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Do biopolymers behave the same as synthetic high polymers?

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Abstract The first measurements in our laboratory of some 55 years ago dealt with adiabatic calorimetry of linear, semicrystalline polyethylene. Quickly it became obvious that *time* needed to be controlled to study the metastable and unstable states. Shortly thereafter, my first students were building our own DTA, capable to give quantitative, time-dependent calorimetric data. Only few years later, we could present the quantitative link between molecular motion and heat capacity in the melting and glass-transition regions. One of these students involved in this study was Prof. Michael Jaffe. His study dealt with semicrystalline polyoxymethylene, a synthetic carbohydrate. He could use the first quantitative commercial equipment and modify it to heating with rates of 100 K min^{-1} and more. Today, rates reaching up to 10^7 K min^{-1} and faster are available for the analysis of unstable and small phases. The key question of this beginning study on biopolymer-related materials is the title question of this presentation for this symposium.

Keywords Thermal analysis · Biopolymers · Heat capacity · Molecular motion

Introduction

The first measurements of my career dealt with adiabatic calorimetry of linear, semicrystalline polyethylene, PE. They were done more than 50 years ago in the laboratory of Prof. Malcolm Dole [2]. Quickly it became obvious that *time* needed to be controlled to study the metastable and unstable states in PE. This led me to develop scanning adiabatic calorimetry [2, Fig. 3]. Shortly thereafter, my first students and I were building our own DTA, capable to give quantitative, time-dependent calorimetric data. Only few years later, working with a high-school teacher spending his summer on research at Cornell University and two undergraduate students, I could present the quantitative link between molecular motion and heat capacity in the melting [3] and glass-transition regions [4]. One of these students was Prof. Michael Jaffe, whom we honor in this symposium. After this early work at Cornell University, he became one of my first graduate students at Rensselaer Polytechnic Institute and worked on poly(oxymethylene), POM [5]. Semicrystalline POM is a synthetic carbohydrate chosen already by Staudinger as a synthetic model to understand the biopolymers starch and cellulose [6]. For Mike's PhD thesis he could use the first quantitative commercial equipment, the DuPont, DTA 900 (1963) and the Perkin Elmer DSC-1 (1964). The DTA was easily modified to heat with rates of 100 K min^{-1} and more [7]. Today, rates reaching $>10^7$ K min^{-1} and faster [8, 9] are available for the study of unstable and small phases and should be of special importance for biopolymers and pharmaceutical products.

Thermal analysis of biological macromolecules

Many polymers and small molecules were analyzed following our early study on PE and POM. These calorimetric

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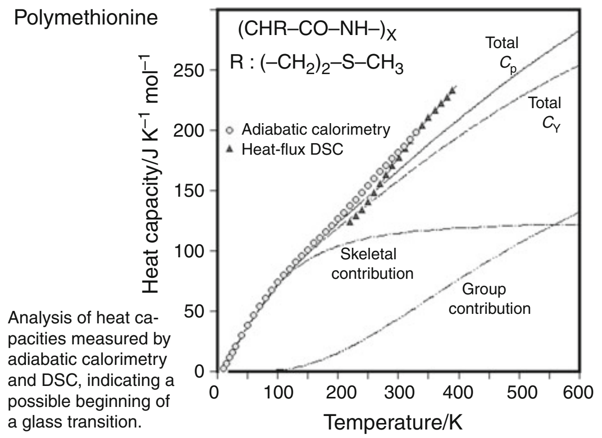
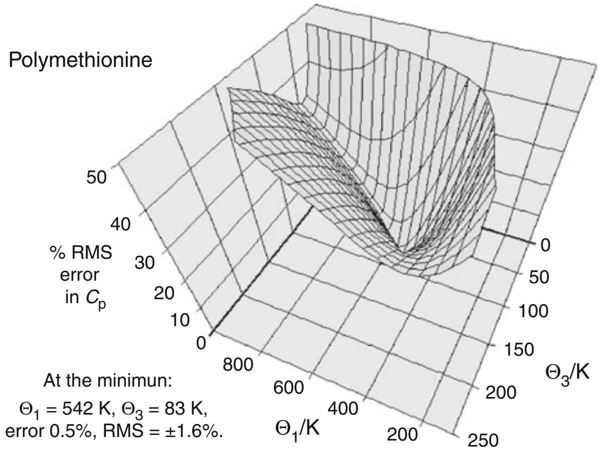


Analysis of heat capacities measured by adiabatic calorimetry and DSC, indicating a possible beginning of a glass transition.

