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Effects of moisture content, molecular weight, and crystallinity on the glass transition temperature of inulin

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ABSTRACT

Effects of moisture content, molecular weight (MW), and crystallinity on the glass transition temperature (T_g) and freeze-concentrated glass-like transition temperature (T_g') of a fructan (inulin) were investigated using differential scanning calorimetry. The T_g of inulin samples decreased with increasing moisture content. The T_g of semi-crystal inulin was higher than that of amorphous inulin. These results were fitted to the Gordon–Taylor equation, and k values, reflecting the sensitivity to the water plasticizing effect, were obtained. The k value was plotted against anhydrous T_g, and the relationship of amorphous inulin was described with a linear function. T_g of anhydrous inulin samples and T_g' of inulin–water mixtures increased with increasing MW, and the results were described empirically by a stretched exponential equation. These results will help to predict T_g and T_g' of inulin, depending on the moisture content, MW, and crystallinity.

1. Introduction

Inulin is a fructan that is linked by β(2–1) glycosidic bonds and contains either a terminal β-D-fructose or an α-D-glucose. The degree of polymerization (DP) of inulin is usually 2–60 units with an average DP = 12. Inulin has attracted much attention in the food and pharmaceutical industries for its multiple benefits, such as dietary fiber (Carabin & Flamm, 1999; Causey, Feirtag, Gallaher, Tungland, & Slavin, 2000; Davidson, Maki, Synecki, Toni, & Drennan, 1998; Kim, 2002) and prebiotic nature (Buriti, Cardarelli, Filisetti, & Saad, 2007; Corradinia et al., 2004; Fooks & Gibson, 2002; López-Molina et al., 2005; Rao, 2001). In addition, inulin–water mixtures show fat-mimetic properties. In order to produce fat-free foods, extensive efforts have been undertaken to investigate the rheological properties of inulin mixtures (Akalm, Karagözlü, & Ünal, 2008; Fagan, O'Donnell, Cullen, & Brennan, 2006; Gonzalez-Tomás, Coll-Marqués, & Costell, 2008; Hennelly, Dunne, O'Sullivan, & O'Riordan, 2006; Kim, Faqih, & Wang, 2001; Tárrega & Costell, 2006; Tseng & Xiong, 2009; Villegas & Costell, 2007; Zimeri & Kokini, 2003a).

Inulin exists, at least partially, in an amorphous state and thus glass transition occurs during dehydration/rehydration and/or freeze/thaw processing. Since various physical properties (*e.g.*, viscoelasticity) are changed drastically by the glass transition (Levine & Slade, 1988; Roos, 1995; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002), it is important, from a practicality viewpoint, to understand the glass transition temperature (T_g) and freeze-concentrated glass-like transition temperature (T_g'). There have been many studies on the glass transition properties of inulin (Chiavaro, Vittadini, & Corradini, 2007; Hinrichs, Prinsen, & Frijlink, 2001; Ronkart et al., 2006; Ronkart, Deroanne, Paquot, Fougnies, & Blecker, 2010; Ronkart, Deroanne, et al., 2007; Ronkart, Paquot, Fougnies, Deroanne, & Blecker, 2009; Zimeri & Kokini, 2002, 2003b). For example, Hinrichs et al. (2001) investigated the glass transition properties of various types of inulin of varying DP, and reported the T_g of anhydrous inulin and T_g' of an inulin–water mixture; however, the effect of moisture content on the T_g of inulin sample was not investigated. Zimeri and Kokini (2002) investigated the T_g of inulin–water mixtures, and the dependence of T_g on moisture content was characterized using a T_g-curve, by plotting T_g versus moisture content, although the DP or molecular weight (MW) of inulin sample was unclear. More recently, Ronkart et al. investigated the glass transition properties of inulin samples having a DP = approx. 10 (2006) and a DP = approx. 30 (2009), and reported the T_g-curve of the inulin–water mixture. Although there have been many efforts to understand the glass transition properties of inulin, the published data were limited for prediction of glass transition properties, because both T_g-curve and T_g' depend on DP or MW and

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its crystallinity. Therefore, further systematic study in addition to application of the obtained results is required.

