

# **Solid/Liquid Phase Behavior of the 1,2-Propanediol, Water System**

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## Abstract

Binary systems of 1,2-propanediol and water are commonly used in a range of commercial and professional applications including a food preservative, cryopreservative, and as antifreeze; therefore, a detailed understanding of the phase behavior under conditions below room temperature is of great importance to manufacturers and researchers alike. The phase behavior of pure 1,2-propanediol and a binary mixture of 0.136 mol fraction (40 w/w%) propanediol in water were analyzed using Differential Scanning Calorimetry (DSC) and a homemade thermal analysis device. DSC analysis of pure 1,2-propanediol indicated a glass transition with no crystallization, and no cold crystallization was observed. Thermal analysis using a larger sample of pure 1,2-propanediol exhibited a consistent glass transition and an inconsistent melting peak indicating a small likelihood of crystal formation.

## Introduction

Aqueous solutions of diols are of specific interest to chemists due to their impact on the properties of water. 1,2-propanediol based systems are common in commercial applications like antifreeze and food additives, and they are also used in pharmaceutical applications as a bactericidal and preserving agent among other uses.<sup>1,3</sup> 1,2-propanediol is a simple model structural unit of a polyol. Like other polyols, 1,2 propanediol contains both hydrophobic and hydrophilic moieties; therefore, it is expected to behave as an amphiphilic compound. Because of the applications for this binary mixture and its relevance to theoretical analysis for other polyols, a study of the properties of 1,2 propanediol/water mixtures is of particular interest.

Previous research into the effect of 1,2-propanediol on the properties of water have found that 1,2-propanediol exhibits both hydrophobic and hydrophilic behavior.<sup>1</sup> For example, the partial derivative of the molar volume of 1,2-propanediol is negative in the region of low concentration which is typically consistent with hydrophobic molecules. Alternatively, it lowers the temperature of maximum density of water which is typical of hydrophilic molecules. Researchers have also studied the stability of the amorphous state of 1,2-propanediol/water mixtures.<sup>2</sup> Based on their findings, 1,2-propanediol creates a much higher stability and resistance to freezing than many other cryopreservatives in aqueous systems. They also reported a phase diagram for 1,2-propanediol/water systems based on weight percent of propanediol. Their results were obtained with a Perkin-Elmer DSC 4 and published in 1979. Their results were also further investigated in a paper published in 1992.<sup>3</sup> Using the same model DSC, a more complete phase diagram was constructed (Figure S1); however, they did not make further analysis of the system.

We hope to provide further insight into the phase behavior of 1,2-propanediol-water systems. The TA Instruments DSC 2000 available for use in our lab is newer and more precise; therefore, we will be able to confirm or correct prior analyses of the phase behavior. We will also

be able to provide additional confirmation of the phase behavior at a larger scale using our in-house thermal analysis device. Considering the particular behavior of these systems in preventing ice formation, this research will be of great use for theoretical and practical applications.

## Experimental Methods

1,2-propanediol (CAS 57-55-0, Aldrich, mass fraction purity 0.99+) was used as purchased without additional purification. Binary mixtures were formed with nanopure water, sonicated, and stirred overnight to form a homogenous mixture. Thermal analysis of samples was performed with a TA Instruments DSC 2000 and Dr. Milosavljevic's (Dr M's) homemade glass thermal analysis apparatus (Figure S2). In the glass apparatus, samples were loaded into a cuvette, and a thermocouple was placed into the sample and a metal reference. Temperature vs. time data was recorded as liquid nitrogen was added to the apparatus and the sample was cooled to  $-200^{\circ}\text{C}$ . Due to the limitations of the thermocouples, temperatures below  $-200^{\circ}\text{C}$  could not be accurately measured. Once this point was reached, the liquid nitrogen was released from the apparatus, and the apparatus was sealed to allow the sample and reference to slowly warm to room temperature.

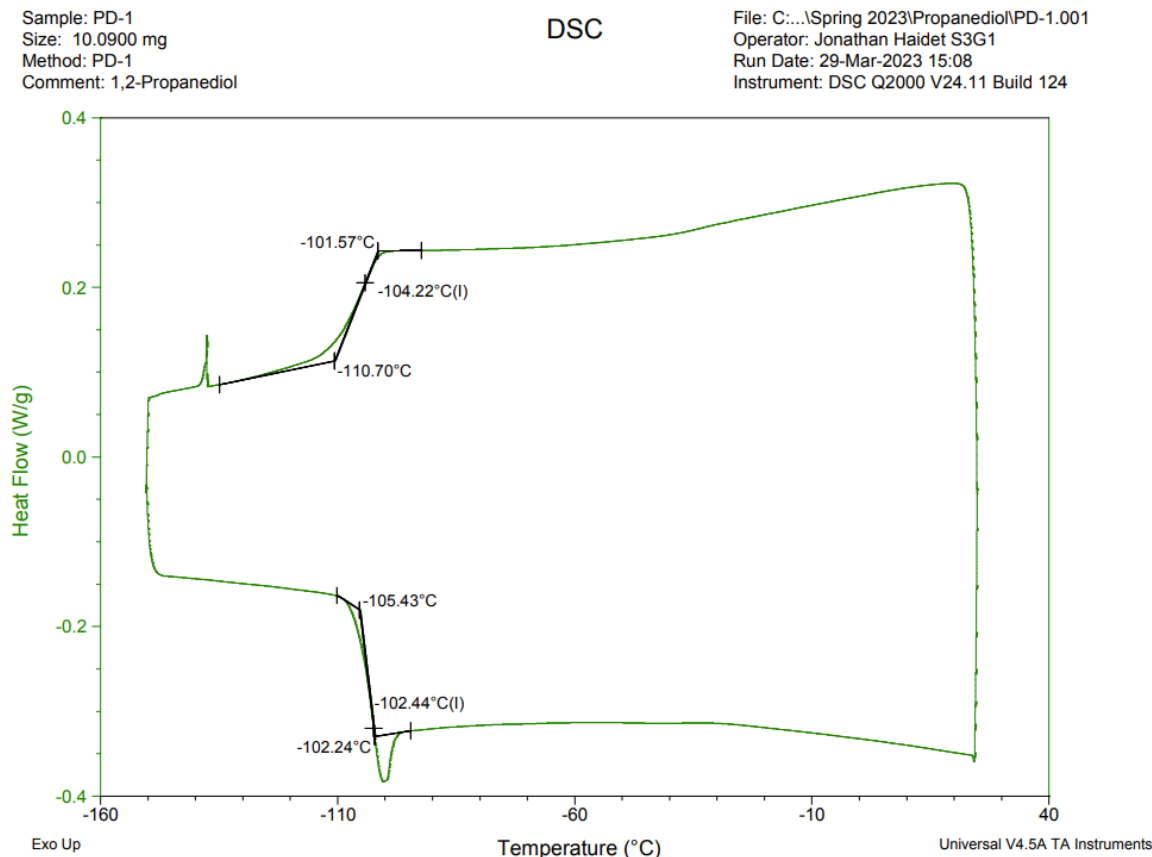
First, pure samples of 1,2-propanediol were analyzed by DSC and by thermal analysis. Two separate DSC procedures were used for analysis of pure 1,2-propanediol. For the first run, the sample was cooled from room temperature at a rate of  $-10^{\circ}\text{C}/\text{min}$  to a minimum temperature of  $-150^{\circ}\text{C}$ , then it was heated back to room temperature at a rate of  $10^{\circ}\text{C}/\text{min}$ . For the second run, the same cooling procedure was used, and the heating procedure was switched to  $1^{\circ}\text{C}/\text{min}$  from  $-150^{\circ}\text{C}$  to  $-40^{\circ}\text{C}$  then  $10^{\circ}\text{C}/\text{min}$  from  $-40^{\circ}\text{C}$  to room temperature. Thermal analysis of pure 1,2-propanediol was then performed for 2 separate runs using the standard procedure shown above.

