capacities can serve as equilibrium baselines for the quantitative thermal analysis of semi-crystalline P3HB. Also, the integral thermodynamic functions of enthalpy, entropy and free enthalpy for the equilibrium condition were calculated using estimated parameters of transitions.

1. Introduction

Poly(3-hydroxybutyrate) (P3HB) belongs to the homologous series of aliphatic polyesters and is a semi-crystalline, biodegradable polymer which is biosynthesized and stored by various strains of bacteria such as *Rolstonia eutropha H16*. It is a native polymer of biosynthesis, which has thermoplastic properties and is used in the plastic industry. P3HB can also be used as an alternative polymer to polylactide–glycolides for drug carrier production. The polymer is nontoxic, and organisms seem to tolerate the monomer well in relatively high concentrations. Bacteria living in soil or waste water slowly degrade P3HB into water and carbon dioxide, especially under anaerobic conditions [1].

The structure of the repeating monomer unit is shown below. The chiral center is defined by the carbon atom labeled C^*(Figure 1):

The molar mass of this repeating unit is $86.09\ \text{g} \cdot \text{mol}^{-1}$. Semi-crystalline P3HB has a glass transition between (273 and 300) K [2,3] and melting temperature between (430 and 470) K [2,4]. Literature [5–8] shows that for 100% crystalline P3HB the equilibrium melting temperature is 470 K with an enthalpy of fusion $12.57\ \text{kJ} \cdot \text{mol}^{-1}$. Usually P3HB with degrees of crystallinity in the range (50 to 80)% or amorphous P3HB can be obtained by varying the cooling rate [2]. P3HB can be degraded in the melting temperature range (453 to 463) K. It has a tensile strength of 40 MPa and a softening temperature of around 368 K [9–13].

In order to obtain a quantitative knowledge of the thermal properties of a polymeric material such as P3HB, the fundamental thermodynamic functions, such as heat capacity, C_p, enthalpy, H, Gibbs free energy, G, entropy, S, and temperatures and enthalpy of transition should be measured, calculated, and interpreted with molecular motion models [14–16]. For example, equilibrium solid and liquid properties must be established as a reference to analyze quantitatively the experimental heat capacity of P3HB.

In this paper, the low-temperature heat capacity of P3HB is measured using a quantum design PPMS and used for the calculation of vibrational, solid heat capacity. The equilibrium solid and liquid heat capacities are established and used as reference for the quantitative thermal analysis of the experimental, apparent

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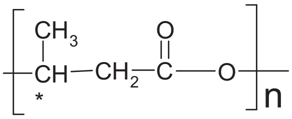

FIGURE 1. Structure of the repeating unit of P3HB.

heat capacity of non-equilibrium semi-crystalline P3HB mostly obtained by differential scanning calorimetry (DSC), and temperature-modulated differential scanning calorimetry (TMDSC).

The quantitative study of P3HB allows for the description of the glass transition and melting process as well as the degree of crystallinity, the mobile amorphous fraction, and the rigid-amorphous fraction in the semi-crystalline material.

1.1. Characterization of the heat capacity

Heat capacity belongs to the fundamental quantities which are used in the evaluation of thermodynamic properties of materials derived from calorimetric measurements [14]. In general, by calorimetry the apparent heat capacity, (C_p^*), is measured and contains heat capacity and latent heat effects, such as enthalpy of fusion, crystallization, reorganization, reaction and others. The description of changes of enthalpy can be given by [14,15]:

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,n} dT + \left(\frac{\partial H}{\partial n}\right)_{p,T} dn, \tag{1}$$

where the first part of equation (1) represents heat capacity, C_p, and the second part $(\partial H/\partial n)_{p,T}$ is the latent heat effect, where dT and dn are the changes in temperature and composition, respectively.

The heat capacity is related to the molecular motion and is a function of temperature. The quantitative study of the heat capacity of P3HB is described, using an adiabatic calorimeter or a more general method using a quantum design PPMS, differential scanning calorimeter (DSC), and temperature-modulated DSC (TMDSC) for measurement, and the ATHAS scheme for analysis [14–17]. The heat capacity of low molar mass [18], solid compounds and polymers [14,17,19–21] is calculated by assuming that at low-temperatures, below the glass transition, only vibrational motion is possible. As the temperature increases conformational, rotational and translational motions appear which can be added to the vibrational heat capacity.

1.2. Calculation of the heat capacity of the solid state

The experimental low-temperature heat capacities of P3HB using a quantum design PPMS are used to calculate the vibrational, solid heat capacities based on an approximate group and skeletal vibration spectrum according to an ATHAS scheme [14–17]. Both approaches are based on the classical Einstein [22], Debye [23], and Tarasov [24] treatments. The vibrational spectrum of a solid polymer consists of 3N vibrational degrees of freedom where N represents the total numbers of atoms in the repeating unit. Theses vibrations are separated into groups (N_{gr}) and skeletal (N_{sk}) vibrations and are expressed by the sum: $3N = N_{gr} + N_{sk}$. Using normal mode vibrations of the chemical structure based on infrared and Raman spectroscopy established in the literature [14,17,25], the types and numbers of group vibrations, are generated. The skeletal vibrations are described as the remaining part of the total numbers of vibrators and are used for fitting the experimental data heat capacity to a Tarasov function [24].

