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Molecular mobility in a homologous series of amorphous solid glucose oligomers

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ABSTRACT

The molecular mobility of amorphous solid biomaterials influences the stability of dried foods and pharmaceuticals, the viability of seeds and spores, and the desiccation-tolerance of organisms during anhydrobiosis. Current understanding of how structure correlates with molecular mobility in the glassy state is inadequate. We used phosphorescence from vanillin dispersed in amorphous films to study the effect of temperature on molecular mobility in the homologous series of oligosaccharides glucose, maltose, maltotriose, maltotetraose, maltopentaose, maltohexaose, and maltoheptaose. Phosphorescence emission spectra and intensity decays were collected from −10 to as high as 130 °C. Emission peak energy, a measure of the extent of dipolar relaxation around the excited state prior to emission, decreased monotonically with temperature, decreasing more significantly in the glassy state in larger sugars (higher degree of polymerisation). The intensity decays were well fitted with sums of either four (glucose, maltose, maltotriose) or three exponentials (maltotetraose, maltopentaose, maltohexaose, maltoheptaose); fit lifetimes at each temperature varied over nearly two orders of magnitude, suggesting a comparable range in matrix dynamic heterogeneity. The lifetimes decreased monotonically with temperature, while the lifetime amplitudes favoured the long lifetime components at lower and short lifetime components at higher temperatures near T_g. Arrhenius analysis indicated that the rate of non-radiative decay, which reflects coupling of probe vibrations with matrix motions and thus provides an estimate of the matrix molecular mobility, increased with molecular size in the glassy state. Both apparent activation energy and activation entropy increased systematically with temperature in all sugars. These data provide additional evidence that the rate and extent of molecular mobility in glassy state carbohydrates is higher in sugars of greater molecular size (mass) and thus higher glass transition temperature and provides additional insight into the molecular dynamics of the glassy state in carbohydrates.

1. Introduction

Vitrification of sugars and other carbohydrates from the melt or from concentrated aqueous solutions is important in the manufacture of confections, in stabilising dried and frozen foods, and in the desiccant-tolerance of spores, seeds and anhydrobiotic organisms (Buitink & Leprince, 2004; Crowe, Carpenter, & Crowe, 1998; Fennema, 1976; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Roos, 1995). The amorphous solids that form are rigid, brittle glasses at low temperature and supercooled melts, or (in the case of polymers, rubbers) at high temperature; softening from the glass to the melt occurs at a characteristic glass transition temperature (T_g). The glass transition is a dynamic rather than a structural transition; it is most simply described as the onset temperature for macroscopic flow (Zallen, 1998). The T_g is often considered as the standard reference temperature for stability in amorphous biomaterials, which are often considered stable below T_g due to slow structural rearrangements (Rawson, 1991); however, evidence suggests that biomaterials are unstable with respect to some degradative reactions, even in the glassy state (Yoshioka, Hancock, & Zografi, 1994). At T_g and above, full molecular mobility is activated, leading to an acceleration of a variety of physical and chemical changes that may be detrimental to quality. For example, structural collapse or sticky phenomena (Dowton, Flored-Luna, & King, 1982), caking (Lloyd, Chen, & Hargreaves, 1996) and volatile diffusivity are greatly increased above T_g (Whorton & Reineccius, 1995). Consequently, much work is devoted to characterising the glass transition temperature of amorphous biomaterials. The T_g of sugars, for example, appears to be more dependent on molecular mass than on structure (Orford, Parker, & Ring, 1990).

The changes in molecular mobility occurring in the glass, below and in the melt above T_g, are important in defining the shelf-life and quality of amorphous foods, pharmaceuticals and biomaterials (Bell & Hageman, 1992, 1996; Buera, Chirife, & Karel, 1995; Buera & Karel, 1995; Roos, 1995, 2003). These motions are of strong concern as they affect rates of molecular diffusion, and thus chemical reaction rate as well as the rates of other physical processes in amorphous foods and pharmaceuticals (Ludescher, Shah, McCaul, & Simon, 2001).

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The phosphorescence intensity of the food dye erythrosin B (FD& C No. 3, acid red 51) embedded in amorphous solids is sensitive to molecular mobility in amorphous sugars (Pravinata, You, & Ludescher, 2005; Shirke, Takhistov, & Ludescher, 2005; You & Ludescher, 2006) and proteins (Draganski et al., 2010; Nack & Ludescher, 2006; Sundaresan & Ludescher, 2007). We have recently shown that phosphorescence of vanillin embedded in amorphous sucrose is especially sensitive to molecular mobility in the glassy state and changes in mobility at the glass transition temperature (Tiwari & Ludescher, 2010). We here report vanillin phosphorescence studies of the effect of temperature on molecular mobility in amorphous films of the homologous series of sugars, glucose, maltose, maltotriose, maltotetraose, maltopentaose, maltohexaose and maltoheptaose. These data indicate that mobility actually increases with molecular mass, and thus with glass transition temperature, in the glassy state of this homologous series of sugars.