Following pure 1,2-propanediol analysis, a mixture of 0.136 mol fraction (40 w/w%) 1,2-propanediol in water was analyzed by DSC and thermal analysis. 5 separate runs were conducted using DSC with varying parameters indicated in the thermogram results. Thermal analysis of the binary 1,2-propanediol/water mixture was performed using the standard procedure shown above.

## Results

### DSC Analysis of Pure 1,2-Propanediol

From the initial DSC run for pure 1,2-propanediol using a 10°C heating rate, the following thermogram (Figure 1) was obtained.

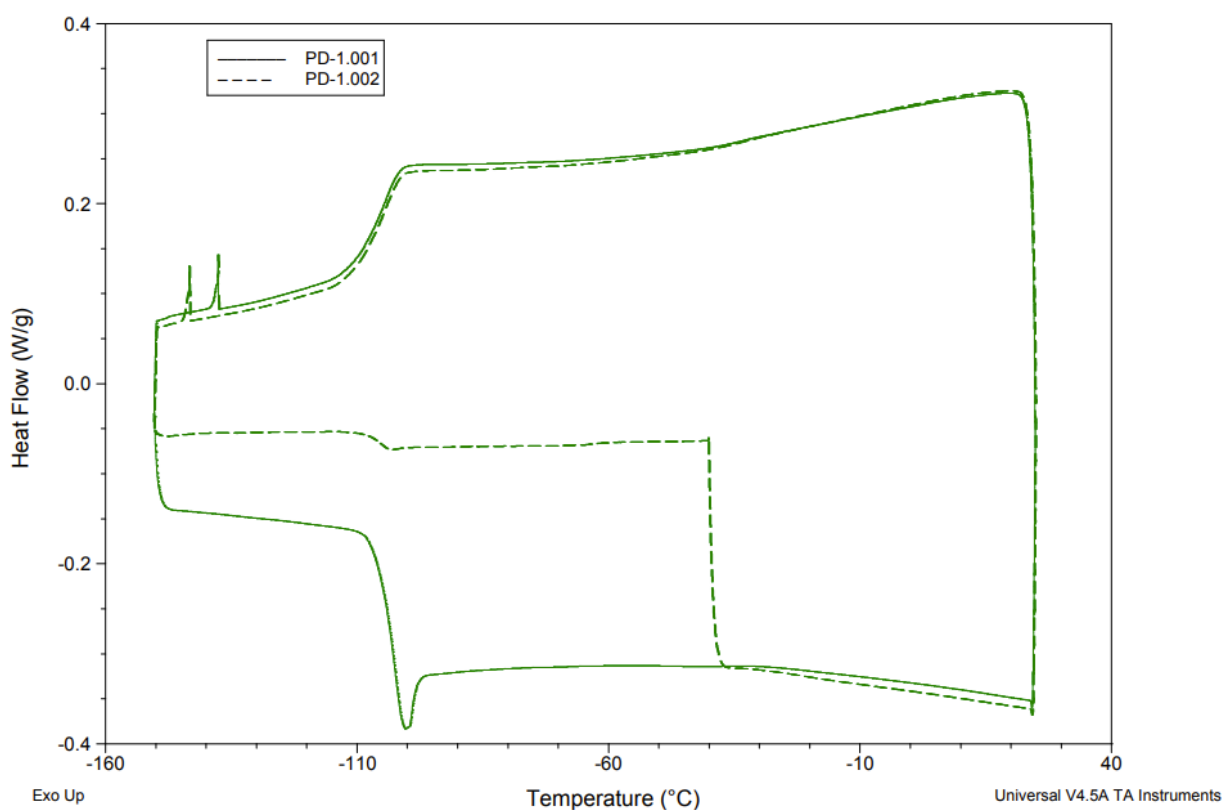


**Figure 1.** DSC 2000 Thermogram for Pure 1,2-Propanediol with 10°C/min Heating Rate.

Analysis of the thermogram shows a clear glass transition at a temperature of -103.33 °C as shown by the sigmoidal curve present in both the heating and cooling cycles. The temperature of the glass transition was obtained by the average of the inflection temperatures for the heating and cooling cycles. In the heating cycle, the glass transition also appears to exhibit a small endothermic peak which was integrated to give a value of 3.603 J/g. This peak resembles what would be expected for melting; however, it occurs below the melting temperature and no crystallization was observed upon cooling of the sample. Therefore, the origins are not entirely clear. Additionally, there is a small upward peak in the cooling cycle. This peak is likely

attributable to a physical change in the sample such as cracking as opposed to a phase change, and it was not examined further. No melting or crystallization peaks occur in the thermogram.

For the second DSC run of pure 1,2-propanediol, the heating rate between  $-150^{\circ}\text{C}$  and  $-40^{\circ}\text{C}$  was slowed to  $1^{\circ}\text{C}/\text{min}$ . By using slower heating over a longer period, the sample was able to further equilibrate at each temperature and thus the chances of “cold crystallization” were increased. Cold crystallization is a phenomenon where a sample that is supercooled exhibits crystallization during heating at temperatures below its melting point. Cold crystallization would be observed in a DSC thermogram as an exothermic crystallization peak occurring during the heating cycle at temperatures below the melting point of  $-59^{\circ}\text{C}$ . The new thermogram (Figure 2) was overlaid on the original thermogram to examine differences resulting from the altered heating rate.



