Nr 5 (281–340) MAJ 2024 Tom LXIX

POLIMERY

Liquid heat capacity of an amorphous poly(lactic acid)

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DOI: https://doi.org/10.14314/polimery.2024.5.1

Abstract: The experimental and computed liquid heat capacity of an amorphous PLA was presented. The liquid heat capacity of PLA above the glass transition 333 K (60°C) is linked to the molecular motions and computed as the sum of vibrational, external (anharmonic), and conformational contributions. The largest contribution to the liquid heat capacity, C_p(liquid) of PLA comes from the vibrational motions calculated as the group and skeletal vibrational heat capacity. The external contribution to C_p(liquid) was calculated as a function of temperature from experimental data of the thermal compressibility and expansivity of the liquid state. The contribution of conformational heat capacity to the total heat capacity of an amorphous liquid PLA was calculated by fitting the experimental liquid heat capacity, after subtracting the vibrational and external parts, to the obtained heat capacity based on a one-dimensional Ising-type model with two discrete states. The parameters described in these states can characterise the macromolecule's stiffness, cooperativity, and degeneracy. The computed and experimental data of C_p(liquid) showed good agreement at the investigated temperature region.

Keywords: PLA, amorphous phase, liquid heat capacity, conformational heat capacity, glass transition.

Pojemność cieplna ciekłego amorficznego poli(kwasu mlekowego)

Streszczenie: W pracy przedstawiono eksperymentalna i obliczoną pojemność cieplną ciekłego amorficznego PLA. Pojemność cieplna cieczy PLA powyżej temperatury przejścia szklistego 333 K (60°C) jest powiązana z ruchami molekularnymi i została obliczona jako suma składników wibracyjnych, zewnętrznych (nieharmonicznych) i konformacyjnych. Największy wkład w pojemność cieplną cieczy, C_p(liquid) PLA, pochodzi z ruchów wibracyjnych, obliczonych jako pojemność cieplna wibracji grupowych i szkieletowych. Zewnętrzny wkład do C_p(liquid) został obliczony jako funkcja temperatury na podstawie danych eksperymentalnych z użyciem parametrów ściśliwości i rozszerzalności cieplnej cieczy. Wkład konformacyjnej pojemności cieplnej do całkowitej pojemności cieplnej amorficznego ciekłego PLA został obliczony przez dopasowanie eksperymentalnej pojemności cieplnej cieczy, po odjęciu

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części wibracyjnych i zewnętrznych, do otrzymanej pojemności cieplnej opartej na jednowymiarowym modelu typu Ising z dwoma dyskretnymi stanami. Parametry opisane w tych stanach mogą charakteryzować sztywność, kooperatywność i degenerację makrocząsteczki. Obliczone dane C_p(liquid) wykazały zgodność z danymi eksperymentalnymi w badanym zakresie temperatury.

Słowa kluczowe: PLA, faza amorficzna, pojemność cieplna cieczy, konformacyjna pojemność cieplna, temperatura zeszklenia.

The quantitative thermal analysis of polymers requires knowledge of equilibrium quantities and parameters as references. The heat capacity (C_p) is one of the macroscopic, thermodynamic quantities that can give information about the thermal behaviour of macromolecules. Differential Scanning Calorimetry (DSC) is the method that can measure thermodynamic heat capacity and apparent heat capacity (sum of C_p and heat of transition). To analyse the C_p and apparent C_p of crystalline, amorphous and semicrystalline polymers, the solid and liquid heat capacity references equilibrium baselines in an entire range of temperatures must be established [1]. It should be noted that polymers' heat capacity arises from molecular motions, mostly from vibrational, conformational, and anharmonic (external) [1, 2]. The solid heat capacity was obtained from the low-temperature experimental C_p of crystalline or semicrystalline polymers and linked to the approximate vibrational spectrum of molecular motion of materials [1–3]. The solid heat capacities and vibrational states are collected in the ATHAS (Advanced THermal Analysis System) Data Bank [2–5].

The second equilibrium baseline is the liquid heat capacity, which can be obtained from experimental measurements of C_p above the glass transition temperature (T_g) for fully amorphous polymers and above the melting temperature (T_m), for fully crystalline and semicrystalline materials. A fit of experimental data for the liquid heat capacity of polymers often shows a linear function of temperature [2, 4, 5]. Furthermore, an empirical addition scheme based on the group contribution of the constituent chain segments of macromolecules is available from the ATHAS Data Bank [4–6]. The interpretation of liquid heat capacity of macromolecules on a microscopic level, based on molecular motions, still has been of interest and has been investigated by many scientists (Flory [7–9], Sanchez [10–12], and Simha [13–15], Prigogine [16], O'Reilly [17], Gibbs and DiMarzio [18–20], Wunderlich [21]). Previously, our works on the liquid heat capacity, C_p (liquid), were based on the link of the experimental heat capacity of fully amorphous polymer above the T_g to molecular motions and the computation of C_p as the sum of vibrational, external (anharmonic), and conformational contributions [2, 22–23]. Such an approach was applied to characterise some macromolecules, e.g., polyethylene, polypropylene, poly(vinyl methyl ether) and others [22] with good agreement, in a few per cent errors, close to the experimental precision at the temperature region. The full description of the calculation of liquid heat capacity C_p^{cal} (liquid) of polymers developed by Wunderlich and co-workers is presented in [2, 3, 22], and a general scheme is also given in the "Methods" section.

