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THERMODYNAMIC BEHAVIOR OF GLASS FORMING POLYMERIC MELTS

Physics

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ABSTRACT

Polymer molecules segments can exist in two specific physical structures. They can exist in either crystalline form or amorphous form.Crystalline polymers are possible in such conditions if there is a regular chemical structure (e.g., homopolymers or alternating copolymers), and the chains possess a highly ordered arrangement of their segments. Symmetrical polymer chains are never 100% and crystallity in polymers is due to symmetrical polymer chains. Thus, polymers form mixtures of small crystals and amorphous material. These semi-crystalline polymers have a kind of typical liquifiction pathway, having their solid state until they reach their melting point at T_m. So it is interesting to study the thermodynamic behavior of polymers.

The temperature dependence of the Gibbs free energy difference (ΔG), enthalpy difference (ΔH) and entropy difference (ΔS) between the undercooled melt and the corresponding equilibrium solid has been analysed for glass forming polymeric materials. It is done by calculating ΔG for one sample of glass forming polymeric melt ; polyethylene terephthalate (PET) and two simple organic liquids: tri-α-naphthyl benzene(tri-α-NB) phenyl salicylate (salol) in the entire temperature range T_m (melting temperature) to T_g (glass transition temperature). The expression for ΔS and ΔH has been derived assuming hyperbolic dependence of ΔC_p on T. The calculation of enthalpy difference (ΔH) and entropy difference (*ΔS*) is made for two samples of glass forming polymeric melts ; polyamid-6 (PA-6), polypropylene oxide (PPO) and one simple organic liquids: tri-α-naphthyl benzene (tri-α-NB).

KEYWORDS

polymeric glasses, thermodynamics of undercooled melts, thermodynamic parameters

Introduction

Most of polymers possess semi-crystalline morphology. There is no long range order in the amorphous or glass-like structure and the chains are tangled. The crystalline material shows a high degree of order formed by folding and stacking of the polymer chains. Thus, polymers form mixtures of small crystals and amorphous material. They melt over a range of temperature instead of melting at a single melting point.

All kinds of materials can form glasses irrespective of their physical and chemical properties with the rapid solidification technique. The thermodynamic behavior is important for understanding the viscosity, glass forming abilities, nucleation and growth kinetics etc of the undercooled melt. For predicting the glass forming ability, the Gibbs free energy difference (ΔG) between the undercooled liquid and the corresponding equilibrium solid phases is found to be an important parameter. The estimation of ΔG is often critically important when used in the analysis of nucleation phenomena because the nucleation frequency has an exponential dependence on ΔG. If the temperature dependences of the heat capacities of the liquid and crystalline phases are known, the temperature dependence of ΔG in the undercooled region can be acquired. But the experimental determination of the specific heat of the undercooled melt is always tough and sometimes impossible (due to) by cause of their strong tendency to crystallize. It can measure close to the melting temperature T_m and at the glass transition temperature T_g in the case of glass forming melts. It would be needed (desirable) to have solid analytical expressions for the estimation of the thermodynamic parameters.

Several investigators [1-5] have suggested expressions for heat of fusion ΔH_m, T_m etc. There is not any expression of ΔG which is universally applicable. If specific heat data is not available then the choice of the approximation depends on the type of material i.e. pure metal, glass forming alloys or organic substances. The aim of the present investigation is to study the thermodynamic behaviour of the glass forming polymeric melts. The study is made by analyzing the temperature dependence of ΔG, ΔS and ΔH in the temperature range T_m to T_g.

In the present work, ΔG for polymeric melts and simple organic liquids are calculated using the Mishra and Dubey expression [6, 7, 8] and two earlier proposed equations by Lad et al [9] and Dhurandhar et al [10]. It is done by calculating ΔG for one sample of glass forming polymeric melt; polyethylene terephthalate (PET) and two simple organic liquids: tri-α-naphthyl benzene (tri-α-NB) and phenyl salicylate (salol). Calculation of ΔG for two samples of glass forming polymeric melts; polyamid-6 (PA-6), polypropylene oxide (PPO) is also done by Prapti et al [11]

A novel expression has been obtained for the entropy difference ΔS and the enthalpy difference ΔH between the liquid and solid phases. The entropy difference (ΔS) between the liquid and solid phases has a significant role in the study of viscosity of the undercooled melts. The expression for ΔS and ΔH has been derived assuming hyperbolic dependence of ΔC_p on T. The calculation of entropy difference (*ΔS*) and enthalpy difference (ΔH) is made for two samples of glass forming polymeric melts; polyamid-6 (PA-6), polypropylene oxide (PPO) and one simple organic liquids: tri-α-naphthyl benzene (tri-α-NB).