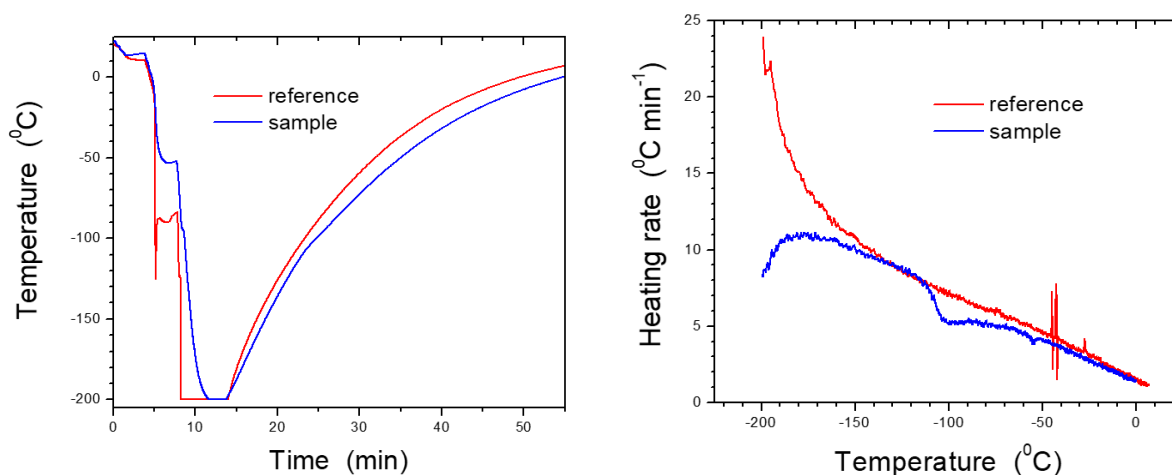
**Figure 2.** DSC 2000 Thermogram for pure 1,2-propanediol with  $1^{\circ}\text{C}/\text{min}$  heating rate (dotted line) overlaid on original results.

Despite the slowed heating rate, no exothermic peaks were present in the thermogram. This result indicates that cold crystallization of pure 1,2-propanediol is probabilistically unlikely. Additionally, using the slowed heating rate, the glass transition during the heating cycle still exhibited a small endothermic peak. The observed peak in the glass transition was much smaller however, and its presence may be an artifact of the faster heating rate. Therefore, in order to determine the shape of the glass transition upon heating, additional testing is required.

### Glass Apparatus Thermal Analysis of Pure 1,2-Propanediol

Further examination of the phase behavior of pure 1,2-propanediol was performed using the glass thermal analysis device. The absence of a cold crystallization peak in the DSC thermogram indicates that it is probabilistically unlikely; however, due to the larger sample volume of the glass apparatus, there is an increased likelihood of observing this phenomenon. Additionally, physical observations of the pure 1,2-propanediol sample can be recorded due to the transparency of the device.

From the thermocouple data, the plot of temperature vs time was recorded. This data was then processed by plotting the first derivative against temperature to show the heating rate of the sample and reference. From the thermocouple data for the first run, the following thermograms (Figure 3) were obtained.

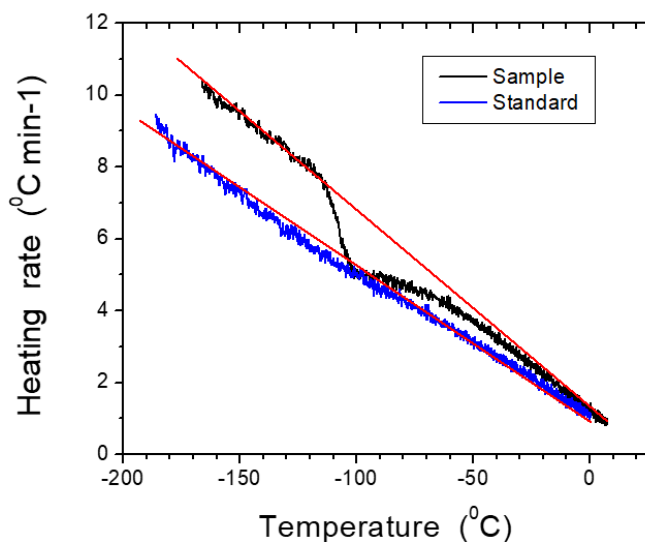


**Figure 3.** Temperature vs time (left) and Heating Rate vs Temperature (right) for pure 1,2-propanediol, run 1.

As can be seen in the reference, the heating rate vs temperature of a sample that does not undergo a phase transition will exhibit a linear trend. This occurrence is the result of Newton's law of cooling which states that the temperature of an object at a different temperature than ambient conditions will approach the ambient temperature as an exponential.<sup>5</sup> When the slope of the exponential temperature vs time is taken and plotted against temperature, this results in a linear fit. The heating rate data provides a significant advantage for phase behavior analysis over the temperature vs time data that is commonly used in thermal analysis. Because of the linear fit, any deviations from normal warming behavior are highlighted and can be clearly examined.

Based on the obtained heating rate data, the glass transition of pure 1,2-propanediol can be clearly seen to occur around  $-105^{\circ}\text{C}$  as indicated by the deviation from linear behavior. The decrease in the heating rate is additionally indicative of an endothermic event which is consistent with devitrification. At the melting point of a material, the temperature does not change as heat energy is added while the material is changing phase. In the heating rate data, this would manifest as a sharp downward peak in the heating rate at the melting temperature. Upon examination of the heating rate, a small downward bump can be seen in the sample data around  $-55^{\circ}\text{C}$ . This deviation may be indicative of a small amount of crystallized 1,2-propanediol melting in our sample.

For the second run, a larger metal piece was used as a reference. By using a larger metal piece, the reference is expected to heat more slowly due to the larger mass and thus larger specific heat. From the processed thermocouple data, the following thermogram (Figure 4) was obtained.



**Figure 4.** Heating Rate vs Temperature for Pure 1,2-Propanediol, run 2.

From the heating rate data, the same sigmoidal behavior corresponding to a glass transition can be observed around  $-105^{\circ}\text{C}$ . In contrast to run 1, no melting peak is seen in the thermogram. The difference in the results across different runs may indicate that crystal formation is highly probabilistically unlikely, or it may be the case that crystal formation very precisely depends on the conditions under which the sample is cooled.