This paper presents the calculated liquid heat capacity of amorphous poly(lactic acid), providing valuable insights into its thermal properties. The experimental heat capacities at the liquid state, above the glass transition temperature 333.15 K (60°C), were linked to the molecular motions and computed as the sum of vibrational, external (anharmonic), and conformational contributions. The experimental and computed data results of liquid C_p were compared. Our approach can provide a better understanding and prediction of the macroscopic physicochemical properties of the system under study.

EXPERIMENTAL PART

Materials

Poly(lactic acid), PLA, with high stereochemical D-isomer (16.4%, PLA-*H*) was obtained from Cargill Dow LLD, Chem. Co. (Minnetonka, MN, USA). The average molar mass was 180 000–220 000 Da.

Methods

Heat capacities of amorphous PLA at $T = 5–250$ K were measured with an automated adiabatic calorimeter, which was described previously [24]. Briefly, the sample's heat capacity was 60–70% of the total heat capacity of the calorimeter and substance over the whole temperature range. The sample weight was around 1.0 g. The calorimetric ampoule was a cylindrical vessel of platinum with a volume of around $15 \cdot 10^{-6}$ m^3. The heat capacity of an unloaded calorimetric ampoule increased gradually from 0.0045 to 1.440 J · K^{-1} with increasing temperature from $T = 5–250$ K. The temperature was measured with a platinum resistance thermometer. Liquid helium and nitrogen were used to obtain low temperatures. Heat capacities were calibrated with the benzoic acid standard. The precision was estimated to be 0.5% from $T = 5–250$ K.

The high-temperature DSC results were measured from $T = 190–470$ K. For standard DSC experiments, the Q1000™ calorimeter from TA Instruments, Inc. (New Castle, DE, USA) equipped with a refrigerator was used to obtain the apparent heat capacities. The experiments were performed at the heating rate of 10 K min^{-1}. All measurements were carried out in a nitrogen atmosphere with a constant flow rate of around 50 mL min^{-1}.

Temperature calibrations were carried out at the phase transitions of indium onset melting temperature of $T_{m(\text{onset})}$ = 429.75 K (156.6 °C), and enthalpy of fusion of ΔH_f = 3.281 kJ · mol^{-1} (28.45 J g^{-1}).

For C_p measurements by standard DSC, samples of 10–15 mg were used. For C_p calibration, single-crystalline sapphire (Al_2O_3) was used for each measurement temperature.

Scheme of calculating liquid heat capacity for polymers

In this section, a general scheme for the calculation of the liquid heat capacity of polymers, developed by Wunderlich and co-workers is presented [1–3, 21–23]. A starting point to compute a liquid heat capacity is to obtain the data of an experimental heat capacity of polymeric material. The experimental heat capacity can be described by the Equation 1 [1–3, 21–23]:

$$C_p(\text{liquid}) = C_V(\exp) + TV\frac{\alpha^2}{\beta} \qquad (1)$$

where C_p (liquid) is the experimental heat capacity at constant pressure above the glass transition temperature for fully amorphous polymer or above the melting temperature for semicrystalline or fully crystalline polymeric material and is used to calculate liquid heat capacity. In Eq. 1 the expression C_v (exp) + TV(α^2/β_c) is the standard thermodynamic relationship, where C_v(exp) is the experimental heat capacity at constant volume, T is the temperature in kelvin, V is volume, α is the thermal expansivity $\alpha = V^{-1}(\partial V/\partial T)_p$ and β_c is the compressibility, $\beta_c = V^{-1}(\partial V/\partial_p)_T$, derived from the experimental P-V-T (pressure-volume-temperature) diagram for the liquid-like state collected from literature [1, 22, 25].

The right side of Eq. 1 of the liquid heat capacity, C_p(liquid) of polymers can be approximated as the sum of three heat capacity's contributions as described in Equation 2 [1, 2, 20–23]:

$$C_p(\text{liquid}) = C_V(\exp) + TV\frac{\alpha^2}{\beta} \approx C_v(\text{vibration}) + C_V(\text{conf}) + C_V(\text{ext}) \qquad (2)$$

where C_v (vibration), is the vibrational heat capacity and is the same as in the solid state, C_v (conf), is the conformational heat capacity, and C_v (ext) is the external (anharmonic) contribution. It should be noted that according to Equation 1 C_v (exp) corresponds to two parts of contributions, the sum of C_v (vibration) and C_v (conf). The C_v (ext) is equal to TV(α^2/β_c). All contributions of liquid heat capacity in Eq. 2 need to be known as a function of temperature.