Formulation of Theoretical expression

The difference in Gibbs free energy between the liquid and crystalline phases is given by

$$\Delta G = \Delta H - T\Delta S \qquad (1)$$

where

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \qquad (2)$$

and

$$\Delta S = \Delta S_m - \int_T^{T_m} \Delta C_p \frac{dT}{T} \qquad (3)$$

where, T_m is the melting temperature, S_m is the entropy of fusion and H_m is the enthalpy of fusion.

Putting Eq(2) and Eq(3) in Eq(1) and solving , we get,

$$\Delta G(T) = \left[\Delta Hm - \int_T^{Tm} \Delta CpdT\right] - T\left[\Delta Sf - \int_T^{Tm} \Delta Cp \frac{dT}{T}\right] \qquad (4)$$

$\Delta C_p^{\,m} = C_p^l - C_p^x$ is the difference in specific heats of the liquid and corresponding crystalline phases of metallic alloy.

Thus, if we have experimental specific heat data for the undercooled liquid and the corresponding equilibrium solids, experimental ΔG can be calculated using Eq(4).

However, due to metastable nature of both undercooled liquid and the corresponding solid, it is difficult to obtain accurately the heat capacity data experimentally.

Due to scarcity of specific heat data in under cooled region, the functional dependence of ΔG on under cooling has to be estimated theoretically.

The expression for Δ*G* is given by Mishra and Dubey [8] based on hole theory [12, 13] of liquids leads to the following expression for ΔG*:*

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{2T}\left(1 - \frac{2}{3}\frac{T_k}{T_m}\frac{\Delta T}{T}\right) \qquad (5)$$

Where T_k= Kauzmann temperature, $\Delta T = T_m - T$

Another expression proposed by Lad et al [9] for bulk glass forming alloy is;

$$\Delta G = \frac{\Delta H_m \Delta T}{T_m}\left[\frac{4T^2}{(T+T_m)^2}\right] \qquad (6)$$

Eq. (6), gives good account of Δ*G* in most of the systems. But, since the derivation again involves the approximation of the logarithmic term, the results obtained are not in good agreement with the experimental points. In the derivation of above equation, ΔC_p has been to be constant and it also involves the limitations of the validity of above equation to small undercooling. It is well known that to evaluate Δ*G* accurately, choice of proper ΔC_p variation is important. It has been observed that C_p does not remain constant in the entire under cooled region and instead it increases with increased under cooling (i.e. towards lower temperature).

For such systems, in which the specific heat increases considerably with undercooling, ΔC_p at any temperature $T_k<T<T_m$ in the undercooled region can be expressed as

$$\Delta Cp(T) = \frac{\Delta Cp^m Tm}{T} \qquad (7)$$

ΔC_p^m being the difference in the specific heats at the melting point. Putting this value of ΔC_p in Eq (2) and Eq (3) and then solving Eq (1), we can get

$$\Delta G = \frac{\Delta Hm\Delta T}{Tm} - \Delta Cp^m Tm\left[\ln\frac{Tm}{T} - \frac{\Delta T}{Tm}\right] \qquad (8)$$

the Δ*G* values for glass forming systems is calculated by Dhurandhar et al [10].

Plots of Gibbs free energy differences *(*ΔG) and Temperature (T) of various polymeric melts have been given in the following fig.1 to fig.3.

Expression for ΔS and ΔH:

Mishra and Dubey [8] have proposed the expression for the entropy difference ΔS based on the hole theory of liquid;

$$\Delta S = \Delta S_m - \frac{\Delta C_p^m}{4\delta^2}\left[(1+2\delta) - \left(1 + 2\delta\frac{T_m}{T}\right)e^{-2\delta\Delta T/T}\right]$$

$$\text{Where } \Delta T = T_m - T \text{ and } \delta = \frac{T_k}{T_m} \qquad (9)$$

The novel expression for S in case of hyperbolic dependence of ΔC_p on T can be obtained by partial differentiation of Dhurandhar et al [10] Eq. (8)

$$\Delta S = -\frac{\partial \Delta G}{\partial T} \qquad (10)$$

one gets the following expression for ΔS through Eq. (8)

$$\Delta S = \frac{\Delta Hm}{Tm} - \Delta C_p^m \frac{Tm}{T} + \Delta C_p^m \qquad (11)$$

Mishra and Dubey proposed the expression for enthalpy difference ΔH is given bellow:

$$\Delta H = \Delta H_m - \Delta C_p^m T_m \frac{\Delta T}{T}\left(1 - \delta\frac{\Delta T}{T}\right) \text{where } \Delta T = T_m - T \text{and } \delta = \frac{T_k}{T_m} \qquad (12)$$

The novel expression for ΔH can be obtained using Heena et al. Eq. (8) and (11) in Eq (1)

$$\Delta H = \Delta Hm - \Delta C_p^m Tm \ln\left(\frac{Tm}{T}\right) \qquad (13)$$

Plots of the entropy difference ΔS and the enthalpy difference ΔH with Temperature (T) of various polymeric melts have been given in the following fig.4-9.