Fig. 1 The heat capacity of solid, dry polymethionine and its interpretation on the basis of its skeletal and group vibrations [12, 13]



At the minimun:
Θ_1 = 542 K, Θ_3 = 83 K,
error 0.5%, RMS = ±1.6%.

Fig. 2 The fit of the heat capacity of polymethionine to a Tarasov-type treatment of the skeletal vibrations [13, 17]

data can be found in the *ATHAS Data Bank*, which includes also critically reviewed literature information [10]. Only a single measurement for *natural rubber* was documented from the 19th century and few data exist from before 1950 on other biological polymers like *carbohydrates* and *proteins*. Our protein study started with the study of poly(-amino acids). First, all the homopolymers from the 20 naturally occurring amino acids were analyzed [11–13]. This was followed by a number of copoly(amino acid)s [14]. Figures 1 and 2 illustrate one set of the generated data and the fit of the heat capacities of polymethionine to the ATHAS scheme of analysis. As expected, the same precision was possible as was found for synthetic polymers [10]. By then, we thought it was time to also investigate some proteins and carbohydrates to accomplish a similarly broad phase-characterization as was possible for synthetic polymers [15]. When trying to raise funds for the new research direction by turning to NIH, we were told,

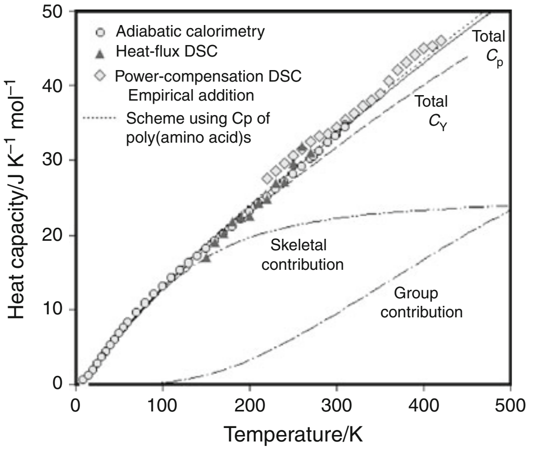
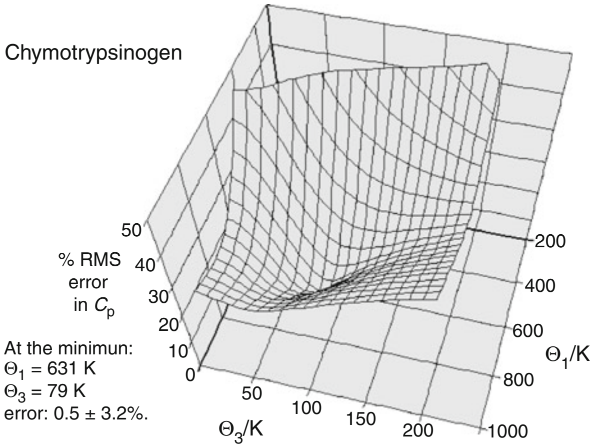


Fig. 3 The heat capacity of solid, dry bovine α-chymotrypsinogen and its interpretation on the basis of its skeletal and group vibrations [18]



At the minimun:
Θ_1 = 631 K
Θ_3 = 79 K
error: 0.5 ± 3.2%.

Fig. 4 The fit of the heat capacity of polymethionine to a Tarasov-type treatment of the skeletal vibrations [17, 18]

however, that (at that time?) this topic was of their lowest priority [16]. Fortunately, we were not of this opinion, and we could continue with our study without direct support and prove the same precision also for a number of proteins, as documented with reference [17], and the Figs. 3 and 4 [13, 18].

These first steps toward a more detailed look into the proteins were done on dry samples in analogy to the synthetic polymers. The only literature data at that time were collected on samples with unknown moisture content. When compared to the dry samples, major deviations occurred in the wet samples, starting at 150 K and reaching more than 100% at room temperature when major evaporation of the water began, as is discussed in [11]. The technique proposed was to first establish the dry heat capacity, and then try to find the partial molar quantities

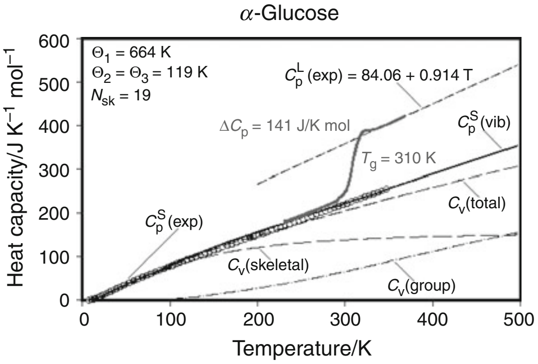


Fig. 5 The experimental heat capacity of solid and liquid α-glucose and their ATHAS-analysis [21]