The conformational and external contribution comes from large-amplitude motion. The calculation of the conformational heat capacity, C_v (conf) is based on the one-dimensional Ising-type model [26] with the assumption that the conformational states of flexible segments of the macromolecule can occur in only two discrete states, a ground state or an excited state and an energy difference between the two states is equal B. Energy B can be modified by the energy A, describing the interaction of the nearest conformational neighbours. The parameter B corresponds to stiffness, and parameter A corresponds to cooperativity.

The total energy, E_I of the chain conformations of a macromolecule with a total number N of rotatable segments can be described according to the one-dimensional Ising-type model, as presented in Equation 3 [2, 9, 22]:

$$E_I = A\sum_{j=1}^{N} m_j m_{j+1} + B\sum_{j=1}^{N} m_j \qquad (3)$$

where m_j is the conformation number and is equal zero ($m_j = 0$) for the ground state with energy zero and degeneracy g_o. The excited state of the conformation is described by the number $m_j = 1$ with energy B and degeneracy g_1. In Equation 3, the energy of the conformation state can be modified by the energy A, depending on the neighbour's state, and can be negative or positive.

Knowing of energy E_I, and using of the transfer-matrix method for the estimation of the partition function and the free energy per bond, the conformational heat capacity, C_v (conf) can be calculated. The C_v (conf) can be presented in the closed-form solution as follows (Equation 4) [2, 22–23]:

$$C_V(\text{conf}) = R\frac{\Gamma[\frac{B}{k_BT}]^2 e^{\frac{-B}{k_B}T}}{[\Gamma e^{\frac{-B}{k_BT}} + 1]^2}[1 + \upsilon(B, A, \Gamma, T)] \qquad (4)$$

where R is the gas constant, k_B, is the Boltzmann constant, Γ is the ratio of the degeneracies of the conformational states ($\Gamma = g_1/g_o$), and T is the temperature in kelvin. The first part in Equation 4 describes the heat capacity of the rotational isomers model [1, 2, 22], and the second part in Equation 4 describes the contribution to C_v(conf) from the interaction of the nearest conformational neighbours. The expression υ(A, B, Γ, T) in Equation 4 is too extensive to present here in detail. The full description of the calculation of C_v (conf) is given in the cited literature [2, 22].

More details regarding the computation of the vibrational heat capacity C_v (vibration), based on group and skeletal contribution, can be found in the references [1–3, 27–31].

RESULTS AND DISCUSSION

The measurement of heat capacity for amorphous poly(lactic acid) was carried out by adiabatic calorimetry (AC) and standard DSC. Figure 1 shows this experimental heat capacity of fully amorphous PLA-*H* at solid and liquid states [31, 32]. The evaluation of the solid heat capacity of PLA-*H* was analysed according to the ATHAS method