In addition to the thermocouple data, observations of the sample's macroscopic behavior were recorded. During cooling on both runs, the glass was observed to spontaneously crack at  $-150^{\circ}\text{C}$  (Run 1, Figure S3) and  $-141^{\circ}\text{C}$  (Run 2, Figure S4). The spontaneous cracking of the 1,2-propanediol glass was attributed to be a result of the Kauzmann paradox. The Kauzmann

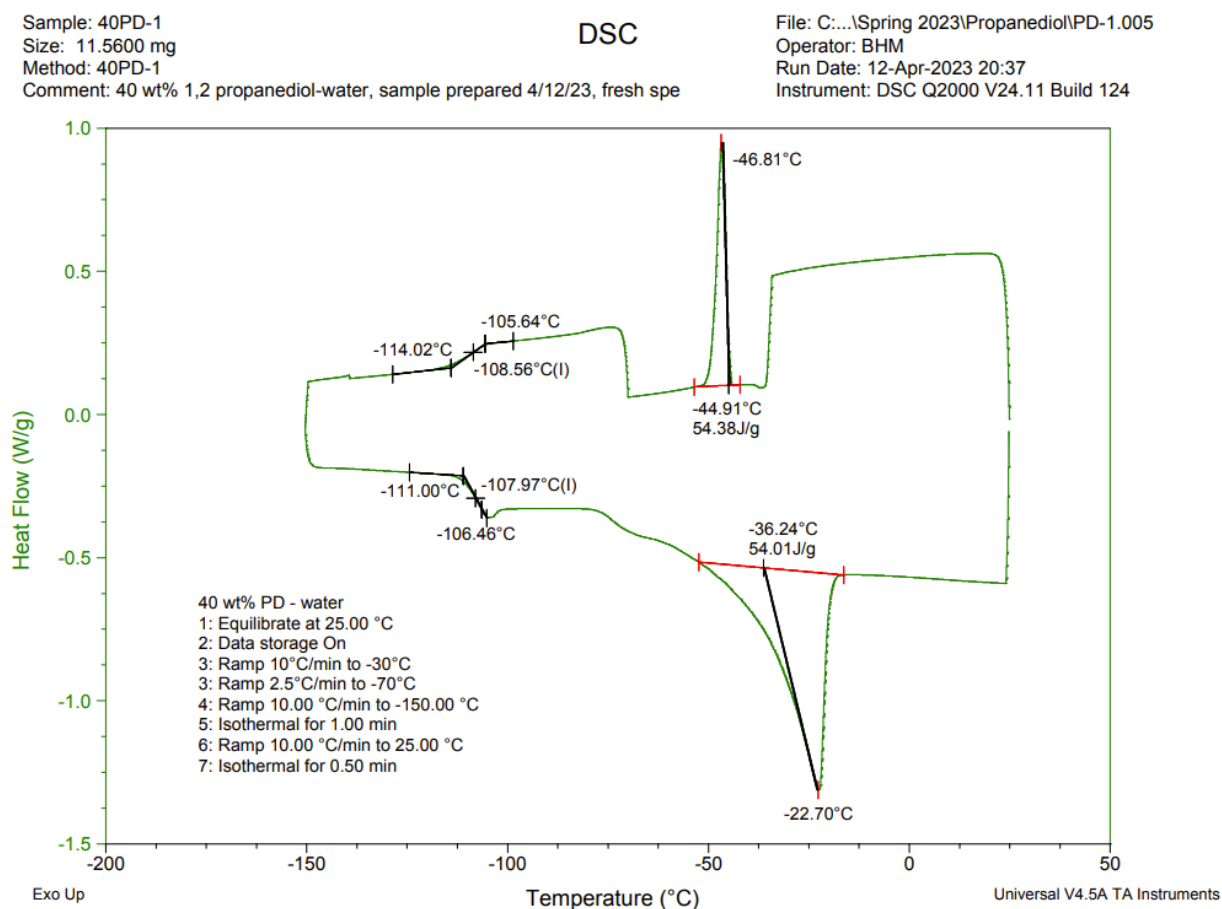
paradox is a result of the different specific heats of crystals compared to liquids and glasses. Liquids and glasses have a larger specific heat than crystals; therefore, if a liquid sample is cooled below its melting point without crystallization, the entropy of the supercooled liquid or glass will decrease faster than the crystal state since entropy change can be calculated by integrating  $C_p/T$ . At some temperature, the entropy of the supercooled liquid or glass phase is equal to that of the pure crystal, so further cooling would result in a theoretically negative entropy value. Since this is thermodynamically impossible, the glass around this temperature must spontaneously expand and crack to increase the entropy and avoid a paradoxical situation. The glass cracking initially occurred only on the bottom half of the sample. This is most likely due to a temperature gradient in the sample since the liquid nitrogen was only in contact with the bottom of the sample. The cracks extended to the top of the sample as the sample was further cooled.

Additional photographs from run 2 were taken of the sample at certain critical temperatures such as when the glass transition was passed ( $-100^{\circ}\text{C}$ ), when the melting point was passed ( $-60^{\circ}\text{C}$ ), and 30 degrees after the melting point was passed ( $-30^{\circ}\text{C}$ ) (Figure S5). From the images, it can be seen that the cracks vanished as the glass temperature was surpassed. This is reflective of the devitrification of the propanediol and the reformation of a supercooled liquid state. However, it is also observed that the liquid state below the melting point is significantly opaque, and the observed opacity decreases after the melting point is passed. The opacity of the supercooled liquid state may be representative of the presence of microscopic crystals in the liquid. This would account for the scattering of light which clouds the sample, and the disappearance of the cloudiness after the melting point is surpassed would reflect the melting of the crystals and the resumption of a normal liquid state.

#### DSC Analysis of 1,2-Propanediol/Water Mixture

5 separate DSC experiments were performed to analyze the phase behavior of a 40 w/w% 1,2-propanediol/water binary mixture. From the DSC results, two distinct phase behaviors were observed in each sample: crystallization and a glass transition. An example of the DSC data is shown in Figure 5.