In this study, the T_g of various types of inulin was investigated using differential scanning calorimetry (DSC), and the effects of MW, crystallinity, and moisture on T_g of inulin were revealed in order to predict T_g and T'_g of fructan. These results were compared with those of a glucan reported in previous studies (Kawai, Hagiwara, Takai, & Suzuki, 2005; Levine & Slade, 1988; Orford, Parker, Ring, & Smith, 1989; Roos, 1995).

2. Materials and methods

2.1. Materials and sample preparation

Three types of inulin reagent, Instant® (native), fiblose® (low-MW), and XL® (high-MW) were provided from San-ei Sucrochemical, Co., Ltd., Aichi, Japan. It was preliminarily confirmed that the average molecular weight of low-MW, native, and high-MW inulins was 1197, 2175, and 4395 g/mol (DP = 7, 13, and 27), respectively, by gel permeation chromatography (HLC-8220GPC; Tosoh Co., Ltd., Osaka, Japan).

First of all, crystallinity of the inulin reagents was investigated by X-ray. As shown in afterwards, it was found that only the high-MW inulin was a semi-crystal polymer, and thus amorphous high-MW inulin was also prepared, according to previous studies (Zimeri & Kokini, 2002, 2003b; Ronkart et al., 2009). In brief, a high-MW inulin–water mixture (40%, w/w) was hydrolyzed thermally at 90 °C, and then quenched by dropping it into liquid nitrogen. The frozen mixture was freeze-dried for 2 days, and the obtained solid was disintegrated using a rotary mixer. Four types of inulin samples (native, low-MW, non-treated (NT) high-MW, and pre-melted (PM) high-MW) were employed in this study.

2.2. X-ray diffraction (XRD)

The crystallinity of the inulin samples was investigated using X-ray diffraction (RINT-UltimaIII; Rigaku Co., Tokyo, Japan). The sample was placed in the aluminum sample stage. XRD measurement was carried out with 40 kV × 40 mA wavelength of CuKα = 1.54 Å and scanned at a rate of $2\theta = 10^\circ$/min with a 3–30° scanning range of the diffraction angle.

2.3. Isothermal water sorption

The samples were vacuum-dried at 60 °C for 48 h for sufficient water removal, and then held under various relative humidity (RH) conditions at 298 K. The equilibrium of water sorption was confirmed gravimetrically. A portion of the samples was used for DSC measurement, as is shown below. The others were used for the measurement of moisture content. The samples were dehydrated at 105 °C for 12 h, and the moisture content was evaluated gravimetrically.

2.4. DSC measurement

T_g and T'_g of the inulin samples were investigated using a DSC (DSC8230; Rigaku Co., Tokyo, Japan). In order to investigate the effect of moisture content on T_g, the inulin samples held under various RH conditions were prepared as mentioned above. Furthermore, 3–10% (w/w) aqueous solution was prepared in order to investigate T'_g of the inulin samples. An empty aluminum pan was used as a reference, and the temperature and heat flow were calibrated using indium and distilled water. The sample (2–10 mg) was placed in an aluminum pan and hermetically sealed. In order to evaluate anhydrous inulin T_g, inulin that had been vacuum-dried at 60 °C for 12 h was put into the pan and held at 105 °C for 2 h prior to sealing. DSC measurement was performed at 5 °C/min in the temperature range of −40 and 180 °C.

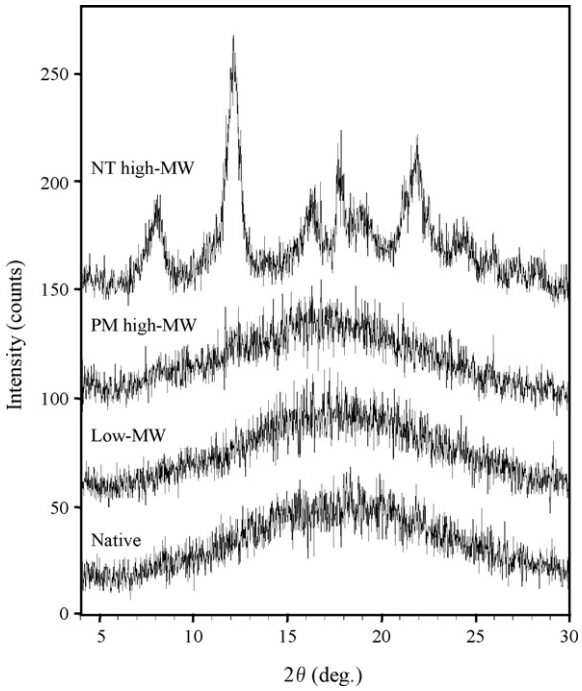

Fig. 1. X-ray diffraction pattern of inulin samples.

