

## GLASSY STATE IN 2-AMINO-2-METHYL-1,3 PROPANEDIOL PLASTIC CRYSTAL

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### Abstract

Heat capacity measurements between 293 K and 363 K have been carried out in order to elucidate the different states appearing in 2-amino-2-methyl-1,3 propanediol (AMP) plastic crystal. The results allowed one of them to be identified as a glassy crystal.

The changes of enthalpy, entropy and Gibbs free energy thermodynamic functions with temperature have been calculated from the experimental heat capacity values.

**Keywords:** 2-amino-2-methyl-1,3 propanediol plastic crystal, glassy crystal, kinetics

### Introduction

In a previous paper [1] we have determined the different phases appearing in 2-amino-2-methyl-1,3 propanediol (AMP): Three equilibrium (brittle crystalline *II*, plastic crystalline *I* and liquid *L*) and two non-equilibrium states ( $I_g'$  and  $L'$ ). Apparently, one of these non-equilibrium states,  $I_g'$ , was a glassy crystal (frozen – in state of orientational disorder in plastic phase [2]).

Adiabatic calorimetry [2–5], in order to determine the jump in  $C_p$  at the glass transition temperature and the residual entropy at 0 K, together with nuclear magnetic resonance for molecular motions studies in glassy and plastic states [6–9] are the most widely used techniques.

In this work we present heat capacity measurements on the sample between 293 and 363 K (upper limit of temperature in our AC calorimetric device since the crucible cannot be hermetically sealed and sublimation becomes important), showing the transformation of *II* to *I* (in the first heating) and of *I* to  $I_g'$  (in cooling runs). As the glass transition is dynamic in nature, the glass transition temperature ( $T_g$ ) and the shape of the heat capacity jump ( $\Delta C_p$ ) depend on the cooling and heating rates as well as on the degree of disorder which has been frozen [4]. In our case, due to the quenching temperature (293 K, since

the nucleation rate of phase *II* becomes important at lower temperatures [1]) and to the fact that only orientational disorder can be frozen from a plastic phase [2, 4] the  $I_g' < = > I$  glass transition is very smooth.

## Experimental

### Calorimetry

#### AC

$C_p$  measurements have been carried out in a home-made AC calorimeter working in a dynamic range [10, 11] which allowed the continuous measurement of the heat capacity vs. temperature.  $Al_2O_3$  was used as standard in the calibration runs. Sample masses about 100 mg, 22 mHz of alternating power signal and scanning rates of  $1 \text{ deg}\cdot\text{h}^{-1}$  were used as experimental conditions. Numerical acquisition of sample temperature was done with a sampling period of 3 s and then, a heat capacity value was obtained each 6 mK.

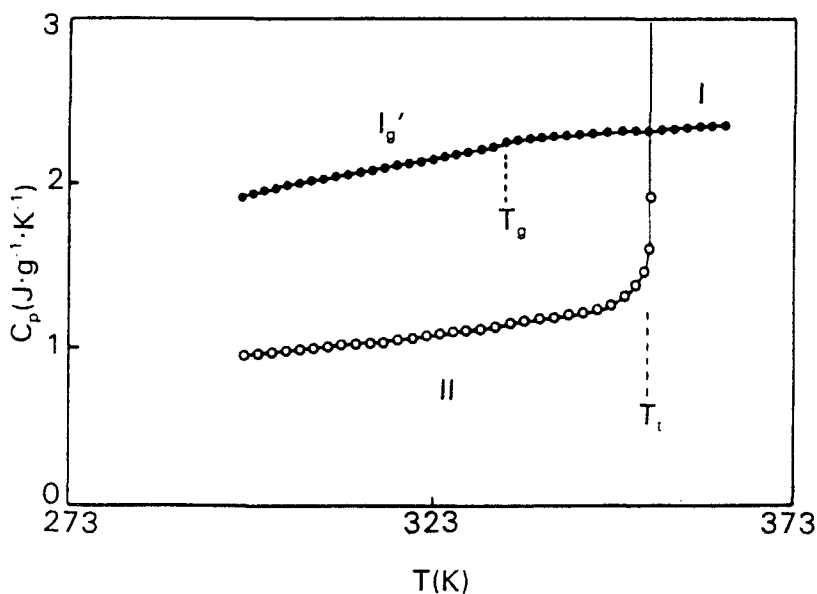
#### Differential

Differential scanning calorimetry was performed in a Perkin-Elmer DSC-7 device. Aluminium crucibles and scanning rates from 2 to  $50 \text{ deg}\cdot\text{min}^{-1}$  were used.

## Results and discussion

The experimental heat capacity values of AMP are given in Fig. 1. The *II*→*I* process at 351 K, in heating run, is clearly a first order phase transition [1] (solid ordered crystalline phase to orientationally disordered crystalline phase). The plastic to liquid transition at 383 K cannot be attained by means of our calorimetric device, as we have mentioned above. In cooling, no first order *I*→*II* process occurs; only a variation in the slope of  $C_p(T)$  at approximately 333 K is detected. On reheating the sample from room temperature up to 363 K, no differences were found with respect to the cooling run. We have associated this behaviour with the existence of a quenched state (glassy crystal  $I_g'$ ) of plastic phase *I* [1], the glass transition temperature  $T_g$  being 333 K.