**Figure 5.** DSC analysis of 40 w/w% 1,2-propanediol/water exhibiting crystallization during cooling.

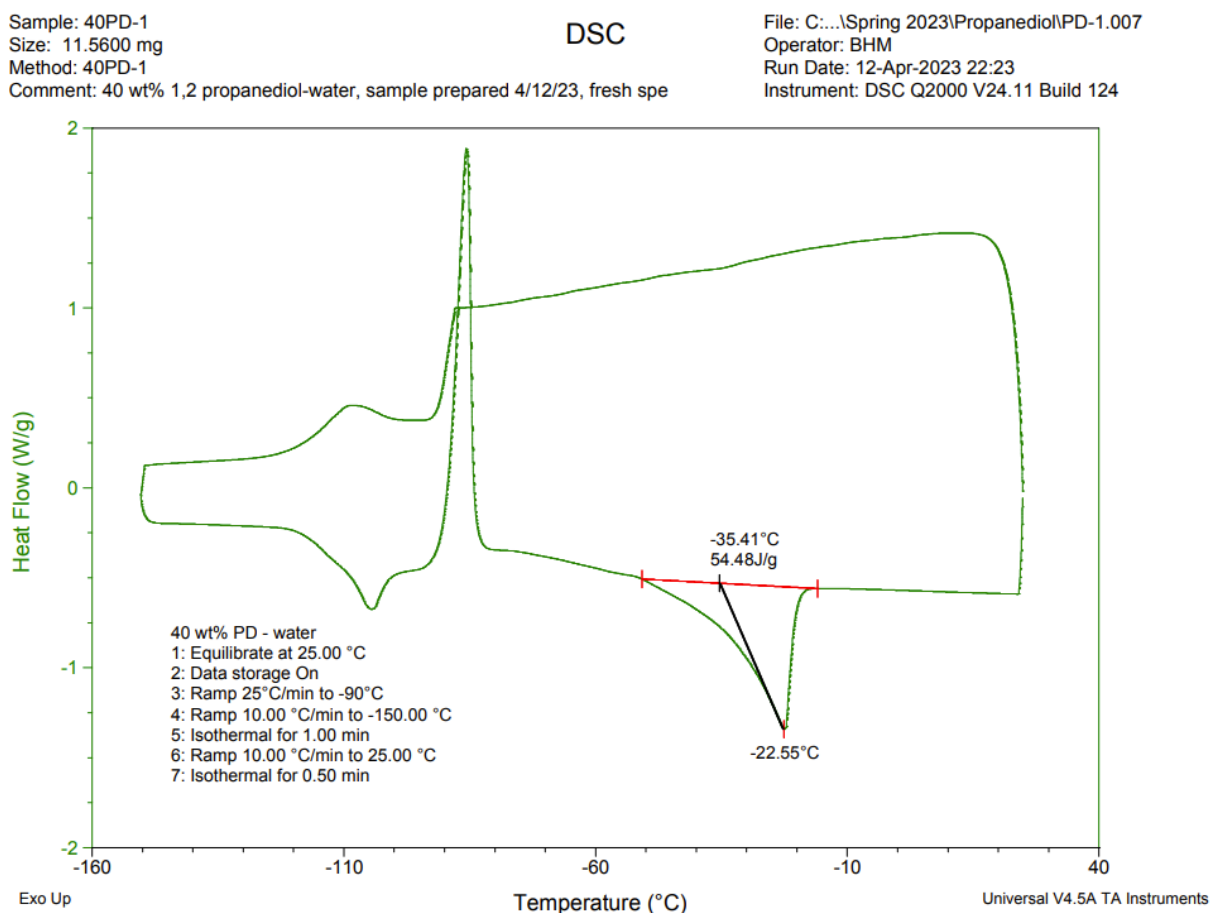
In the DSC procedure, the cooling rate of the sample was decreased from 10°C/min to 2.5°C/min between -30°C to -70°C. Based on prior research, the complex was expected to crystallize in the given temperature range. Since crystal formation is a probabilistic event, decreasing the cooling rate gives the sample more time to equilibrate at each temperature and for seed crystals to form. In the DSC thermogram, a large crystallization peak was observed at -44.91°C. Integration of the crystallization peak showed the enthalpy of crystallization to be 54.38 J/g. Similarly, a large, broad melting peak was observed in the warming cycle at -36.24°C with an integrated enthalpy of melting of 54.01 J/g. The percent difference of the enthalpy of crystallization and enthalpy of melting were 0.7% indicating good agreement. For both the crystallization and melting peaks, the temperature of the phase transition was determined by the intersection of a line which crosses the top of the peak with the same slope as the leading edge and the basal line of the peak similar to the procedure used in the chemical literature.<sup>2,3</sup>

The average melting temperature across all DSC experiments was determined to be -35.8°C. This experimental melting temperature has a 48% difference from the literature value of

-22°C;<sup>2</sup> however, the literature value coincides closely with the average experimental peak melting temperature of -22.6°C. In the literature experiments, the melting peak was observed to be much narrower, and the peak broadening in our experiments was likely a product of a faster heating rate. Additionally, the average enthalpy of fusion determined by DSC for the binary mixture was 54.195 J/g. This result is lower than the enthalpy of fusion of water which is 334 J/g,<sup>6</sup> and it is also lower than the enthalpy of fusion of 1,2-Propanediol which is 110 J/g.<sup>7</sup> The difference in the experimental enthalpy of fusion compared to the pure substance enthalpies of fusion indicates that the crystallization corresponds to a complex of water with 1,2-propanediol as opposed to a single substance crystallizing out of the solution.

In addition to melting and crystallization, the sample also exhibits a glass transition at -108.27°C as shown by the inflection in the heating and cooling cycles of the DSC curve. The presence of this glass transition was consistent throughout all DSC experiments of 40 w/w% 1,2-propanediol samples, regardless of the positions or sizes of the melting and crystallization peaks. The presence of a glass transition indicates that solid crystallizes out of the solution leaving behind an amorphous state. The temperature of the glass transition has a relatively small percent difference of 4.6% from the pure 1,2-propanediol sample. This result may indicate that the amorphous state corresponds to 1,2-propanediol that is excluded when the complex crystallizes. Alternatively, the mixture may be heterogeneous and contain pure 1,2-propanediol domains that correspond to the amorphous state. Additionally, the heating cycle glass transition shows some peak-like behavior which is consistent with the DSC curve for pure 1,2-propanediol. According to the chemical literature, it has been verified by X-ray diffraction that this peak-like phase behavior does indeed correspond to a glass transition.<sup>2</sup> The presence of this small peak indicates a weakly endothermic change corresponding with devitrification of the glass. This change may be the result of the molecules relaxing during devitrification and the distance between molecules increasing.

Comparable DSC curves exhibiting crystallization upon cooling, a glass transition, and a melting peak were observed with 10°C/min and 5°C/min cooling rates as shown in Figure S6 and Figure S7. However, when the cooling rate was increased to 25°C/min, no crystallization peak was observed in the cooling cycle. Instead, a large cold crystallization peak occurred during the heating cycle of the sample. An example of this phase behavior is shown in Figure 6.

