

Observation of Liquid-Crystal Formation during Melting of D-(+)-Glucose

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ABSTRACT: Liquid crystals, observed as maltese crosses under cross-polarized light, form in D-(+)-glucose immediately upon melting, at ~ 416 K, and become an isotropic liquid at ~ 500 K. Differential scanning calorimetry (DSC) results show two overlapping endothermic peaks corresponding to the formation and disappearance of the liquid crystals. Thermogravimetric analysis (TGA) confirmed that D-(+)-glucose undergoes thermal decomposition upon melting. Cooling and reheating isotropic samples previously heated to 500 K do not lead to the reappearance of the liquid crystals. The formation of liquid crystals is irreversible. Further study is required to determine which components among the decomposition intermediates or products of D-(+)-glucose are responsible for the formation of liquid crystals and whether they have process or product applications.

KEYWORDS: glucose, melting, liquid crystals, polarized microscopy, differential scanning calorimetry

INTRODUCTION

The melting behavior of sugars such as glucose is complex. Melting temperatures are sensitive to water and other impurities and to sample crystallinity.¹ Sugars decompose on melting. Orsi² distinguished three reaction stages occurring during the melting of glucose. Lee et al.^{3,4} showed that the loss of crystalline structure in glucose, sucrose, and fructose is due to the kinetics of thermal decomposition, termed apparent melting, rather than thermodynamic melting. They proposed the term “apparent melting” to distinguish the loss of crystalline structure due to a kinetic process, such as thermal decomposition, from thermodynamic melting. The work of Hurtt et al.¹ showed that the melting of sugars is a multiphased phenomenon with outcomes affected by both the determination method and the origin and quality of samples. Differences were observed among samples of the same sugar. Melting point values alone cannot be used for identification of sugar samples in all cases.

The presence of liquid crystals in carbohydrate derivatives has been reported previously^{5,6} and has attracted considerable interest.⁷ A carbohydrate-based mesogen typically consists of a hydrophilic (polar) headgroup attached to one or more lipophilic (nonpolar) chains. Carbohydrates are a significant source of liquid crystals, and practically every conversion of a carbohydrate moiety containing one or two alkyl attachments longer than C₇H₁₄ can result in the observation of mesogenic properties.⁸ For example, D-(+)-glucose has been used as a starting material for the synthesis of liquid crystals.⁹ Even though the melting and thermal decomposition of D-(+)-glucose lead to the formation of many products, liquid-crystal formation during this process has not been reported previously.

Hot-stage microscopy is a powerful technique for the characterization of liquid crystals together with differential scanning calorimetry (DSC) and X-ray diffraction. Hot-stage microscopy is the combination of a furnace, a temperature controller, and a polarizing optical microscope between crossed polarizers.¹⁰ This technique permits visual observation of samples subjected to a temperature program. In situ observations of phase transitions from solid to liquid crystal and from liquid crystal to isotropic liquid

are obtained.¹¹ Here, the observation of liquid-crystal formation upon melting of D-(+)-glucose is reported for the first time. Liquid-crystal formation in D-(+)-glucose was observed using hot-stage microscopy and confirmed with DSC measurements.

MATERIALS AND METHODS

D-(+)-Glucose ($\geq 99.5\%$) was purchased from Sigma-Aldrich Co.

Hot-Stage Microscopy. Figure 1 shows a schematic of the hot-stage placed on an adjustable platform above an inverted microscope. With this atypical arrangement, samples are viewed from below through an yttrium–aluminum–garnet (YAG) window (Figure 2a). With a conventional hot-stage cell, samples sit on a heated metal substrate and are viewed from above (Figure 2b). Samples (5–10 mg) were loaded into the hot-stage cell by placing them on the (YAG) window and then inserting the window into the bottom of the hot-stage cell. A silver-plated O-ring was used to seal the YAG window to the cell. The hot-stage was then heated using heating tape. The temperature was measured using a thermocouple in contact with the YAG window. The hot-stage was heated at 5–10 K/min under nitrogen. A Zeiss Axio-Observer inverted reflective microscope equipped with cross polarizers was used for in situ observation of the samples. The combined magnification of the system was 200 \times or 500 \times depending on particle size. This apparatus was used previously to observe liquid crystals in petroleum fractions.¹¹

