

Starch Gelatinization

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Synopsis

The dependence of the melting temperature of starch on its concentration in a polymer-diluent mixture was determined. The resultant data were analysed by application of the thermodynamic equations appropriate to a first-order phase transition. It is suggested that this analysis may be used to explain certain features of starch gelatinization.

INTRODUCTION

When an aqueous suspension of starch granules is heated, the granules swell to form a paste. This process of gelatinization has been described in detail in various tests.^{1,2} Despite the commercial significance of starch, there is little information concerning thermodynamic aspects of gelatinization.

Starch consists largely of linear and branched polymers of D-glucose. The chains of these polysaccharides form a continuum of crystalline and amorphous arrangements in the granule. The crystalline character accounts for the birefringence and the relatively sharp bands observed in x-ray powder patterns of intact starch particles. When starches are completely gelatinized, they lose birefringence and give diffuse x-ray patterns, though in some cases a weak V-type pattern may arise due to complexing of linear starch molecules with traces of lipid.^{1,2} Flory has demonstrated that under appropriate conditions the conversion of a polymer from a partly crystalline to an amorphous state may be treated as a first-order phase transition.³ In such cases, the equilibrium temperature, T_m , at which the last traces of polymer crystallinity disappear is related to the concentration of diluent by the following equation:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} (\nu_1 - \chi_1 \nu_1^2) \quad (1)$$

where T_m^0 is the melting point of pure polymer, ΔH_u is the heat of fusion of polymer repeat unit, V_u and V_1 are the molar volumes of repeat unit and diluent, respectively, ν_1 is the volume fraction of diluent, χ_1 is a dimension-

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less quantity characterizing the solvent-polymer interaction energy, and R is the gas constant. Equation (1) has been employed in the analysis of crystal-liquid transformation in both simple polymers and complex macromolecular systems such as fibrous proteins.⁴ The following report describes an attempt to use this expression to explain certain features of starch gelatinization.

EXPERIMENTAL

Wheat starch was washed from a flour dough, collected by centrifugation, and dried at room temperature. Samples were kindly supplied by the Lord Rank Research Centre, Bucks., England.

Gelatinization of starches was detected using a polarizing microscope fitted with a hot stage. Heating was conducted at a rate of 1°C/30 min near the melting temperature, though at lower temperatures rates of up to 20°C/hr were used. The temperature was recorded at which birefringence was lost by all granules. Triplicate determinations of T_m were made; in general, results agreed to within $\pm 1^\circ\text{C}$.

The volume fraction of polymer was calculated using a value of 1.55 g/ml for the density of starch.¹

RESULTS AND DISCUSSION

Starch granules were found to lose crystallinity over a temperature range of approximately 15°C. This result is probably due in part to sample inhomogeneity¹; however, a diffuse melting process would be expected in a relatively complex macromolecular system such as starch.⁴ In a typical experiment, the gelatinization temperature T_m varied from 70°C to 82°C as the volume fraction of diluent was altered from 0.88 to 0.59. Excessive turbidity prevented measurement of the gelatinization temperatures of more concentrated suspensions, consequently T_m^0 cannot be estimated from a graph of $1/T_m$ versus ν_1 .³ The thermal instability of starch precludes the accurate determination of its melting temperature by other methods. Since T_m^0 is unknown, it is advantageous to rearrange eq. (1) into the following form⁴:

$$\left(1 - \frac{T_m}{T_m^0}\right) / \nu_1^2 = \left(\frac{R}{\Delta H_u} \frac{V_u}{V_1}\right) \frac{T_m}{\nu_1} - \left(\frac{R}{\Delta H_u} \frac{V_u}{V_1}\right) \chi_1 T_m. \quad (2)$$

If ΔH_u and the product $\chi_1 T_m$ are assumed to be constant over the temperature range investigated,⁵ then, according to eq. (2), the term $(1 - T_m/T_m^0)/\nu_1^2$ should be a linear function of T_m/ν_1 . The variance about the regression line in the graph of $(1 - T_m/T_m^0)/\nu_1^2$ versus T_m/ν_1 was computed for a series of values of T_m^0 . For the samples tested, the best fit was ob-

tained with the temperatures shown in Figure 1. These values of T_m^0 are consistent with studies demonstrating that the crystallinity of starch is destroyed by heating to 200–220°C.

Taking T_m^0 to be 210°C, the heat of fusion ΔH_u calculated from eq. (2) is 7000 cal/mole while the entropy of fusion ΔS_u ($\Delta S_u = \Delta H_u/T_m^0$) is 14.5 cal/deg/mole. The interaction parameter B , defined by $B = \chi_1 RT/V_1$, is of the order of 2 cal/ml, and therefore water is a poor solvent for starch.³ Similar

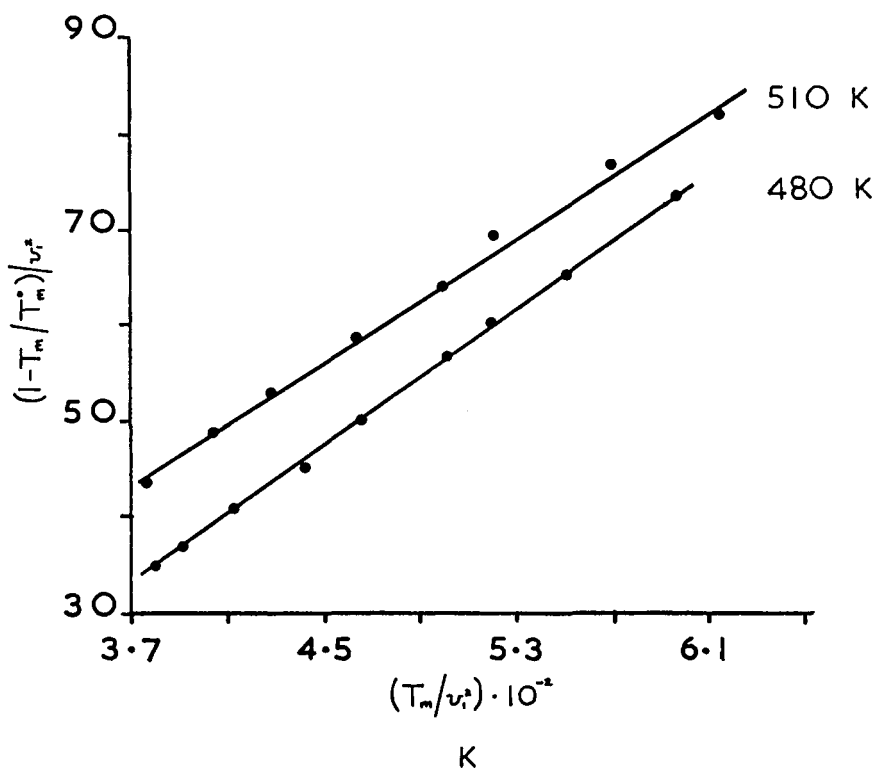


Fig. 1. Gelatinization temperature data for two samples plotted according to eq. (2) with the values of T_m^0 (°K) giving the best fit to a linear plot.

values of the thermodynamic parameters characterize other polymer systems.⁴

The analysis outlined above suggests that the theory of crystalline–amorphous phase transitions may be used to explain some features of starch gelatinization.

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