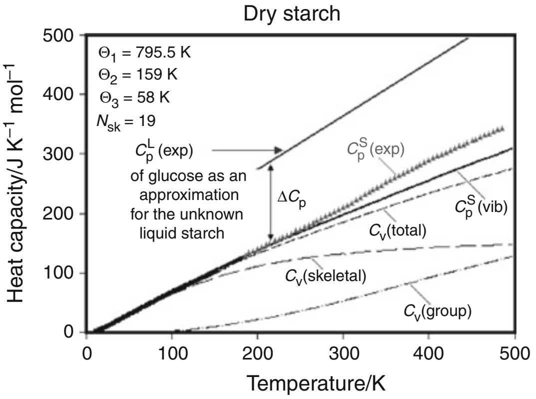


Fig. 6 The experimental heat capacity of solid and liquid dry starch and their ATHAS-analysis [22, 23]

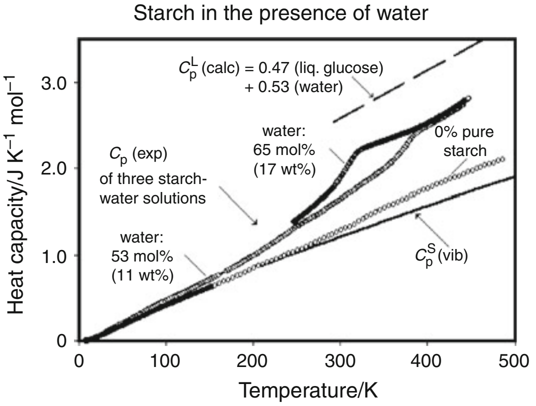


Fig. 7 Changes of the heat capacity of starch caused by the presence of water [24, 25]

with increasing water content, as was later accomplished for silk [19].

It is interesting to note that for the polymethionine a beginning glass transition is seen in Fig. 1 [20]. For the heat capacity of dry protein chymotrypsinogen as shown in Fig. 3 (denatured, molar mass 25,646 Da), it is noteworthy to see that after the contributions from all optical vibrations were subtracted (as estimated from the spectra of the 20 poly(amino acids), the remaining 3005 skeletal vibrations could be fitted to the unique Θ_1 and Θ_3 parameters of the Tarasov expression, as listed in Fig. 4 [13, 17]. In addition, their theta-values are similar to the poly(amino acid)s and not much different from the synthetic polymers of similar backbone structures.

Similar experiments as with the proteins were carried out with dry, amorphous, and semicrystalline starch, and extended by a study of the influence of water on starch [21–23]. Figures 5, 6, and 7 show a comparison of the data and analysis of starch with the better-known monomer glucose. The beginning of a broad glass transition can be seen in Fig. 7 even for the dry starch. The transition broadens to lower temperature in the presence of water, but still does not reach the level of complete devitrification, expected from the model glucose.

Conclusions

Having answered the title question with a clear: "Yes," the next step would involve developing a picture of the phase structure from the macrophase to nanophase scale, as was done for synthetic macromolecules [24–26]. Most urgent is to map the multiphase-structure of semi-ordered systems. As in semicrystalline polymers, one can expect rigid-amorphous nanophases, detectable by detailing the glass-transition analysis. These could be of importance for regulating the strength of the materials, as well as govern the mobility, the basis for possible chemical reactions [26]. Both for poly(amino acids) [20] and starches [22, 23], the observed broad partial glass transitions are in need of detailed, modern quantitative analyses requiring the use of temperature-modulated DSC [24], as well as fast scanning calorimetry [8, 9].

References

1. Wunderlich B. Thermal Analysis of Materials, published via the Internet (2005–2007). Available by downloading through: http://www.scite.eu (under Books and more), http://athas.prz.rzeszow.pl (under Teaching), and http://www.evitherm.org/index.asp (from their home page, go to Thermal analysis & calorimetry).
2. Wunderlich B, Dole M. Specific heat of synthetic high polymers. VIII. Low pressure polyethylene. J Polym Sci. 1957;24:201–13.
3. Wunderlich B, Kashdan WH. Thermodynamics of crystalline linear high polymers. I. Comparison of the melting transitions of solution and melt-crystallized polyethylene. J Polym Sci. 1961;50:71–8.
4. Wunderlich B, Jaffe M, Stahl ML. Bestimmung von sekundären Einfriererscheinungen aus Messungen der spezifischen Wärme. Kolloid Z Z Polym. 1962;85:65–6.