In the initial calculations of the heat capacity of the solid state, the experimental heat capacities at constant pressure C_p(exp) are converted into the heat capacities at constant volume C_v(exp) using the following equation [14,24,26]:

$$C_p(\mathrm{exp}) - C_v(\mathrm{exp}) = \frac{TV\alpha^2}{\beta}, \tag{2}$$

where V is the molar volume, α the expansivity, and β represents the compressibility, and all parameters are functions of the temperature, T.

In case the experimental data of parameters from equation (2) are not available for the solid state, C_p(exp) is converted to C_v(exp) by the Nernst–Lindemann equation in the form [24,27,28]:

$$C_p(exp) - C_v(\mathrm{exp}) = 3RA_0\frac{C_v^2(\mathrm{exp})}{C_v(\mathrm{exp})}\frac{T}{T_m}, \tag{3}$$

where A_o is approximately equal to the universal constant ($\approx 0.0039\ \mathrm{K \cdot mol \cdot J^{-1}}$), T is the temperature in Kelvin, T_m is the equilibrium melting temperature, and R is the gas constant.

Assuming that the heat capacity at constant volume C_v(exp) contains only vibrational contributions below the glass transition temperature, it can be separated into the heat capacities from group vibrations $C_v(gr)$ and skeletal vibrations $C_v(sk)$ [14]:

$$C_v(exp) = C_v(gr) + C_v(sk). \tag{4}$$

$C_v(gr)$ can be described as a sum of normal modes having a box-like distribution, C_v(box), and single frequencies approximated by separate Einstein modes C_v(Einstein), and presented by the following equation [14,24]:

$$C_v(gr) = C_v(\mathrm{box}) + C_v(\mathrm{Einstein}). \tag{5}$$

The heat capacity, C_v(Einstein) can be written as [14,24]:

$$\frac{C_v(\mathrm{Einstein})}{NR} = \sum_i E\left(\frac{\Theta_{Ei}}{T}\right) = \sum_i \frac{(\Theta_{Ei}/T)^2 exp(\Theta_E/T)}{[exp(\Theta_{Ei}/T) - 1]^2}, \tag{6}$$

where $\Theta_{Ei} = h\nu/k$, represents the given Einstein frequencies in Kelvin, and h and k are Planck's and Boltzmann's constants, respectively.

The heat capacity of a box-distribution, C_v(box) can be described as a one-dimensional Debye function, D_1, and set of frequency intervals from Θ_U, to Θ_L which can be calculated by the following equation [14,24,29]:

$$\begin{aligned}\frac{C_v(box)}{NR} &= B\left(\frac{\Theta_U}{T}, \frac{\Theta}{T}\right)\\ &= \frac{\Theta_U}{\Theta_U - \Theta_L}\left[D_1\left(\frac{\Theta_U}{T}\right) - \left(\frac{\Theta_L}{\Theta_U}\right) D_1\left(\frac{\Theta_U}{T}\right)\right],\end{aligned} \tag{7}$$

where N is the number of vibrational modes for the frequency distribution, R is the gas constant, B can be called the box function, T is the temperature in Kelvin, and Θ_U, Θ_L are upper and lower frequencies, respectively.

At low temperatures, the difference between the experimental heat capacity at constant volume and the heat capacity from group vibrations is approximated by the general Tarasov function, T [14,24,30,31]:

$$\begin{aligned}\frac{C_v(sk)}{NR} &= T\left(\frac{\Theta_1}{T}, \frac{\Theta_2}{T}, \frac{\Theta_3}{T}\right)\\ &= D_1\left(\frac{\Theta_1}{T}\right) - \left(\frac{\Theta_2}{\Theta_1}\right)\left[D_1\left(\frac{\Theta_2}{T}\right) - D_2\left(\frac{\Theta_2}{T}\right)\right]\\ &\quad - \left(\frac{\Theta_3^2}{\Theta_1\Theta_2}\right)\left[D_2\left(\frac{\Theta_3}{T}\right) - D_3\left(\frac{\Theta_3}{T}\right)\right],\end{aligned} \tag{8}$$

TABLE 1
Addition scheme of liquid heat capacity of structure-group contribution of P3HB.

Structure-group of polymers	C_p(liquid) of group [$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$]
Methylene[($-CH_2-$)]	$13.91 + 0.0487T$
Methylmethylene [$-CH(CH3)-$]	$25.06 + 0.108T$
Carboxyl [$-(CO)O-$]	$64.32 + 0.002441T$