Results & Discussion

The result of ΔG for PET (fig.1), our result (Eq.8) slightly overestimate particularly at large undercooled region. The result of tri-α-NB (fig.2) shows excellent match with experimental data. This is simple organic liquid and no polymerization undergoes. So we can say that polymerization may have effect on Glass Forming Ability (GFA) of material. Lad et al (Eq.6) are somewhat closer and the possible reason is ΔCp may not vary much. The results of SALOL (fig.3) appear to be close to experiment almost in entire undercooled region.

Figures 1-3 show the results of ΔG as function of T in the undercooled region for three polymeric melts and two simple organic liquids obtained using Eq (5), (6) and (8).The parameters used for the calculations of ΔG for these systems are given in table.1. The results for these systems (fig.1-3) are calculated with our present Eq. (8), Lad et al Eq.(6) and compared with the experimental results of [8]. We can see the fair agreement of the present results obtained through Eq. (8) with experimental data.

The tri-α-NB (fig.2) shows the good agreement and close matching of our present Eq.(8) with experimental curves up to large degrees of undercooling. The results of PET (fig.1) and SALOL (fig.3) show much better agreement of our present Eq.(8) and Mishra et al Eq.(5) with experimental curves. All three polymeric and simple organic liquid samples (fig.1-3) have a large deviation of the curves obtained using the formulation given by Lad et al Eq.(6).

Figures 4-6 show the result of ΔS as function of T in the undercooled region for two samples of glass forming polymeric melts and one simple organic liquid obtained using our present Eq. (11) and Mishra et al Eq. (9). The graphs for PA6 (fig.4), PPO (fig.5) and tri-α-NB(fig.6) show results for ΔS of our present Eq.(11) and seem to be matching with experimental curve.

In the result for ΔS of PA6 (fig.4), our result (Eq.11) and results obtained by Mishra et al(Eq.9) match with experimental data qualitatively. However, quantitatively they deviate from experimental points.

Figures 7-9 are presenting the results of ΔH as a function of T in the undercooled region for two samples of glass forming polymeric melts and one simple organic liquid obtained using our present Eq. (13) and that of Mishra et al Eq (12). The PA6 (fig.7), PPO (fig.8) and tri-α-NB(fig.9)show excellent result for ΔH. The results using our present Eq. (13) for both the systems are much nearer to experimental results.

Conclusion

It is found that the expression for the thermodynamic parameter ΔG based on the hyperbolic variation of ΔCp expresses the correct temperature dependence for glass forming polymeric as well as simple organic materials. A novel expression for ΔS and ΔH has been derived assuming hyperbolic dependence of Δ Cp on T which shows fairly reasonable results and very small deviation from experimental data. These polymeric and simple organic liquid samples have fairly good glass forming tendency with smaller value of ΔG.

Table 1Parameters used for calculations [8]

System	$T_i=T_g$ (K)	*Tk* (K)	T_m (K)	Tk/T_m (K)	ΔH_m (kJ/mol)	ΔC_p^m (kJ/mol-K)	ΔS_m (kJ/mol-K*)*
tri-α-NB	342	255.4	472	0.54	42.489	0.09086	0.09002
Salol	230	209.5	316.6	0.66	9.799	0.02368	0.03095
PET	342	253.6	543	0.47	22.600	0.0088	0.04162
PA6	323	252.5	496	0.51	21.814	0.03815	0.04396
PPO	198	156.7	350	0.45	8.4	0.02198	0.024

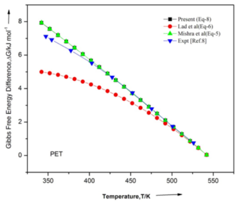

Fig. 1 Gibbs free energy difference ΔG as a function of temperature T for Polyethylene terephthalate (PET)

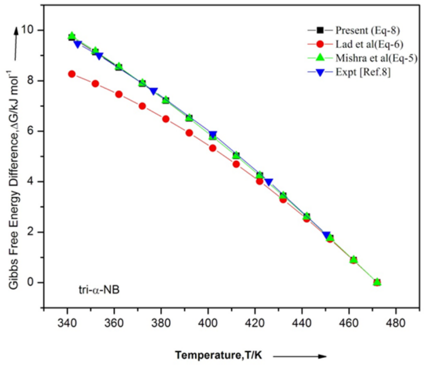

Fig. 2 Gibbs free energy difference ΔG as a function of temperature T for tri-α-naphthyl benzene (tri-α-NB)