Differential Scanning Calorimetry. Sample heat capacities were measured in a differential scanning calorimeter TG-DSC 111 (Setaram, France) in the temperature range from 300 to 570 K. Temperature calibration to ITS 90 was performed using indium, tin, lead, and zinc (mass fractions of 0.99999, Sigma-Aldrich Co.) as recommended by Gesellschaft für Thermische Analyse (GEFTA).^{12–16} Energy calibration was performed using the Joule effect method in the factory and checked by measuring the heat of fusion, $\Delta_{\text{fus}}H_m$, of naphthalene, indium, and tin. The agreement with recommended literature values^{14–17} was within 2%. Heat capacity c_p (heat flow rate) calibration was performed using

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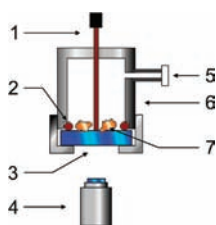


Figure 1. Schematic for the hot-stage cell used in this study: (1) thermocouple; (2) O-ring; (3) YAG window; (4) objective lens of the inverted microscope; (5) gas inlet for purging the cell; (6) cell body; (7) powder sample placed on the hot-stage window.

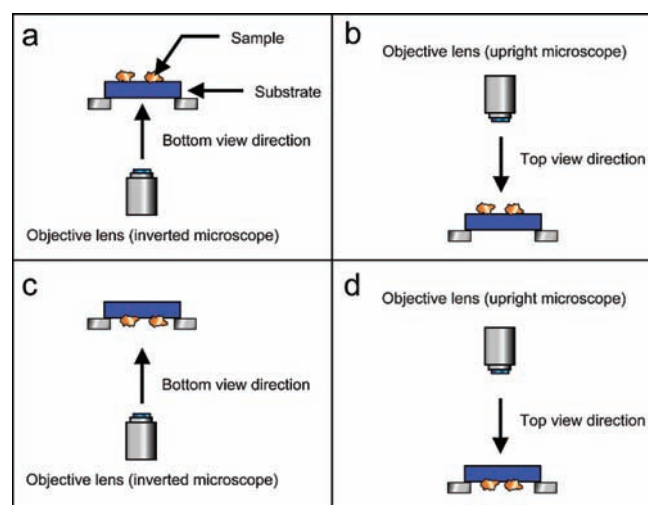


Figure 2. View directions applicable for liquid crystal observation using reflective microscopes: (a) substrate–sample interface view direction for an inverted reflective microscope with a transparent substrate; (b) gas–sample interface view direction for an upright reflective microscope with an opaque reflective substrate; (c) gas–sample interface view direction for an inverted reflective microscope with an opaque reflective substrate; (d) substrate–sample interface view direction for an upright reflective microscope with a transparent substrate.

synthetic sapphire, a primary reference material according to the National Institute of Standards and Technology (NIST) (SRM 720) and the International Confederation for Thermal Analysis and Calorimetry (ICTAC).¹⁷ The uncertainty of the c_p measurements was estimated to be <2% ($0.02 \text{ J K}^{-1} \text{ g}^{-1}$) in the studied temperature range. All heat capacity data were obtained using a continuous three-step method,¹⁸ "(1) empty – (2) reference material (sapphire) – (3) sample under study", for a measuring cell. An empty reference cell was present for all three runs. The measurements were carried out with a heating rate of 2 K min^{-1} with isothermal periods of 3600 s at the beginning and end of each trial. Hermetically sealed stainless steel cells, with a maximum pressure of 10 MPa at 573 K, were applied in experiments.

Thermogravimetric Analysis (TGA). Thermogravimetric measurements were performed using a Thermo Cahn TherMax 400 thermogravimetric analyzer (TGA) (Thermo Electron Corp., Waltham, MA). Samples (4–5 mg) were heated at 5 K/min in a nitrogen atmosphere.