3. Results and discussion

3.1. Crystallinity of the inulin samples

The results of XRD are shown in Fig. 1. The native and low-MW inulins showed a halo pattern, indicating an amorphous form. NT high-MW inulin, on the other hand, showed some peaks indicating the existence of ordered structure in the XRD pattern. The peaks disappeared in PM high-MW inulin. From these results, it was confirmed that low-MW, native, and PM high-MW inulins were amorphous and NT high-MW inulin was in a semi-crystal state.

3.2. Isothermal water sorption behavior

The results of isothermal water sorption are shown in Fig. 2. The solid line was obtained by fitting the Guggenheim, Anderson and de Boer (GAB) equation (Eq. (1)) to the data,

$$W = \frac{W_m CK(RH/100)}{(1 - K(RH/100))(1 - K(RH/100) + CK(RH/100))} \quad (1)$$

where W_m, C and K represent the moisture content of the monolayer, a factor correcting the sorption properties of the first layer with respect to the bulk liquid, and a factor correcting the properties of the multilayer with respect to the bulk liquid, respectively (Zimeri & Kokini, 2002, 2003b). The obtained GAB parameters are listed in Table 1. It was found that the GAB parameters were affected by inulin MW and crystallinity. The W_m of PM high-MW inulin was much larger than that of low-MW, native, and NT high-MW inulins. This can be attributed to the difference in the number of hydration-sites. The C and K increased and decreased with increase in MW, respectively. Increases in crystallinity caused increases in C and K. The moisture content of low-MW and native inulins was much higher than that of NT and PM high-MW inulins at a RH > 60%. The drastic increase in the moisture content of low-MW and native

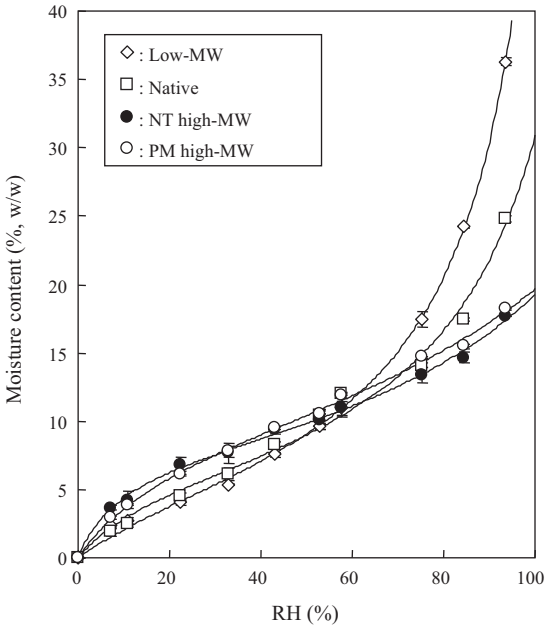

Fig. 2. Isothermal water sorption behavior of inulin samples at 298 K. The solid lines were obtained by fitting Eq. (1) to the data.

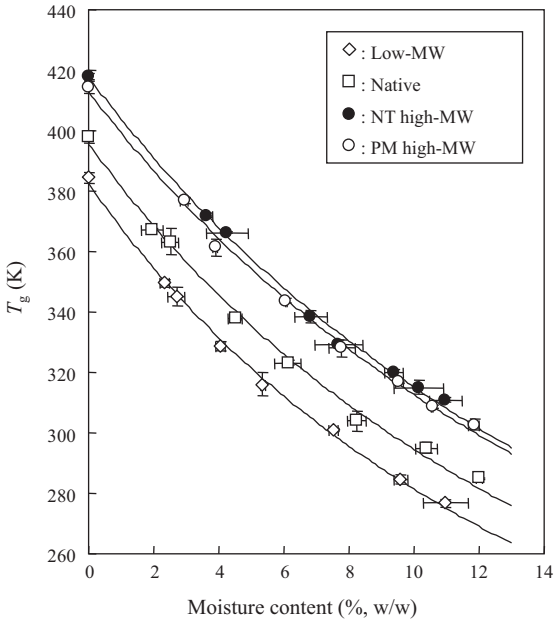

Fig. 3. Effect of moisture content on T_g of inulin sample. The solid lines were obtained by fitting Eq. (2) to the data.

inulins can be related to the glass transition at 298 K, as shown in the next section.