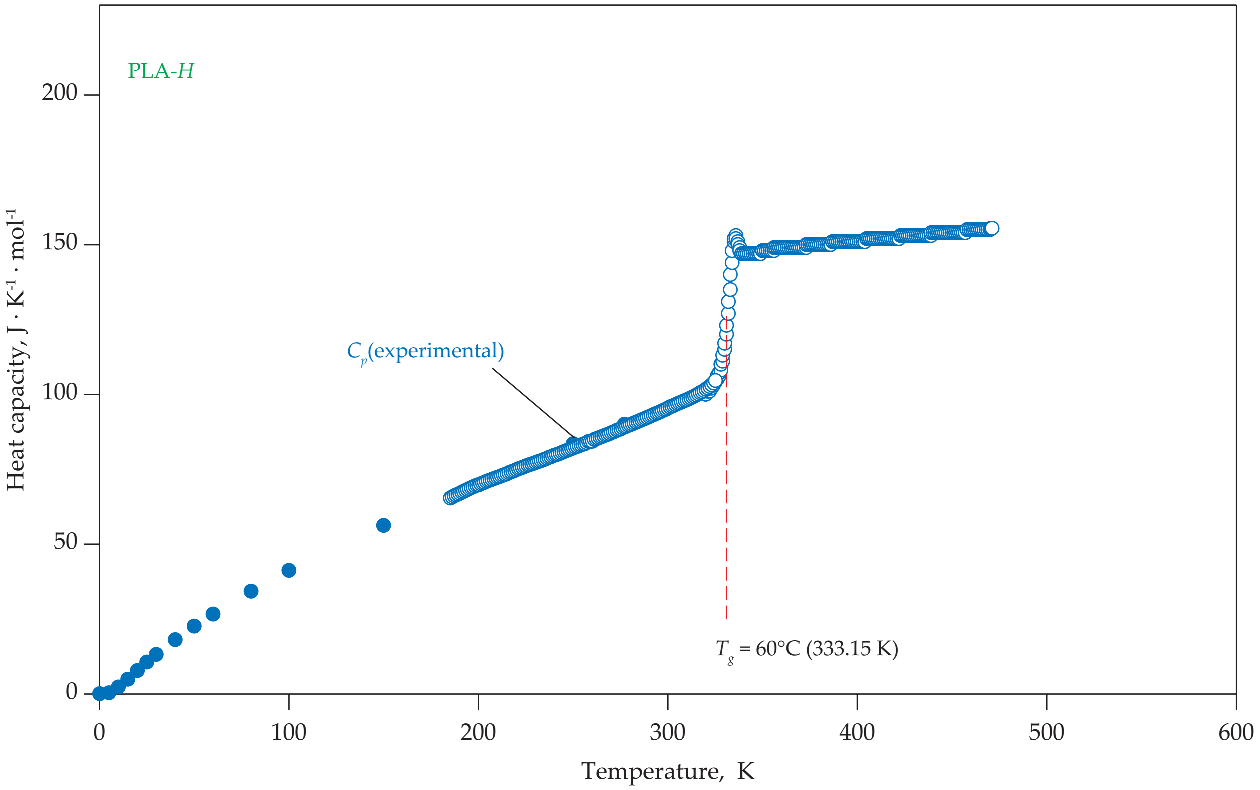

Fig. 1. Experimental heat capacity of amorphous poly(lactic acid) (PLA-*H*) at solid and liquid states [31]

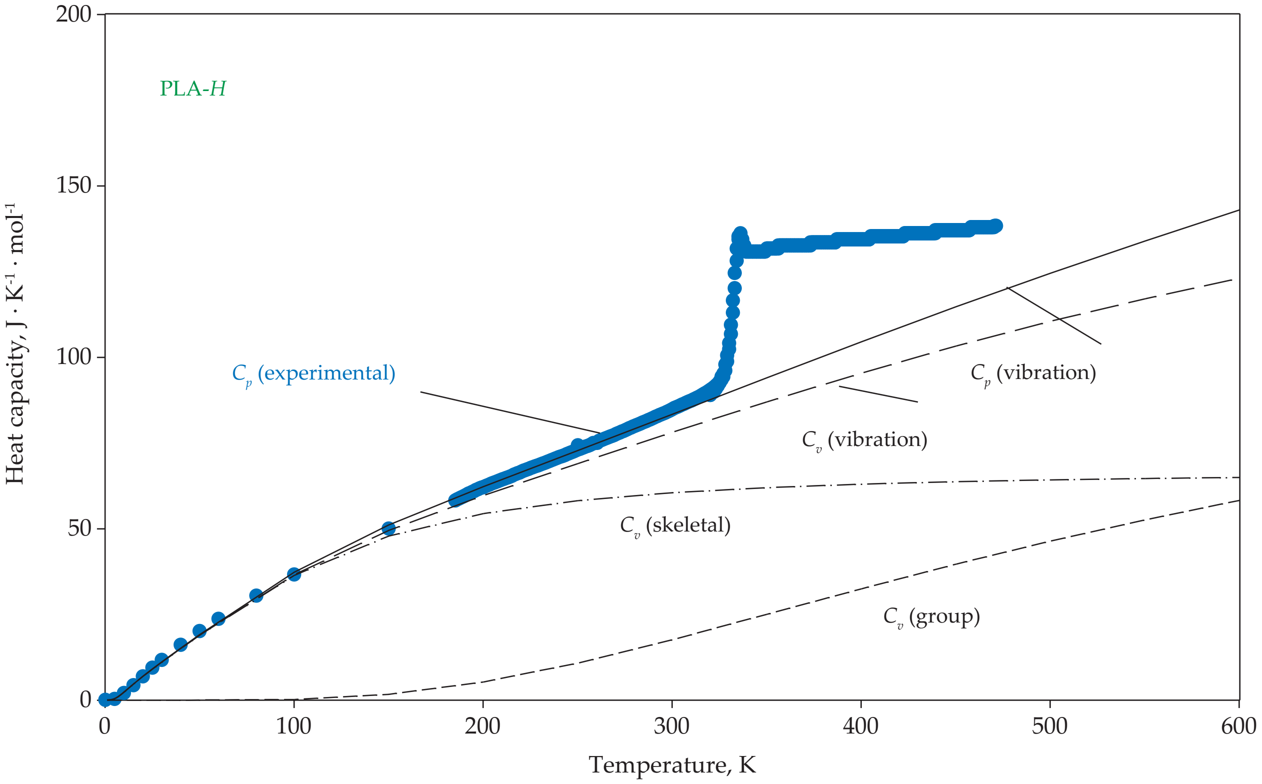

Fig. 2. Experimental and calculated, vibrational heat capacity C_p(vibration) of amorphous poly(lactic acid) and its contributions: the group, C_v(group) and skeletal, C_v(skeletal) vibration [31]