RESULTS AND DISCUSSION

The glucose sample was observed in the hot-stage cell from room temperature to 550 K. At 295 K, the powder included domains of optical order. These appeared as bright domains

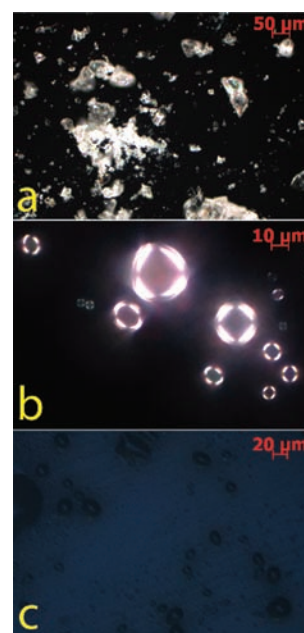


Figure 3. Liquid-crystal formation on a glass surface observed from below the sample–glass interface: (a) fresh glucose sample at 295 K; (b) liquid crystals at 430 K; (c) isotropic liquid at 505 K.

under cross-polarized light (Figure 3a). Above 416 K a phase transition occurred, and the first liquid-crystal domains appeared. The Maltese crosses (or disclination with four dark brushes) shown in Figure 3b are usually observed in concentric lamellar liquid crystals comprising surfactant, cosurfactant, and solvent.¹⁹ The Maltese cross rotated in the direction of the polarizer and analyzer rotation, indicating radial symmetry of the liquid-crystal molecules (mesogens). As the temperature was increased further, the number of domains increased and then decreased upon further heating. The sample became isotropic at $\sim 500 \text{ K}$ (Figure 3c). Once the liquid-crystal phase appeared, it remained stable upon cooling. However, when samples were heated above 500 K and became isotropic, they remained isotropic on cooling and during a subsequent heating cycle to 550 K. Thus, the formation and disappearance of liquid crystals in D-(+)-glucose is irreversible. Liquid crystals formed and disappeared similarly under nitrogen and oxygen atmospheres.

The liquid-crystal images are consistent with thin layers of liquid-crystalline material forming on the exterior surface of particles, making up a small portion of the total mass of the sample (Figure 4b). A detail is shown in Figure 5 under cross-polarized light (Figure 5a) and normal light (Figure 5b). The behavior appears to be independent of particle size (Figures 4b and 5a), from diameters of $<10 \mu\text{m}$ to $>300 \mu\text{m}$. As the glucose sample did not form domains larger than $350 \mu\text{m}$ upon melting, no comments can be made on the behavior of larger particles.

With the inverted microscope, liquid crystals were observable form beneath the sample–YAG window interface (Figure 2a) but were not observable from above the gas–sample interface using a typical upright microscope geometry (Figure 2b). The experiments were repeated with a glass window, and the result was the same. However, liquid crystals formed on a reflective surface, aluminum in this case, were observable from above the gas–sample interface using a typical upright microscope geometry (Figure 4). Thus, to observe the liquid crystals found in

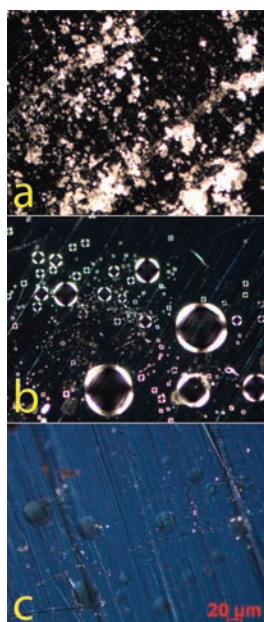


Figure 4. Liquid-crystal formation on an aluminum surface observed from above the sample–gas interface: (a) fresh glucose sample at 295 K; (b) liquid crystals at 430 K; (c) isotropic liquid at 505 K. The three images share a common scale.