3.3. Effects of moisture content, MW and crystallinity on T_g of linulin

DSC thermogram of the inulin samples showed an endothermic shift due to glass transition, and T_g value was evaluated from the onset point of the shift (data not shown). Some glassy samples (T_g > 298 K) showed the recovery of enthalpy relaxation depending on the thermal history. In order to cancel the effect of the thermal history on T_g, the samples were re-scanned after cooling, and T_g was evaluated from the DSC thermogram obtained from the second scanning (Haque, Kawai, & Suzuki, 2006; Kawai et al., 2005). The obtained T_g was plotted against moisture content as shown in Fig. 3. As expected, T_g decreased with an increase in moisture content and a decrease in MW. In addition, T_g of NT high-MW inulin (semi-crystal form) was slightly higher than that of PM high-MW inulin (amorphous form), similarly to amorphous starch (Chung, Lee, & Lim, 2002; Thanatuksorn, Kawai, Kajiwara, & Suzuki, 2009). This might be because the crystalline regions play a role in crosslinking amorphous regions of the polymeric network and thus suppress the mobility of amorphous regions. In addition, since the semi-crystal inulin can contain some water molecules in the structure (André, Mazeau, et al., 1996; André, Putaux, et al., 1996; Ronkart et al., 2006), there is a possibility that the water molecules in the crystal structure did not contribute to the plasticizing to the amorphous region.

The solid line in Fig. 3 was obtained by fitting the Gordon–Taylor (GT) equation (Eq. (2)) to the T_g data,

$$T_g = \frac{W_{(i)}T_{g(i)} + kW_{(w)}T_{g(w)}}{W_{(i)} + kW_{(w)}} \quad (2)$$

where $T_{g(i)}$ and $T_{g(w)}$ are T_g of the anhydrous inulin and water, $W_{(i)}$ and $W_{(w)}$ are the mass fraction of inulin and water, and k is a constant depending on the system, respectively. The k value represents the sensitivity to the water plasticizing effect; the higher the k value, the greater the moisture content dependence of T_g. T_g and $T_{g(i)}$ were evaluated experimentally. The $T_{g(w)}$ was obtained as 136 K from previous publications (Johari, Hallbrucker, & Mayer, 1987; Sastry, 1999), and k was obtained as a fitted parameter. The obtained k value and T_g of the anhydrous inulins are listed in Table 1.

It is known that the k value of mono- and di-saccharides increases linearly with an increase in T_g (Crowe, Reid, & Crowe, 1996; Roos, 1995). In order to understand the relationship between k and T_g of inulin samples, the obtained k value was plotted against T_g of anhydrous inulin, as shown in Fig. 4. From the results, it was found that k of three amorphous inulin samples decreased linearly with increases in T_g. This result is inconsistent with that previously observed in mono- and di-saccharides. However, this is not surprising when we consider that the inulin samples are oligo- or poly-saccharides. For example, it is noted that poly-saccharides have a higher T_g and lower k (*e.g.*, T_g = 516 K and k = 5.2 for amylopectin reported by Roos (1995)) than those of di-saccharides (*e.g.*, T_g = 387 K and k = 7.5 for trehalose reported by Crowe et al. (1996)). This suggests that the relationship between k and T_g differs between mono- and di-saccharides and oligo- and poly-saccharides. The empirical relationship shown in Fig. 4 remains an

Table 1
Resulting parameters for Eqs. (1) and (2).