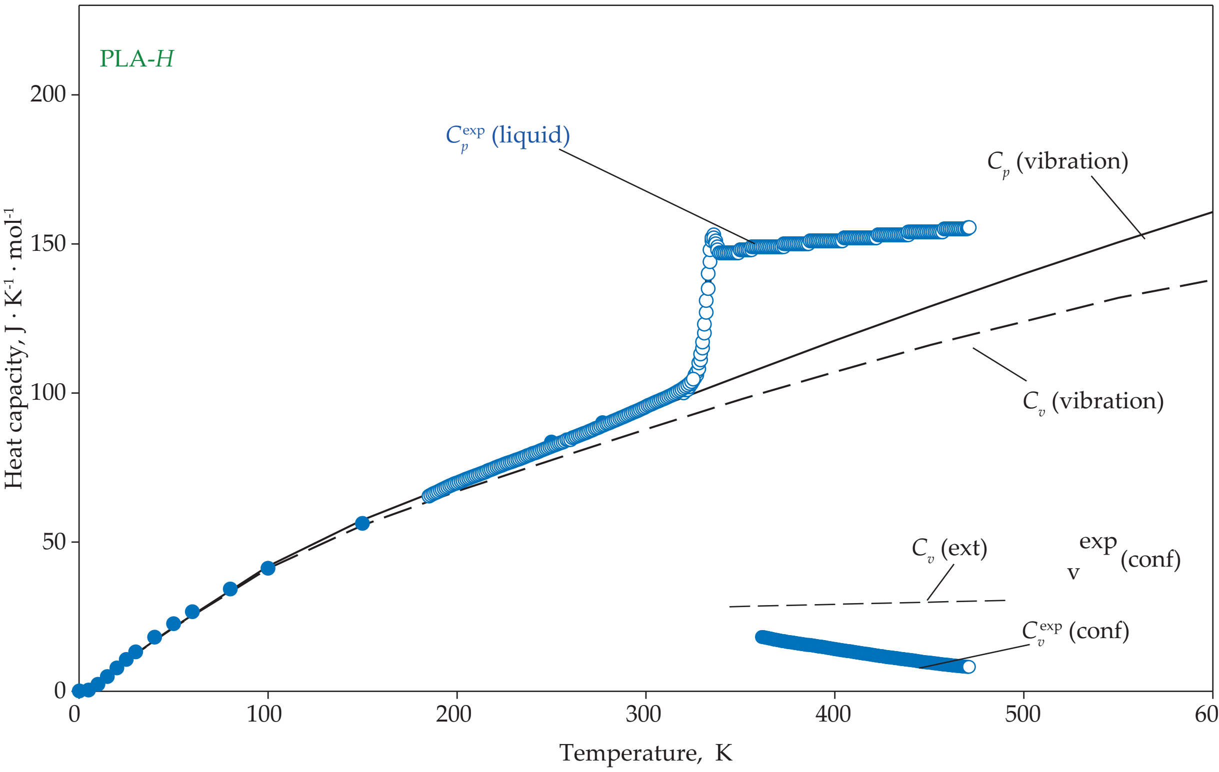

Fig. 3. Evaluation of vibrational, C_p(vibration), external, C_v(ext), and conformational, C_v(conf), parts and experimental heat capacity, C_p^{exp}(liquid) at the liquid state of amorphous poly(lactic acid)

and has already been presented in authors' previous work [31–33].

The heat capacity of C_p(solid) = C_p(vibration) is presented in Figure 2. The results of calculated, solid, vibrational heat capacity C_p(vibration) were provided based on the low-temperature experimental heat capacity of PLA-*H*. The experimental data of C_p(experimental) below T_g of PLA-*H* were linked to vibration motion using an approximate group and skeletal vibrational spectrum, according to the ATHAS scheme for solid state [31]. Figure 2 shows all vibrational contributions: the group, C_v(group) and skeletal, C_v(skeletal), which, as the sum, gives the heat capacity at constant volume C_v(vibration). Conversion from constant volume to constant pressure (C_v to C_p) using the standard thermodynamic relationship [1, 2, 31, 34, 35] gives the total heat capacity of the solid-state, C_p(vibration). This C_p(vibration) line is extended to a higher temperature beyond T_g. It is the equilibrium C_p for quantitative thermal analysis of amorphous and semicrystalline poly(lactic acid). The good agreement between the experimental C_p(experimental) and calculated C_p(vibration) heat capacity below the T_g temperature was observed with a standard deviation of around ±3% from 5 to 300 K [31].