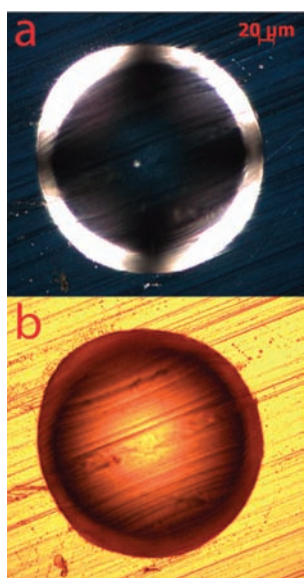


Figure 5. Close-up of a liquid-crystal domain formed at 435 K and cooled to room temperature under (a) cross-polarized light and (b) normal light.

this study, a reflective microscope is necessary. If a transparent slide is used, samples must be observed from the view direction depicted in Figure 2a for an inverted microscope. For an upright microscope the sample must be turned upside down and observed as depicted in Figure 2d. Fine powder usually sticks to the slide surface, and this orientation does not pose a problem for qualitative experimental work. If opaque and reflective solid slides such as aluminum are used, liquid crystals are observed with the view directions depicted in Figure 2c for an inverted microscope and in Figure 2b for an upright microscope.

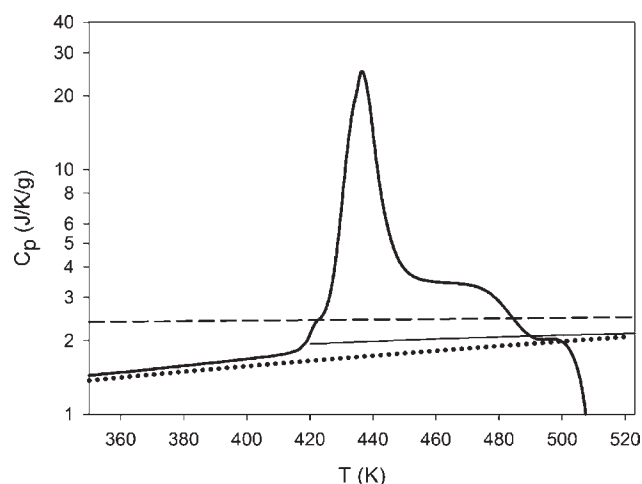


Figure 6. Heat capacity for D-(+)-glucose during the first (—) and second (---) heating cycles. The predicted heat capacity of solid glucose from Lastovka et al.²⁰ (···) and of liquid glucose from Dadgostar and Shaw²¹ (—) are also shown.

The observed transition temperatures and thermal irreversibility of the liquid crystals are consistent with the calorimetric results shown in Figure 6, where the DSC traces for glucose during the first and second heating cycles differ significantly. A broad endotherm comprising two overlapping peaks was observed during the first heating cycle over the temperature interval 416–495 K. The enthalpy of the complex transition, 48.1 kJ/mol, was parsed to obtain values for the enthalpy of fusion, approximately 41.87 kJ/mol, and the enthalpy of the secondary peak, approximately 6.62 kJ/mol. The heat capacities of solid and liquid glucose, calculated using accurate correlations,^{20,21} provide baselines. The absence of peaks during the second heating cycle underscores the irreversible nature of the liquid-crystal formation and subsequent transition to isotropic liquid. Typically, a melting transition from a crystalline solid to a liquid crystal phase or an isotropic phase involves an enthalpy of change of 30 to 50 kJ/mol. Liquid-crystal to isotropic liquid transitions are associated with enthalpy changes of 4 to 6 kJ/mol.²² Reported enthalpy of fusion values for D-(+)-glucose range from 34.05 kJ/mol at a heating rate of 2 °C/min to 37.47 kJ/mol at a heating rate of 50 °C/min. The authors also reported that at low heating rates, there were substantial differences among samples of the same sugar.¹ The difference between the current and prior enthalpy measurements falls outside the typical errors for such measurements and may reflect different choices for the baselines. Baselines employed here are well rooted in theory and experiment.^{20,21} The melting point of glucose has been reported to be 414 K by Parks et al.²³ (with an assigned uncertainty by NIST of 2 K) and 420 K (assigned uncertainty by NIST of 4 K) and 423 K (assigned uncertainty by NIST of 3 K) by Kofler et al.²⁴ The melting point identified in this work, 416 K, with an uncertainty of 2 K, based on prior work,²⁰ falls within the range of these measurements. TGA, reported in Figure 7, shows that the weight loss, resulting from thermal decomposition, starts immediately after melting at ~416 K. By combining all of the data, it is clear that liquid crystals arise during the thermal decomposition of glucose.