	GAB parameters				GT parameters		
	W_m (%)	C	K	R^2	T_g (K)	k	R^2
Low-MW	6.43	3.66	0.944	0.9997	384.4	6.43	0.9985
Native	6.34	6.95	0.852	0.9945	398.0	5.93	0.9973
PM high-MW	9.56	7.69	0.603	0.9986	414.3	5.20	0.9984
NT high-MW	7.61	15.06	0.666	0.9985	418.1	5.18	0.9986

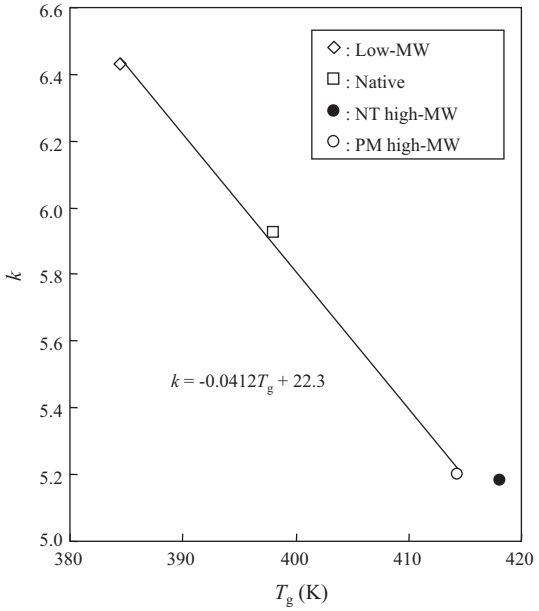

Fig. 4. Relationship between k and T_g. The solid line was obtained experimentally.

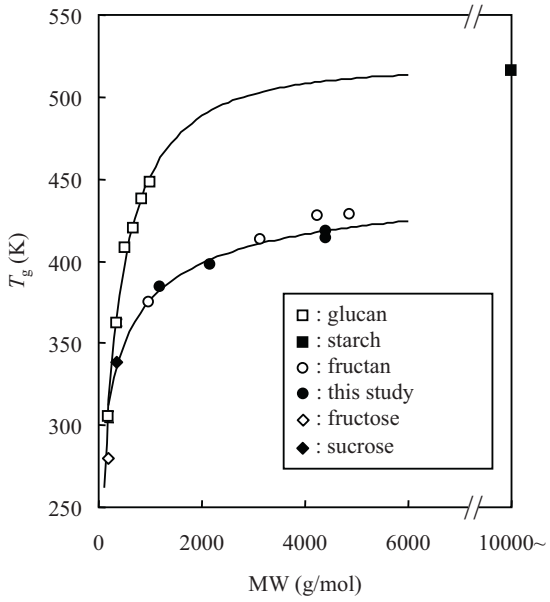

Fig. 5. Effect of MW on T_g of fructan and glucan. The solid lines were obtained by fitting Eq. (4) to the data.

outstanding theoretical problem, but will be of practical use in the prediction of the effect of moisture content on amorphous inulin T_g. NT high-MW inulin, on the other hand, deviated slightly from the empirical relationship between k and T_g observed in the amorphous inulin samples. Since the increase in crystal region causes not only an increase in T_g, but also a decrease in k because of decreasing hydration-sites, the relationship between k and T_g in semi-crystal inulin will have shifted to a higher temperature.

The T_g values of anhydrous inulin (fructan), including previous results (Hinrichs et al., 2001; Ronkart et al., 2009), were plotted against their MW (Fig. 5). For comparison, the T_g values of anhydrous fructose, sucrose and glucan (*i.e.*, polymer of glucose) were included from the literature (Kawai et al., 2005; Levine & Slade, 1988; Orford et al., 1989; Roos, 1995). From the results, it was confirmed that T_g increased with increases in MW. The Fox–Flory equation is a well-known equation used to describe the effect of MW on T_g of amorphous polymer Eq. (3),

$$T_g = T_{g(\infty)} - \frac{B}{\mathrm{MW}} \tag{3}$$

where $T_{g(\infty)}$ and B are maximum anhydrous T_g and constant, respectively. However, the results shown in Fig. 5 did not obey Eq. (3). Therefore, a stretched exponential function Eq. (4) was employed,

$$1 - \frac{T_g}{T_{g(\infty)}} = \exp\left(-\left(\frac{A}{\mathrm{MW}}\right)^n\right) \tag{4}$$

where $T_{g(\infty)}$ is a maximum anhydrous T_g (K), A (g/mol) is a constant, and n is a non-exponential parameter changing between 0 and 1. As seen in Fig. 5, the effect of MW on T_g of fructan and glucan could be reasonably described by Eq. (4). The obtained parameters are listed in Table 2. From the results, it was found that T_g of fructan varies between 338 K (*i.e.*, T_g of sucrose) and 447 K (*i.e.*, obtained $T_{g(\infty)}$) depending on the MW. At each MW, T_g of fructan was lower than that of glucan by up to 70 K. This result indicates that fructan is more flexible than glucan. This difference will be caused by the types of monomer and linkage patterns of the monomer (Levine & Slade, 1988; Orford et al., 1989).