2. Materials and methods

2.1. Sample preparation

Glucose, maltose, maltotriose, maltotetraose, maltopentaose, maltohexaose and maltoheptaose were purchased from Sigma–Aldrich (St. Louis, MO) with minimum purity of 98% and were used without further purification. These compounds were dissolved, to near saturation, in deionised water at room temperature. Vanillin was dissolved in distilled deionised water to make a 66 mM solution. An aliquot of vanillin solution was added to each of the sugar solutions to obtain a solution with dye/sugar mole ratio of $\sim 1{:}10^3$. An aliquot (20 μl) of the dye-containing sugar solution was spread on a quartz slide (3 cm × 1.35 cm) custom built by NSG Precision Cells (Hicksville, NY). After spreading the solutions, the slides were then dried under a heat gun (Vidal Sassoon) for 5 min to a maximum temperature of ~88 °C (measured using a thermocouple probe). The dried films had a thickness of ~0.05 mm. The slides were stored at room temperature against P_2O_5 and DrieRite and protected from light to prevent any photo bleaching for at least 7 days before any phosphorescence measurements were made. The desiccant was refreshed, as needed, to maintain a relative humidity close to 0%. The glass transition temperatures for these sugars, determined from the literature, are summarised in Table 1. The values determined by Imamura et al. (2006) were used in this study.

2.2. Instrumentation

All phosphorescence measurements were made on a Cary Eclipse fluorescence spectrophotometer (Varian Instruments, Walnut Creek, CA). The quartz slides were placed in a standard 1 cm × 1 cm × 3 cm quartz fluorescence cuvette which was capped with a lid having inlet and outlet ports for gas lines. The cuvette was flushed with a gentle stream of nitrogen for 15 min to eliminate oxygen. An oxygen-free nitrogen stream was generated by passage of high purity nitrogen through a Supelco (Bellefonte, PA) gas purifier. The temperature was controlled using a TLC 50 thermoelectric heating/cooling system (Quantum Northwest, Spokane, WA). The TLC-50 sample compartment was fitted with a jacketed cover and the temperature of the cuvette was monitored directly, using a thermocouple in the cuvette. The film was equilibrated for 15 min at each temperature before collecting the data. The Cary Eclipse uses a pulsed lamp and collects emission intensity in analogue mode; data were not collected within the first 0.1–0.2 ms to suppress fluorescence coincident with the lamp pulse.

Table 1
Glass transition temperatures, T_gs, for malto-oligosaccharides.

Sugar	Molecular weight	T_g/°C (from FTIR[a])	T_g/°C (from DSC)
Glucose (G_1)	180.5	38	35[a], 38[b], 31[c]
Maltose (G_2)	343	90	90[a], 93[b]
Maltotriose (G_3)	505	113	110[a],131[b]
Maltotetraose (G_4)	667	133	128[a], 147[b]
Maltopentaose (G_5)	829	143	137[a], 165[b]
Maltohexaose (G_6)	991	146	145[a], 167[b]
Maltoheptaose (G_7)	1153	154	150[a]

[a] (Imamura et al., 2006).
[b] (Orford, Parker, & Ring, 1990).
[c] (Roos, 1993).

2.3. Luminescence measurement

Delayed luminescence emission spectra (10 nm bandwidth) of vanillin in amorphous sugars were collected, from 400 nm to 800 nm, using excitation at 320 nm (20 nm bandwidth) over the temperature range from –10 °C to 150 °C. Each datum point was collected by integrating total emission from a single flash with 0.2 ms delay, 100 ms gate time, and 0.12 s total decay time.

Lifetime measurements were made in the presence of nitrogen as a function of temperature. The samples were excited at 320 nm (20 nm bandwidth) and emission transients collected at 490 nm (20 nm bandwidth) at temperatures ranging from –10 °C to 150 °C. Each decay was an average of 50 cycles and, for each cycle, data were collected from a single flash with a delay of 0.2 ms; windows for gate time and the total decay time were varied at each temperature to compensate for changes in the probe lifetime. All measurements were made in quadruplicate and data reported as means ± standard deviation.

2.4. Emission energy as a function of temperature

Emission spectra were analyzed using the programme Igor (Wavemetrics, Inc., Lake Oswego, OR). The phosphorescence emission spectra were converted to intensity versus frequency (wavenumber, cm^{-1}) and fitted to a log-normal function:

$$I(v) = I_0 \exp[-\ln(2)(\ln[1 + 2b(v - v_P)/\Delta]/b)^2] \quad (1)$$

In this equation I_0 is the maximum intensity of the emission spectrum, v_P is the frequency in cm^{-1} of the emission maximum, Δ is a line width parameter, and b is an asymmetry parameter. The bandwidth of the emission, the full width at half maximum (Γ), is related to b and Δ as follows:

$$\Gamma = \Delta[\sinh(b)/b] \quad (2)$$

2.5. Photophysical scheme

The phosphorescence intensity decays were collected as described above and were fitted using a multi-exponential function (Shamblin, Hancock, Dupuis, & Pikal, 2000):

$$I(t) = I(0) \sum_{i=1}^{n} \alpha_i \exp(-t/\tau_i) \quad (3)$$

In this decay model, I(0) is the intensity at t = 0, τ_i are the emission lifetimes, α_i are the fractional amplitudes of the components at t = 0, and n is the number of decay components (lifetimes), which was either 3 or 4 depending upon the sugar matrix. Least squares iterative fitting to this model was done with the statistical fitting programme Igor (Wavemetrics, Inc., Lake Oswego, OR). Fits were judged satisfactory if the R^2 values were in the range 0.995–1.0