The evaluation and computation of liquid heat capacity C_p^{cal}(liquid) of fully amorphous PLA-*H* above T_g according to the scheme presented above and in extended version was shown in Figures 3–5 [2, 22–23]. For a liquid state above T_g, in the computation of C_p, additional contributions of large-amplitude motion should be considered [2, 22]. Figure 3 shows the evaluation of vibrational, C_p(vibration), C_v(vibration), external, C_v(ext), and conformational, C_v(conf), parts under experimental heat capacity, C_p^{exp}(liquid) of poly(lactic acid) for calculation of the total liquid heat capacity. The vibrational heat capacity for calculating the liquid heat capacity was the same as

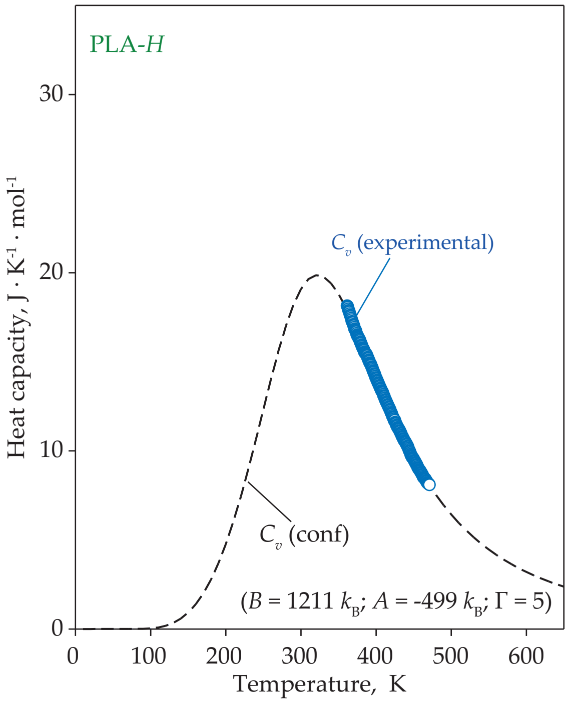

Fig. 4. Comparison of the experimental C_v(experimental) and computed, conformational, C_v(conf) contributions of the liquid heat capacity of an amorphous poly(lactic acid) [36]