The properties of the liquid crystals observed in this study are complex. Their anisotropic texture (Maltese cross), irreversible thermal behavior, and tendency to form on exterior surfaces of particles are similar to the properties of liquid crystals observed, at

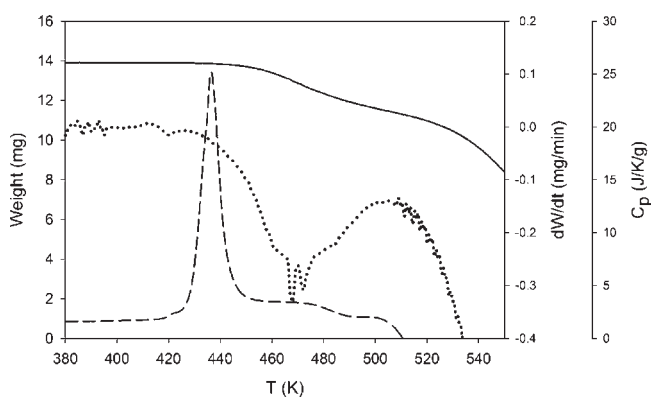


Figure 7. Thermogravimetric analysis: mass loss (—), mass loss temperature derivative (· · ·), and heat capacity of D-(+)-glucose (---) during heating at 5 K/min.

low temperature, in heavy oil fractions.¹¹ Unlike glucose, heavy oil fractions do not degrade thermally in the temperature range at which these liquid crystals form. Heavy oil fractions also form liquid crystals at high temperature,²⁵ as a consequence of cracking reactions, but the formation of these liquid-crystalline domains, termed carbonaceous mesophase, is slow kinetically compared to those formed by D-(+)-glucose and arises at much higher temperatures. Another property, the absence of a liquid-crystal to crystal transition on cooling observed for D-(+)-glucose, has been observed for branched polymers.²⁶ Liquid crystals formed on heating that do not follow an equilibrium path on cooling retain their liquid-like cooperative motion²⁷ to low temperatures. These properties and their analogues from other fields may prove to be useful with respect to the separation of these crystals from the balance of the decomposition products of D-(+)-glucose.

The liquid crystals observed in D-(+)-glucose show a strong kinetic signature and form as a result of thermal decomposition, which produces molecules with appropriate shapes and mobility to form liquid crystals. Further study is required to determine which components among the decomposition products of D-(+)-glucose are responsible for the formation of liquid crystals and whether they have process or product applications. The possible formation of liquid crystals during decomposition of other sugars also warrants investigation.