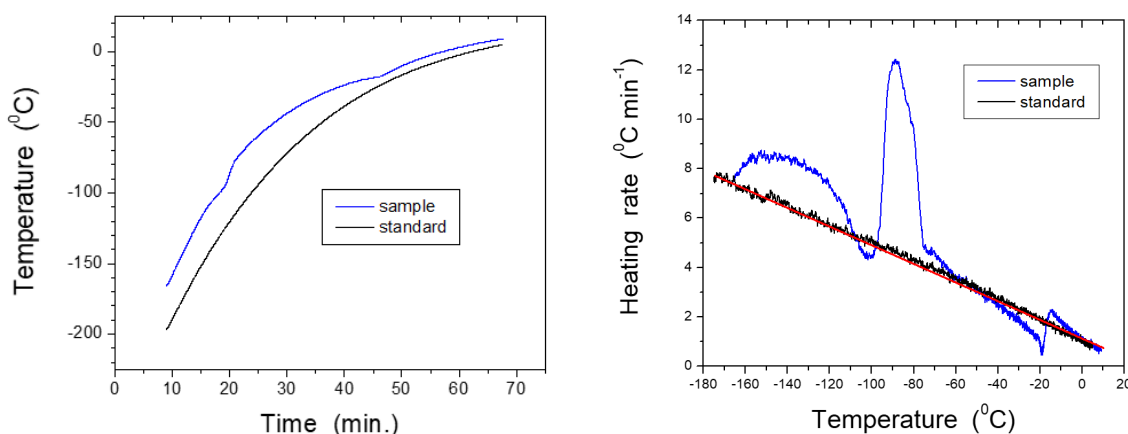


**Figure 6.** DSC analysis of 40 w/w% 1,2-propanediol/water exhibiting crystallization during cooling.

Due to the rapid cooling of the sample, no crystalline phase formed in the solution during the cooling cycle. Instead, an exothermic peak corresponding to the crystallization of the sample was observed in the heating cycle after the glass transition was passed but prior to the melting temperature. This peak corresponds to cold crystallization of the sample, and it confirms the ability of the sample to form a supercooled liquid and crystallize during heating. A similar DSC curve using a rapid cooling rate where cold crystallization was observed is shown in Figure S8. Additionally, the rapid cooling of the sample appears to have impacted the glass transition of the cooling curve. The glass transition in the cold crystallization DSC curves shows the same peak-like behavior as the heating cycle glass transition, and this peak-like behavior is not observed in the samples that crystallized during cooling. This result indicates that there is some weakly exothermic change associated with vitrification and weakly endothermic change associated with devitrification.

### Glass Apparatus Thermal Analysis of 1,2-Propanediol/Water Mixture

After the temperature vs time data was processed as was done in the pure 1,2-propanediol samples, thermal analysis of the 40 w/w% 1,2-propanediol/water mixture reported the following thermogram shown in Figure 7.



**Figure 7.** Thermal analysis using glass apparatus of 40 w/w% 1,2-propanediol/water reported as temperature vs time (right) and heating rate vs temperature (left).

From the heating rate vs temperature thermogram, the same behaviors that were observed in DSC were also observed by thermal analysis. First, around  $-110^{\circ}\text{C}$ , the graph had a sharp dip which resembles the sigmoidal behavior of a glass transition. Based on the location of this behavior and the results of DSC analysis, it can be concluded that the dip in the heating rate resulted from devitrification, and the abnormal graph shape may be related to the abnormal graph shape of the DSC thermogram. Second, around  $-85^{\circ}\text{C}$ , a large upward peak can be observed. The increase in heating rate associated with the peak indicates that an exothermic event has occurred in the sample, and the most probable event is cold crystallization. Considering liquid nitrogen was used to cool the samples and thus there was a rapid cooling rate, this analysis coincides with the observation of cold crystallization in the rapidly cooled DSC thermograms. Finally, the graph is linear until a small downward peak around  $-20^{\circ}\text{C}$ . The decrease in heating rate associated with this peak indicates an endothermic event, and therefore it can be concluded that this represents the melting temperature of the sample. The melting temperature reported by thermal analysis coincides closely with the peak melting temperature present in the DSC analysis and the reported melting temperature in the chemical literature.

## Conclusions

Using both DSC and an in-house thermal analysis device, the phase behavior of pure 1,2-propanediol and a binary mixture of 0.136 mol fraction (40 w/w%) propanediol in water were analyzed. Pure 1,2-propanediol samples exhibited a clear and consistent glass transition around  $-103.33^{\circ}\text{C}$ . A melting peak was also observed for the pure 1,2-propanediol sample in a thermal analysis run, but did not consistently appear in a repeat trial. Analysis of the binary mixture showed crystallization and melting of the solution with an average melting temperature of  $-35.8^{\circ}\text{C}$ . When a cooling rate of  $25^{\circ}\text{C}/\text{min}$  was used, no crystallization occurred during cooling, and cold crystallization of the sample was observed. In addition to crystal formation, a glass transition with a peak-like shape was observed to occur around  $-108.27^{\circ}\text{C}$ , regardless of the position or size of the crystalline peak. The same phase transitions including cold crystallization, a glass transition, and melting was observed by thermal analysis, thus confirming the DSC results. The presence of a glass transition indicates that an amorphous residue is left behind during crystallization of the solution, and the peak-like shapes may be indicative of additional complex behavior worth further exploration.

## Acknowledgements

We would like to thank Dr M for his teaching and assistance in performing these experiments.

## References

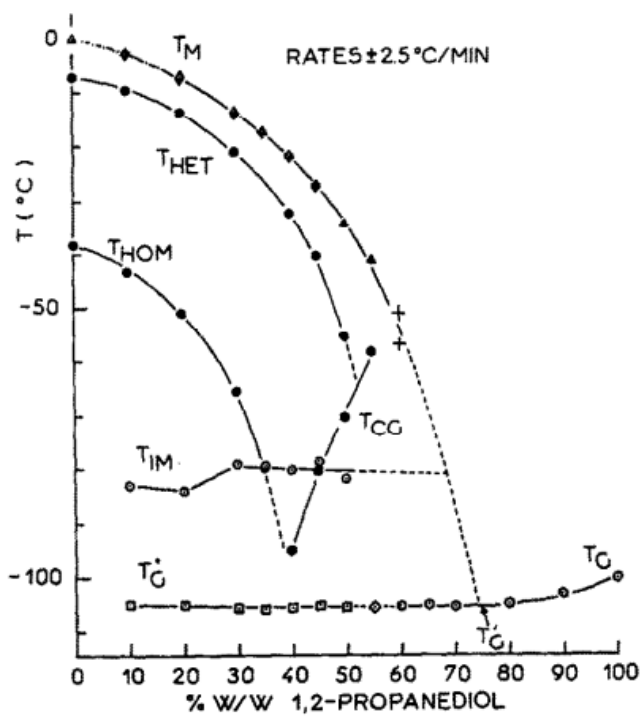
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## Supplemental Information