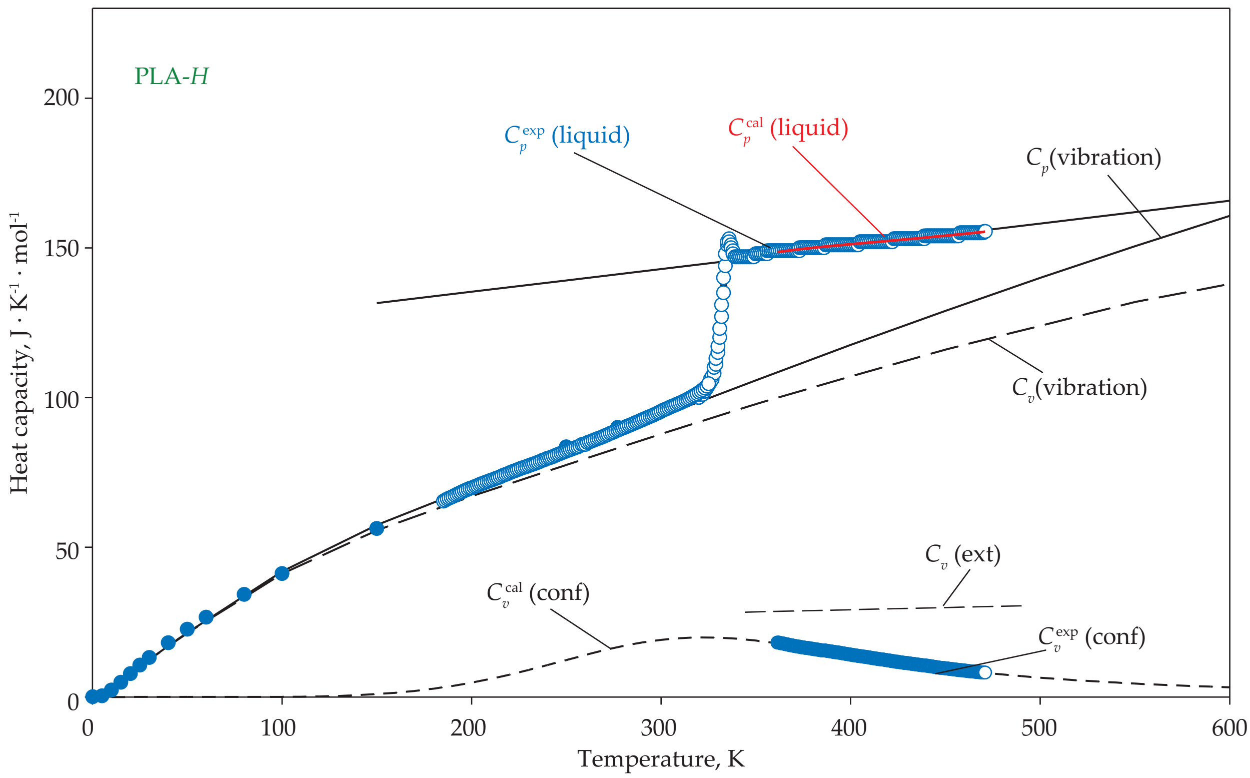

Fig. 5. Evaluation of the calculated liquid heat capacity, C_p^{cal}(liquid) (solid red line) of an amorphous poly(lactic acid) based on the vibrational, C_p(vibration), external, C_v(ext), and conformational, C_v(conf), heat capacity. The calculated liquid heat capacity of PLA-*H* was obtained from the fit of the experimental heat capacity in the liquid state (above T_g) to a linear function

Table 1. Parameters to calculate the external heat capacity C_v (ext) of poly(lactic acid) [37, 38]

Polymer	$V_o \times 10^{-5}$ $m^3\,mol^{-1}$	$\alpha \times 10^{-4}$ K^{-1}	$b_0 \times 10^{-10}$ Pa^{-1}	$b_1 \times 10^{-3}$ K^{-1}
PLA	8.967	7.787	1.88	4.16

the solid heat capacity [31] (see "Methods"). It should be clarified that only the vibrational heat capacity at constant volume, C_v(vib), (not C_p(vibration)) participated in the sum of the total, calculated C_p^{cal}(liquid).

The external heat capacity contribution, C_v(ext), was estimated by using the thermal expansivity (a, in K^{-1}), and compressibility (b_c, in Pa^{-1}) as a function of temperature according to Equations 1 and 2 [$C_p(exp) - C_v \approx C_v(ext) = TV(\alpha^2/\beta_c)$; where $V(T)_{p=0} = V_0 \exp(a\,T)$; $b_c(T) = b_0 \exp(b_1 T)$]. The data were taken from the equation of states, *P-V-T* for the liquid, from [37, 38], where: *P* is the pressure, *V* is the molar volume (in $m^3 \cdot mol^{-1}$), and *T* is the temperature (K). Table 1 presents the values of the constants V_0, α, b_0, and b_1 according to [38, 39]. The calculated C_v (ext) above T_g of PLA in the liquid state is shown in Figure 3.

The conformational heat capacity, C_v(conf), of the total C_p^{cal}(liquid) of PLA-*H* was computed according to the scheme presented in the "Methods" and [2, 22–23]. In order to calculate C_v(conf), the experimental part of heat capacity, C_v^{conf}(experimental), needs to be separated from the total experimental heat capacity at the liquid state. These data were obtained from the subtraction of the vibrational C_v(vib), and external, C_v(ext), heat capacity from total C_p^{exp}(liquid), and were fitted to the Equation 4 [2, 22–23].

The parameter *B* corresponds to stiffness, and parameter *A* corresponds to cooperativity. The first part in Eq. 1 describes the heat capacity of the rotational isomers model [1, 2, 22–23], and the second part in Equation 1 describes the contribution to C_v(conf) from the interaction of the nearest conformational neighbours [the expression $\upsilon(A, B, \Gamma, T)$]. The full description of the calculation of C_v(conf) is given in authors' previous work [2, 22–23].

The values of parameters, energy *B*, the cooperativity energy *A*, and the degeneracies Γ ratio, from the best fit to Equation 1 of the experimental C_v^{conf}(experimental) are presented in Table 2. It should be noted that *A* and *B* are given in terms of temperature (in kelvin), and to convert them to the energy units [$J \cdot mol^{-1}$], both should be multiplicated by the gas constant ($R = 8.314\ J \cdot K^{-1} \cdot mol^{-1}$) then $B = 10.07\ kJ \cdot mol^{-1}$ and $A = -4.15\ kJ \cdot mol^{-1}$. The conformational heat capacity, C_v(conf), was calculated using the values of *B*, *A*, and Γ. Figure 4 and Figure 5 present the results of the comparison between the experimental C_v^{conf}(experimental) and calculated C_v(conf) conformational heat capacity of poly(lactic acid), PLA-*H*. As

T a b l e 2. Fitting parameters used for the calculation of conformational heat capacity C_v(conf), of poly(lactic acid)

