

# DSC and Photophysical Study of Cold Crystallization of Poly(propylene glycol)/Water Mixtures

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## Summary

PPG/Water matrix dynamics was studied using Differential Scanning Calorimetry (DSC), Thermal Analysis (TA), photophysical techniques, and rheology. Supercooling of 29.5 and 31.8 mole percent PPG in water was studied using DSC at cooling/heating rates ranging from 1 to 4 K/min. No regular crystallization was observed at cooling rates above 2 K/min. The fraction of water molecules which experienced regular and cold crystallization were found to be dependent on heating rate. The enthalpy of melting was equal to the sum of the enthalpies of regular and cold crystallization which indicates that the crystalline structure of the ice formed in both types of crystallization was the same. The Kissinger plot for cold crystallization in each solution was found to be linear. The activation energies of the 29.5 and 31.8 mole percent solutions were found to be 63.2 J/mol and 99.9 J/mol, respectively.

A luminescent probe, ruthenium tris-bipyridine [ $\text{Ru}(\text{bpy})_3^{2+}$ ], was used to comment on the matrix dynamics. The rate constant for unimolecular inherent decay of the excited state versus temperature increased when the sample underwent cold crystallization indicating that the probe was more constrained in the glassy state than the crystalline state. This can be attributed to larger void volumes between ice crystals (in which the luminophore is situated) than that in the glassy state. In order to establish a stronger connection between DSC and the photophysical study, the sample heating rate was measured during the laser photolysis experiment. The heating rate data were compared to DSC data; the maxima in the heating rate curve were found to coincide with that of DSC thermogram. Also, the experiment was conducted in a way that visual appearance of the sample could be simultaneously monitored. Upon heating, the (optically transparent) glassy sample crystallized and became opaque, then returned to a transparent liquid state. The temperatures of these transitions were found to be in agreement with DSC data.

Two separate runs of the laser photolysis experiment were conducted and had initial heating rates of approximately 1 and 3 K/min. These could be directly compared to the 1 and 3 K/min DSC thermograms. In producing the 1 K/min thermogram the sample was heated slowly enough to reveal multiple processes which occur after the cold crystallization. At higher heating rates, these processes occur simultaneously and cannot be distinguished. The heating rate data from the photolysis experiments displayed both show the presence of a second exothermic process occurring after melting, which was unexpected. Further DSC and photophysical analysis will be needed to determine the cause of this second peak.

Viscosity versus temperature data was obtained for nine samples of varying PPG mole fractions in water over the range of temperatures from 30 to  $-25$  °C. The dependence of viscosity on PPG mole fraction differed positively from ideality, suggesting hydrogen bonding between the water and PPG molecules. The maximum measured viscosity at 25 °C corresponded to the solution of 85.5 mole percent PPG. This was unusual since adding a fluid liquid to a viscous liquid increased the viscosity of the mixture. It is possible that at low mole fractions of water, the molecules closely associate with the oxygen atoms on the PPG and increase the effective molecular weights of the PPG molecules, increasing the viscosity.

The semi-empirical McAllister equation, which includes terms containing the molecular weights of the pure components, fit the experimental data better when the molecular weight of the repeating unit was used rather than the average molecular weight of the whole PPG molecule. This suggests that the properties of the mixture depend on interactions between water molecules and the oxygen atoms on each repeating unit. Additionally, the solutions become insoluble when the ratio of water molecules to oxygen atoms on PPG molecules is greater than 2:1. Therefore, each oxygen atom can hydrogen bond to no more than 2 water molecules. Above this threshold, the predominantly nonpolar character of the PPG causes it to be insoluble in water.