3.4. Effect of MW on T_g' of inulin–water mixtures

DSC thermogram of an inulin aqueous solution (scanned from 230 K to 300 K) showed an endothermic shift suggesting freeze-concentrated glass-like transition before ice-melting (data not shown). It is known that the DSC thermogram shows two endothermic shifts suggesting a freeze-concentrated glass-like transition (Ablett, Izzard, & Lillford, 1992; Levine & Slade, 1988; MacKenzie, 1977; Ohkuma et al., 2008; Pyne, Surana, & Suryanarayanan, 2003; Roos, 1995; Shalaev & Franks, 1995; Shalaev & Kanev, 1994). It is thought that the shift observed in this study is due to the higher temperature shift. Although the origin of the two freeze-concentrated glass transitions is not completely understood, the glass transition observed at a higher temperature is more important for the prediction of crystallization of ice during freezing storage and structural collapse during freeze-drying processes (Chang & Randall, 1992; Levine & Slade, 1988; Shalaev & Franks, 1995; Wang, 2000). Therefore, only the T_g' observed at the higher temperature was investigated in this study.

The T_g' values of inulin (fructan) including a previous result (Hinrichs et al., 2001), fructose, sucrose, and glucan (Levine & Slade, 1988; Roos, 1995) were plotted against MW in Fig. 6. Similar to the results in Fig. 5, the effect of MW on T_g' was described by three parameters in Eq. (4). The results are listed in Table 2. From the results, it was found that the T_g' of inulin varies between 241 K (*i.e.*, T_g' of sucrose) and 258 K (*i.e.*, obtained $T_{g(\infty)}$) depending on the MW.

Table 2
Resulting T_g and T_g' parameters for Eq. (4).

	T_g				T_g'			
	$T_{g(\infty)}$ (K)	A (g/mol)	n	R^2	$T_{g(\infty)}$ (K)	A (g/mol)	n	R^2
Glucan	517.2	225.6	0.49	0.9981	267.6	21.1	0.32	0.9998
Fructan	446.6	102.8	0.27	0.9849	257.4	2.2	0.19	0.9779

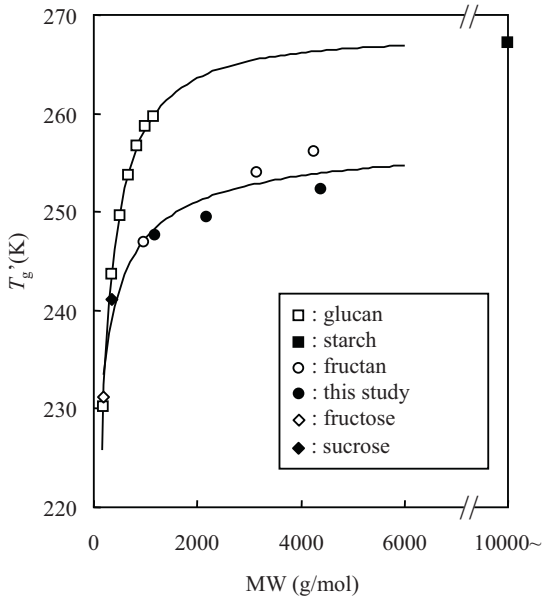

Fig. 6. Effect of MW on T_g' of fructan and glucan. The solid lines were obtained by fitting Eq. (4) to the data.

At each MW, the T_g' of fructan was lower than that of glucan by up to 10 K; the difference in T_g' is lower than that of T_g. This might be because the freeze-concentration of the fructan is higher than that of the glucan, and thus the MW-dependence of T_g' of fructan shifts to a higher temperature.

4. Conclusion

The effects of moisture content, MW, and crystallinity on T_g and T_g' of inulin were manifested. These results will be useful in predicting the T_g and T_g' of inulin. In addition, it was found that T_g and T_g' of fructan including inulin were lower than those of glucan by 70 K and 10 K, respectively. These results may help in understanding the glass transition properties of various carbohydrate polymers.

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