### Sample Calculations

$$\% \text{ Difference} = \frac{|exp - obs|}{\frac{exp + obs}{2}} \times 100\%$$

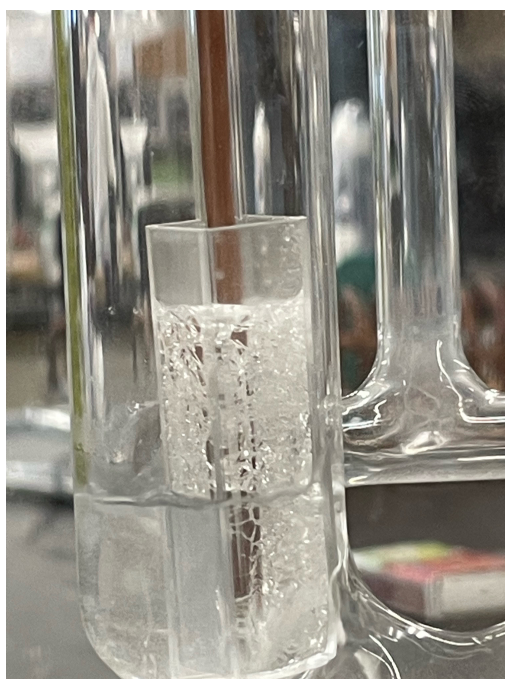
### Supplemental Figures



**Figure S1.** Phase Diagram of 1,2-Propanediol/Water Systems Based on Weight Percent.<sup>3</sup>



**Figure S2.** Experimental glass apparatus setup.

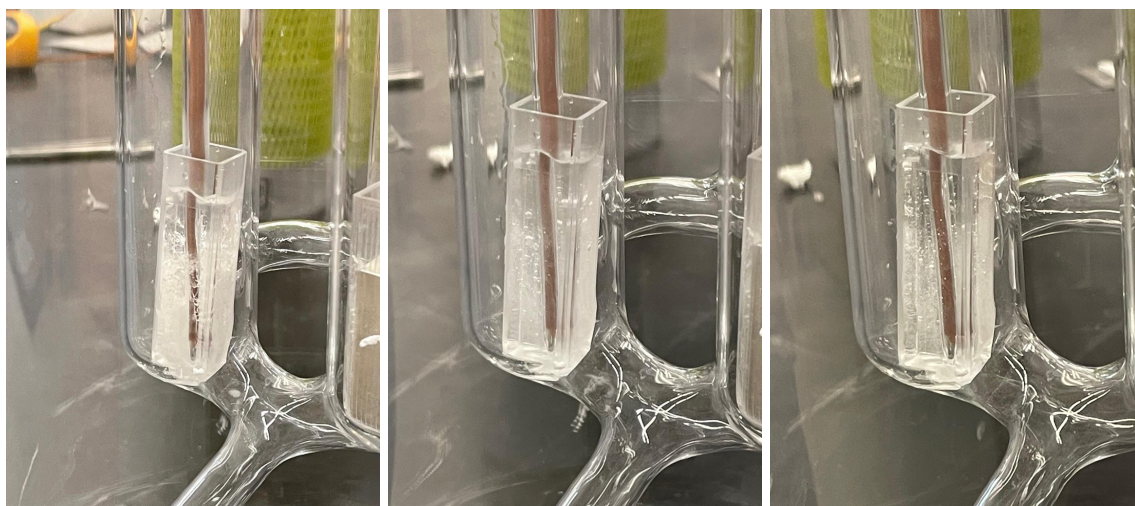


**Figure S3.** Cracked glass of pure 1,2-propanediol at  $-150^{\circ}\text{C}$  during cooling with liquid nitrogen.





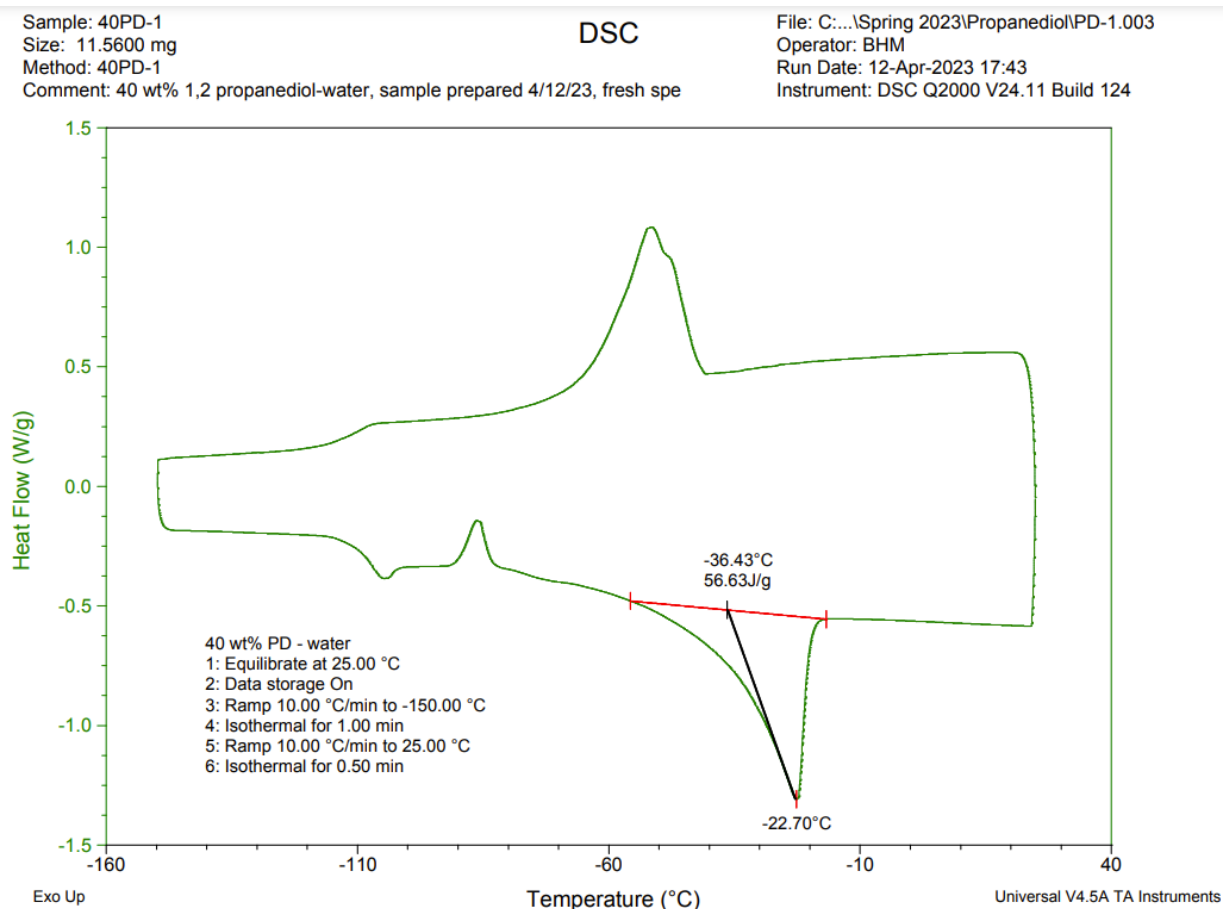
**Figure S4.** Cracked glass of pure 1,2-propanediol at  $-141^{\circ}\text{C}$  during cooling with liquid nitrogen.



**Figure S5.** Images of pure 1,2-propanediol during warming at  $-100^{\circ}\text{C}$  (left),  $-60^{\circ}\text{C}$  (middle), and  $-30^{\circ}\text{C}$  (right).