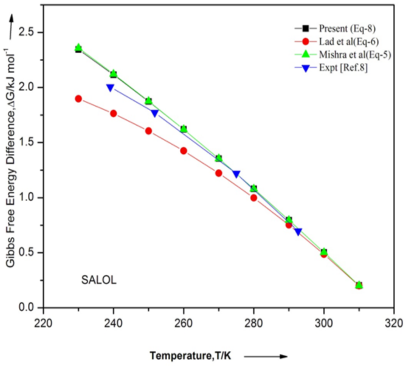

Fig. 3 Gibbs free energy difference ΔG as a function of temperature T for phenyl salicylate (salol)

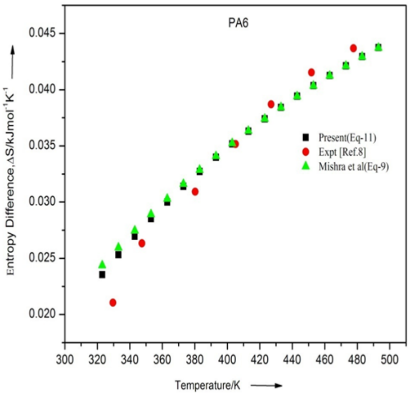

Fig.4 Entropy difference ΔS as a function of temperature T for polyamid-6 (PA-6)

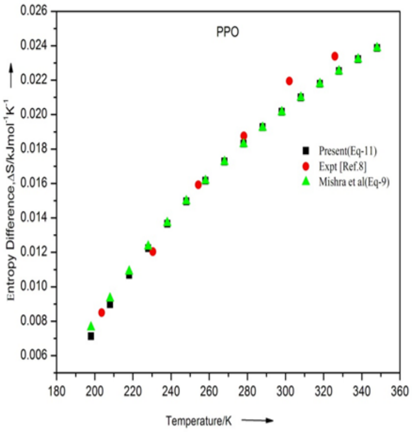

Fig.5 Entropy difference ΔS as a function of temperature T for polypropylene oxide (PPO),

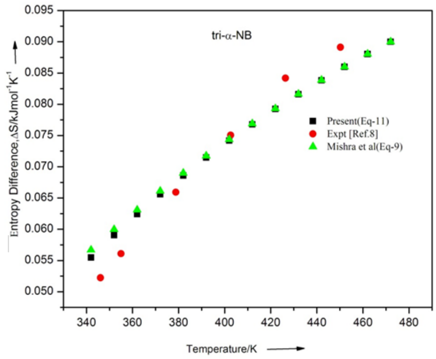

Fig.6 Entropy difference ΔS as a function of temperature T for tri-α-naphthyl benzene (tri-α-NB),

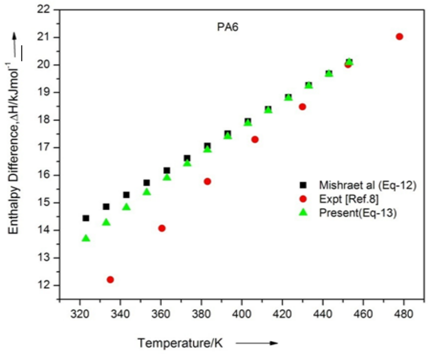

Fig.7 Enthalpy difference ΔH as a function of temperature T for polyamid-6 (PA-6)

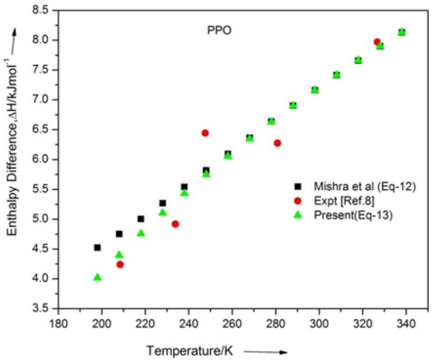

Fig.8 Enthalpy difference ΔH as a function of temperature T for polypropylene oxide (PPO),

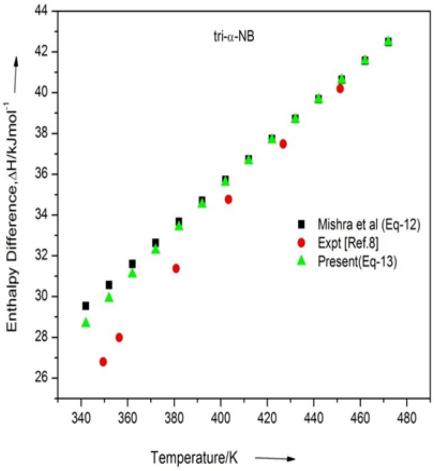

Fig.9 Enthalpy difference ΔH as a function of temperature T for tri-α-naphthyl benzene (tri-α-NB),

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