Polymer	B K	A K	Γ –	Comments
PLA-*H*	1211	–499	5	*A*, *B*, Γ fitting from 360–470 K

seen in Figure 5, the comparison shows good agreement between the experimental C_v^{conf}(experimental) and calculated C_v(conf) heat capacity with errors around ±1% over the temperature range of 360–470 K. The precision of calculation was based on minimising the chi-square statistics function by applying the programming language of "Mathematica 3.0" [2, 22]. Analysis of the conformational heat capacity results shows that the value of the difference between a ground state and an excited conformational state B = (1211 K; 10.07 kJ · mol^{-1}) of PLA-*H* is similar to other polymers such as poly(methyl methacrylate), PMMA, (B = 1452 K; 12.07 kJ · mol^{-1}) or polystyrene, PS, (B = 1438 K; 11.55 kJ · mol^{-1}) and almost the half lower as for polyethylene, PE (B = 696 K; 5.79 kJ · mol^{-1}) or polypropylene, PP, (B = 636 K; 5.29 kJ · mol^{-1}) [2, 22]. The above comparison shows that the stiffness of poly(lactic acid) is similar to PMMA and PS and higher than PE and PP. In order to improve the description of the conformational heat capacity of PLA, a cooperativity effect was included; the difference between two conformational states can be changed. The sum of the energy of the difference between two conformational states B and the cooperative effect energy A, described as effective energy, for PLA-*H* has the value of $B + A$ = 712 K; 5.92 kJ · mol^{-1}. This result suggests that the introduction of the cooperative effect ($A \neq 0$) significantly reduces the stiffness of the PLA chain (from 10.07 kJ · mol^{-1} to 5.92 kJ · mol^{-1}). A similar value of the effective energy ($A + B$) was observed for PMMA (6.2 kJ · mol^{-1}), a little higher for PS (7.5 kJ · mol^{-1}) or poly(vinyl methyl ether), PVME, (8.43 kJ · mol^{-1}) and very high for poly(*n*-butyl methacrylate) (27.7 kJ · mol^{-1}). In the case of the PP, a lower value was obtained (3.7 kJ · mol^{-1}) and a much lower for PE (2.0 kJ · mol^{-1}) [22]. The above comparison suggests that the segments in the PLA in the liquid state are neither soft nor stiff. This observation also indicates that the introduction of the cooperation effect in the whole volume can be enough to soften bones of polymer to allow a phase transition from glass to a liquid state and is related to a change of heat capacity at T_g (in the case of PLA, ΔC_p = 43.8 J · K^{-1} · mol^{-1}) [31]. The ratio of degeneracies g_1 excited (*trans)* state and g_0 ground (*gauche)* state with the value of Γ = 5 indicates that excited conformational states are more readily available than their ground states.

Knowing three contributions of heat capacities: vibrational, C_v(vibration), external, C_v(ext), and conformational, C_v(conf), the calculated liquid heat capacity, C_p^{cal}(liquid) of PLA was obtained as their sum. A good agreement between the experimental C_p(experimental) and calculated C_p^{cal}(liquid) above the glass transition in the temperature range between 360 and 470 K with errors around ±1% was observed (see Figure 5).

Furthermore, an additional estimation of the calculated liquid heat capacity C_p (liquid) of PLA was obtained from the fit of experimental data C_p (experimental) above T_g in the liquid state to a linear function of temperature (T) with a standard deviation of ± 0.5% and can be written as follows [31]:

$$C_p(\text{liquid}) = 120.17 + 0.076T \tag{5}$$

and is shown in Figure 5.

Both approaches show that the liquid heat capacity of poly(lactic acid) increases linearly with temperature. Advanced thermal analysis shows that three contributions to the liquid C_p are nonlinear, but the final result maintains linearity in heat capacity. This behaviour of C_p in liquid state was earlier observed in other macromolecules presented by Wunderlich and co-workers [1, 31]. Finally, we can conclude that the calculated liquid heat capacity of PLA with cooperative approximation in the conformational heat capacity agrees with experimental data and provides a more realistic picture of the molecular level PLA description.

CONCLUSIONS

The calculated liquid heat capacity of poly(lactic acid) on the microscopic level in terms of molecular motions was presented. The heat capacity in the liquid state was measured by calorimetry and characterised by quantitative thermal analysis. The liquid heat capacity at constant pressure for amorphous material above T_g was linked to the molecular motions and was computed as the sum of the vibrational, external, and conformational heat capacity contributions. For the cooperative effect in the description of the conformational C_p, the one-dimensional Ising-like model for two discrete states with three parameters related to stiffness (B), cooperativity (A), and degeneracy (Γ) was applied. A comparison of the experimental and calculated C_p(liquid) for PLA shows a good agreement, is close to the measured precision, and provides a more physical description of the liquid heat capacity of poly(lactic acid).

Knowledge of the liquid and solid heat capacity allows the quantitative thermal analysis to obtain better physical quantities for mobile, rigid glass or melting transition, degree of crystalline of PLA, PLA-water or more complex systems of different polymers [1, 39–44].

Authors contribution

M.S. – writing-original draft, writing review and editing, methodology, conceptualisation; A.CK. – writing review

and editing, methodology, conceptualisation; Z.K. – writing review and editing, methodology, conceptualisation; M.P. – writing-original draft, writing review and editing, methodology, investigation, visualisation, supervision.

Funding
The research received no external funding.

Conflict of interest
The authors declare no conflict of interest.

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Received 24 III 2024.
Accepted 15 IV 2024.

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