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REFERENCES

- Hurtt, M.; Pitkanen, I.; Knuutinen, J. Melting behaviour of D-sucrose, D-glucose and D-fructose. *Carbohydr. Res.* **2004**, *339* (13), 2267–2273.
- Orsi, F. Kinetic studies on thermal-decomposition of glucose and fructose. *J. Therm. Anal.* **1973**, *5* (2–3), 329–335.
- Lee, J. W.; Thomas, L. C.; Jerrell, J.; Feng, H.; Cadwallader, K. R.; Schmidt, S. J. Investigation of thermal decomposition as the kinetic process that causes the loss of crystalline structure in sucrose using a chemical analysis approach (part II). *J. Agric. Food Chem.* **2011**, *59* (2), 702–712.
- Lee, J. W.; Thomas, L. C.; Schmidt, S. J. Investigation of the heating rate dependency associated with the loss of crystalline structure in sucrose, glucose, and fructose using a thermal analysis approach (part I). *J. Agric. Food Chem.* **2011**, *59* (2), 684–701.
- Jeffrey, G. A. Carbohydrate liquid-crystals. *Acc. Chem. Res.* **1986**, *19* (6), 168–173.
- Jeffrey, G. A. Carbohydrate liquid-crystals. *Mol. Cryst. Liq. Cryst.* **1984**, *110* (1–4), 221–237.
- Cook, A. G.; Wardell, J. L.; Imrie, C. T. Carbohydrate liquid crystals: Synthesis and characterisation of the methyl-6-O-(n-acyl)- α -D-glucopyranosides. *Chem. Phys. Lipids* **2011**, *164* (2), 118–124.
- Jeffrey, G. A.; Wingert, L. M. Carbohydrate research. *Liq. Cryst.* **1992**, *12* (2), 179–202.
- Ho, W. M.; Wong, H. N. C.; Navailles, L.; Destrade, C.; Nguyen, H. T.; Isaert, N. Chiral liquid-crystalline compounds from D-(+)-glucose. *Tetrahedron* **1995**, *51* (27), 7373–7388.
- Scharf, T. *Polarized Light in Liquid Crystals and Polymers*. Wiley: Hoboken, NJ, 2007.
- Bagheri, S. R.; Bazyleva, A.; Gray, M. R.; McCaffrey, W. C.; Shaw, J. M. Observation of liquid crystals in heavy petroleum fractions. *Energy Fuels* **2010**, *24*, 4327–4332.
- Hohne, G. W. H.; Cammenga, H. K.; Eysel, W.; Gmelin, E.; Hemminger, W. The temperature calibration of scanning calorimeters. *Thermochim. Acta* **1990**, *160* (1), 1–12.
- Cammenga, H. K.; Eysel, W.; Gmelin, E.; Hemminger, W.; Hohne, G. W. H.; Sarge, S. M. The temperature calibration of scanning calorimeters. 2. Calibration substances. *Thermochim. Acta* **1993**, *219*, 333–342.
- Sarge, S. M.; Gmelin, E.; Hohne, G. W. H.; Cammenga, H. K.; Hemminger, W.; Eysel, W. The calorimetric calibration of scanning calorimeters. *Thermochim. Acta* **1994**, *247* (2), 129–168.
- Sarge, S. M.; Hemminger, W.; Gmelin, E.; Hohne, G. W. H.; Cammenga, H. K.; Eysel, W. Metrologically based procedures for the temperature, heat and heat flow rate calibration of DSC. *J. Therm. Anal.* **1997**, *49* (2), 1125–1134.
- Gmelin, E.; Sarge, S. M. Calibration of differential scanning calorimeters. *Pure Appl. Chem.* **1995**, *67* (11), 1789–1800.
- Sabbah, R.; An, X. W.; Chickos, J. S.; Leitao, M. L. P.; Roux, M. V.; Torres, L. A. Reference materials for calorimetry and differential thermal analysis. *Thermochim. Acta* **1999**, *331* (2), 93–204.
- Höhne, G. W. H.; Hemminger, W. F.; Flammersheim, H.-J. *Differential Scanning Calorimetry*, 2nd ed.; Springer Verlag: Berlin, Germany, 2003.
- Figueiredo Neto, A. M.; Salinas, S. R. *The Physics of Lyotropic Liquid Crystals: Phase Transitions and Structural Properties*; Oxford University Press: New York, 2005.
- Lastovka, V.; Fulem, M.; Becerra, M.; Shaw, J. M. A similarity variable for estimating the heat capacity of solid organic compounds – part II. Application: heat capacity calculation for ill-defined organic solids. *Fluid Phase Equilib.* **2008**, *268* (1–2), 134–141.
- Dadgostar, N.; Shaw, J. M. A predictive correlation for the constant-pressure specific heat capacity of pure and ill-defined liquid hydrocarbons. *Fluid Phase Equilib.* **2011** in press.
- Singh, S.; Dunmur, D. A. *Liquid Crystals Fundamentals*; World Scientific Publishing: London, U.K., 2002.

(23) Parks, G. S.; Thomas, S. B. The heat capacities of crystalline, glassy and undercooled liquid glucose. *J. Am. Chem. Soc.* **1934**, *56*, 1423–1423.

(24) Kofler, L.; Sitte, H. Melting point determination of substances with melt with decomposition. *Monatsh. Chem.* **1950**, *81*, 619–626.

(25) Hurt, R. H.; Chen, Z. Y. Liquid crystals and carbon materials. *Phys. Today* **2000**, *53* (3), 39–44.

(26) Plate, N. A.; Kulichikhin, V. G.; Talroze, R. V. Mesophase polymers in the coming decade - problems and trends. *Pure Appl. Chem.* **1991**, *63* (7), 925–940.

(27) Wunderlich, B. The detection of conformational disorder by thermal analysis. *Pure Appl. Chem.* **1989**, *61* (8), 1347–1351.