### DSC Analysis of 1,2-Propanediol/Water Mixture

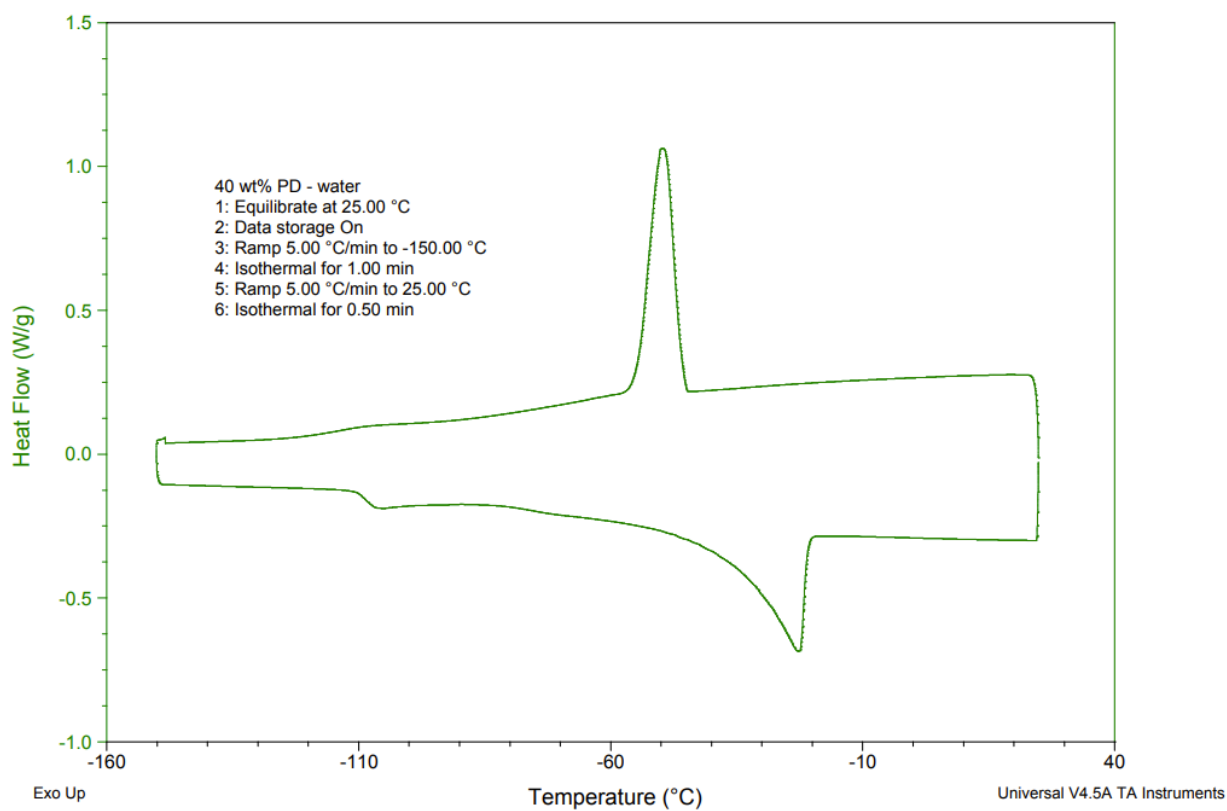


**Figure S6.** DSC Analysis of 40 w/w% 1,2-propanediol in water

Sample: 40PD-1  
Size: 11.5600 mg  
Method: 40PD-1  
Comment: 40 wt% 1,2 propanediol-water, sample prepared 4/12/23, fresh spe

## DSC

File: C:\...\Spring 2023\Propanediol\PD-1.004  
Operator: BHM  
Run Date: 12-Apr-2023 18:54  
Instrument: DSC Q2000 V24.11 Build 124

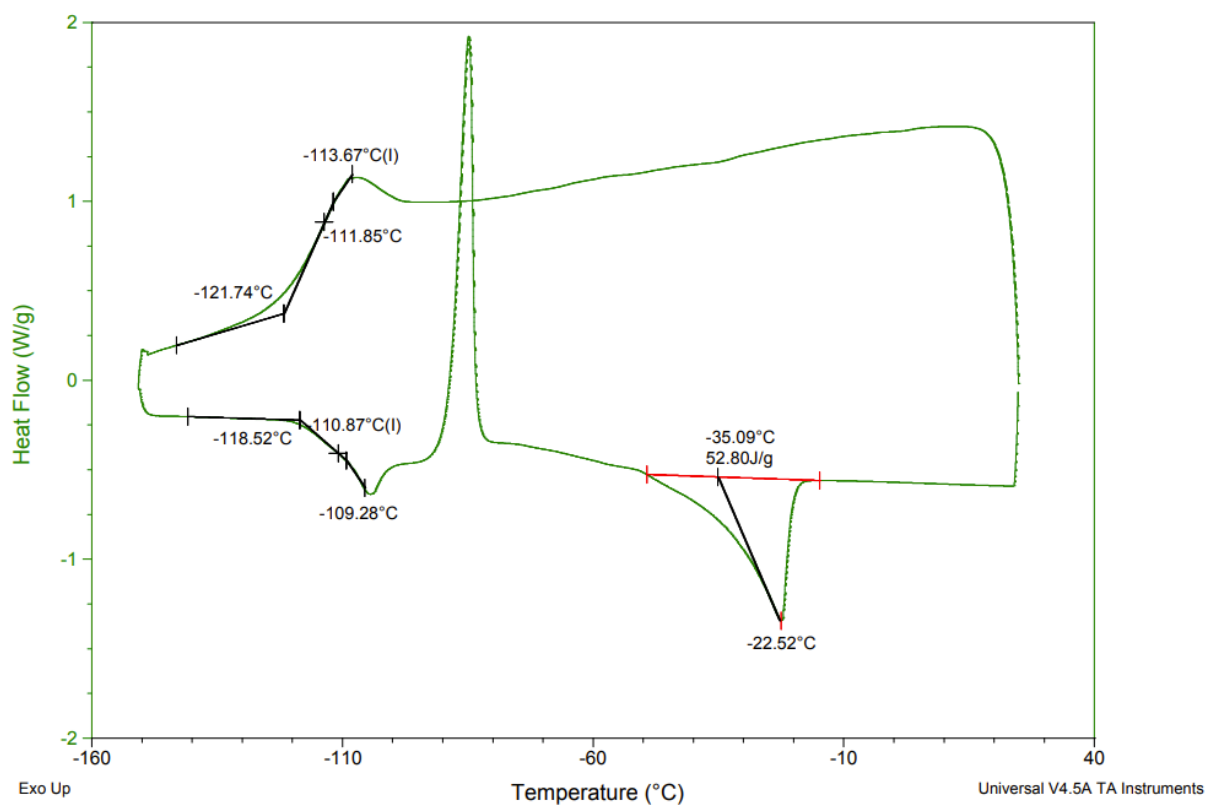


**Figure S7.** DSC Analysis of 40 w/w% 1,2-propanediol in water

Sample: 40PD-1  
Size: 11.5600 mg  
Method: 40PD-1  
Comment: 40 wt% 1,2 propanediol-water, sample prepared 4/12/23, fresh spe

## DSC

File: C:\...Spring 2023\Propanediol\PD-1.006  
Operator: BHM  
Run Date: 12-Apr-2023 21:48  
Instrument: DSC Q2000 V24.11 Build 124



**Figure S8.** DSC Analysis of 40 w/w% 1,2-propanediol in water