From DSC measurements at different heating rates we have obtained an exponential temperature change of the thermal effect associated with the glass transition in front of the scanning rate (see Table 1) showing an activation energy of  $180 \text{ kJ}\cdot\text{mol}^{-1}$ . This behaviour is typical for transitions from a quenched to a stable state [12].



**Fig. 1** Heat capacity values of AMP corresponding to phases II (open circles) and I (full circles and  $I'_g$  state (full circles)

**Table 1** Change of the glass transition temperature with the heating rate. The cooling rate was 20 deg·min<sup>-1</sup> in all cases, starting from liquid phase.

Heating rate/deg·min <sup>-1</sup>	$T_g$ /K
2	327
5	332
10	336
13	337
15	338
20	338
25	338
50	339

The  $C_p$  values shown in Fig. 1 have been fitted to linear equations with the temperature in the following intervals:

a) 293 to 351 K (phase II)

$$C_{p_i}(\text{Jg}^{-1}\cdot\text{K}^{-1}) = 5.147\cdot 10^{-3}T(\text{K}) - 0.601$$

b) 383 to 333 K (phase I)

$$C_p(\text{Jg}^{-1}\cdot\text{K}^{-1}) = 2.709\cdot 10^{-3}T(\text{K}) + 1.316$$

c) 333 to 293 K (state  $I_g'$ )

$$C_{p_i}(\text{Jg}^{-1}\cdot\text{K}^{-1}) = 8.178\cdot 10^{-3}T(\text{K}) - 0.514$$

The changes of the enthalpy, entropy and Gibbs free energy with temperature corresponding to the states  $II$ ,  $I$  and  $I_g'$  have been calculated from the  $C_p$  functions (assuming arbitrary origins  $H_o$  and  $S_o$ ). The corresponding Gibbs free energy curves are represented in Fig. 2.

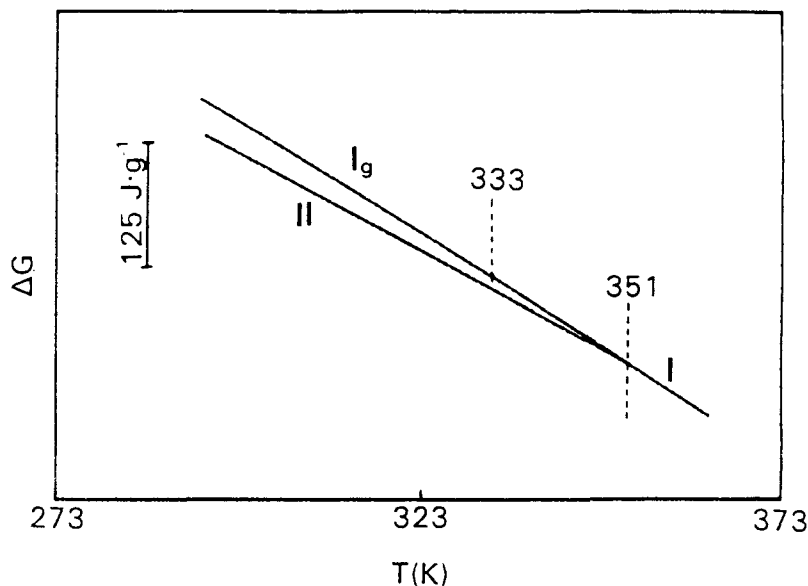


Fig. 2 Gibbs free energy curves corresponding to states  $II$ ,  $I$  and  $I_g'$

In a previous work [1] the results of X-ray diffraction studies as well as the determination of non chemical differences from the initial material, allowed us to consider the state noted  $L'$  as a non-equilibrium amorphous one of AMP, attained only from  $I_g'$ . Additional experiments have revealed that at room temperature  $I_g'$  is more hygroscopic than the brittle crystalline phase  $II$ . This effect, detected as a mass increase, has been confirmed by Karl-Fischer method: for equal masses of  $I_g'$  and  $II$  at room temperature and equal period of time, the absorbed water in the glassy state is about 10 times that absorbed in phase  $II$ . Thus  $L'$  is an aqueous solution of AMP. The crystallisation of  $L'$  (existence of  $L' + II$  noted in reference [1]) may be understood by taking into account the ex-

istence of a binary system  $I_g'$ +water and their transformation to  $II$ +water (at room temperature).

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**Zusammenfassung** — Zur Ermittlung der unterschiedlichen Zustände, die in einem Kunststoffkristall von 2-Amino-2-Methyl-1,3 Propandiol auftreten, wurden im Temperaturbereich von 293 bis 363 K Messungen der Wärmekapazität durchgeführt. Einer von ihnen konnte anhand der Resultate als glasartiger Kristall identifiziert werden.

Anhand der experimentell ermittelten Werte für die Wärmekapazität wurde die temperaturabhängige Änderung der thermodynamischen Funktionen Enthalpie, Entropie und Gibbsscher freier Energie berechnet.