5. Jaffe M, Wunderlich B. Melting of polyoxymethylene. Kolloid Z Z Polym. 1967;216–217:203–16.
6. Staudinger H. Arbeitserinnerungen. Heidelberg: Hüthig Verlag; 1961.
7. Jaffe M, Wunderlich B. Superheating of extended-chain polymer crystals. In: Schwenker EF, Garn PD, editors. Proceedings 2nd ICTA Thermal analysis, vol 1. New York: Academic Press; 1969. p. 387–403.
8. Minakov AA, Schick C. Ultrafast thermal processing and nanocalorimetry at heating and cooling rates up to 1 MK/s. Rev Sci Instrum. 2007;78:073902-1-10.
9. Zhuravlev E, Schick C. Fast scanning power compensated differential scanning nanocalorimeter. 2. Heat capacity analysis. Thermochim Acta. 2010;505:14–21.
10. ATHAS Data Bank: Gaur U, Shu H-C, Mehta A, Lau S-F, Wunderlich BB, Varma-Nair M, Wunderlich B. J Phys Chem Ref Data. 1981;10:89,119,1001,1051. 1982;11:313,1065. 1983;12:29,65,91 1991;20:349. Tables of the thermodynamic functions and transition temperatures are also available via: Pyda M. http://athas.prz.rzeszow.pl. A description of the Data Bank is given in: Wunderlich B. The Athas data base on heat capacities of polymers. Pure Applied Chem. 1995;67:1019–1026.
11. Roles KA, Wunderlich B. Heat capacities of solid poly(amino acid)s. I. Polyglycine, poly-L-alanine, and poly-L-valine. Biopolymers. 1991;31:477–87.
12. Roles KA, Xenopoulos A, Wunderlich B. Heat capacities of solid poly(amino acid)s II. The remaining polymers. Biopolymers. 1993;33:753–68.
13. Zhang G, Lebedev BV, Wunderlich B, Zhang J-Y. Heat capacities of poly(amino acid)s and proteins. J Polym Sci Part B: Polym Phys. 1995;33:2449–55.
14. Roles KA, Wunderlich B. Heat capacities of solid copoly(amino acid)s. J Polym Sci Part B: Polym Phys. 1993;31:279–85.
15. Wunderlich B. Methodology of interpreting thermal analysis of polymers. J Therm Anal Calorim. 2011. doi:10.1007/s10973-010-1270-2.
16. Wunderlich B. A science career against all odds. A life of survival, study, teaching and travel in the 20th century. Berlin: Springer; 2010. p. 9–13, ISBN 978-3-642-11195-2.
17. Wunderlich B, Baur H. Heat capacities of linear high polymers. Fortschr Hochpolymeren Forsch. Adv Polym Sci. 1970;7:151–368.
18. Zhang G, Gerdes S, Wunderlich B. Heat capacities of solid globular proteins. Macromol Chem Phys. 1996;197:3791–806.
19. Pyda M, Hu X, Cebe P. Heat capacity of silk fibroin based on the vibrational motion of poly(amino acid)s in the presence and absence of water. Macromolecules. 2008;41:4786–93.
20. Xenopoulos A, Roles KA, Wunderlich B. A possible glass transition in poly(L-methionine) and poly(L-serine). Polymer. 1993;34:2559–63.
21. Pyda M, Wunderlich B. Quantitative thermal analysis of biomaterial-water Systems. In: Kociba KJ. Kociba BJ, editors. Proceedings 29th NATAS conference in St. Louis, MO, Sept 24–26, 2001;29;76–81.
22. Pyda M. Conformational contribution to the heat capacity of the starch and water system. J Polym Sci Part B: Polym Phys. 2001;39:3038–54.
23. Pyda M. Conformational heat capacity of interacting systems of polymer and water. Macromolecules. 2002;35:4009–16.
24. Wunderlich B. Quasi-isothermal temperature-modulated differential scanning calorimetry (TMDSC) for the separation of reversible and irreversible thermodynamic changes in glass transition and melting ranges of flexible macromolecules. Pure Appl Chem. 2009;81:1931–52.
25. Wunderlich B. Thermodynamics and properties of nanophases. Thermochim Acta. 2009;492:2–15.
26. Wunderlich B. Thermal analysis of polymeric materials. Berlin: Springer; 2005. ISBN 978-3-540-23629-0 (print) 978-3-540-26360-9 (online).