ESRF

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Influence of pressure on hydrogen bonded polymers; polyamides and biopolymers

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Local contact(s):
Peter Boesecke

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Sanjay Rastogi
Ann Terry
Nico van Ruth
Wim de Jeu
Denitza Lambreza
Esther Vinken

Report:

The existence of a re-entrant phase diagram, possessing a high temperature and high pressure maximum, has been reported for a polymer, poly(4-methyl-1-pentene) recently[i,ii,iii,iv]. This re-entrant phase behaviour recalls the general phase diagram proposed by Tammann in 1903[v]. Within this phase diagram a region, referred to as the re-entrant region, exists where the entropy of a crystal is greater than that of its liquid. The existence of a crystal having entropy greater than its liquid is in contradiction to the Kauzmann paradox[vi]. Here we show how a re-entrant phase diagram can exist without invoking a paradox, this requires a detailed study on the origin of the re-entrant phase behaviour. Tammann ascribes the origin of the re-entrant behaviour, depicted in a pressure-temperature diagram, to the existence of a line where the difference in specific volume between the liquid and the crystal is zero ($\Delta V = 0$ line) and another line where the difference in enthalpy between liquid and crystal is zero ($\Delta H = 0$ line). Here we provide direct experimental evidence for the existence of this $\Delta V = 0$ line for the first time. The experimental observations also show the presence of a second $\Delta V = 0$ line at lower temperatures. This second $\Delta V = 0$ line has an essential role in resolving the apparent entropy crisis[vii] in the re-entrant region of the pressure-temperature phase diagram, through a relationship between the specific volume and the entropy. These two $\Delta V = 0$ lines, when combined with the melting and glass transition temperature, describe the shape of the pressure-temperature phase diagram of this polymer.

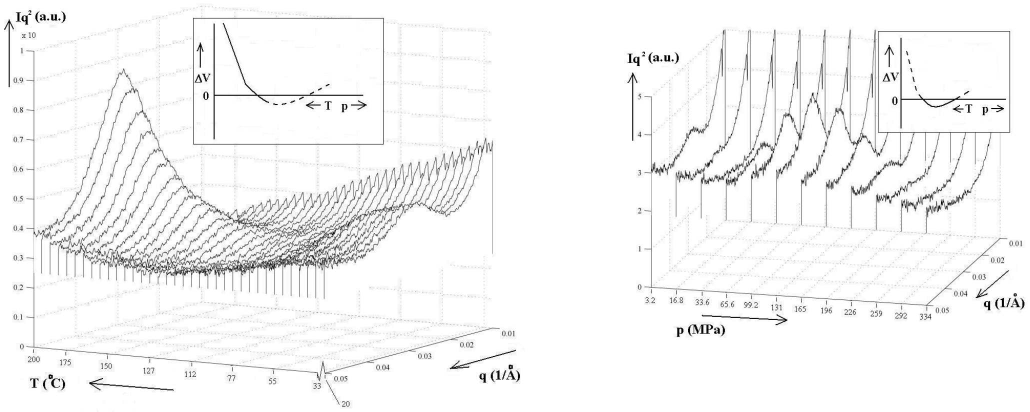

Figure1 Evolution of SAXS patterns during **a**, an isobaric experiment at 32 MPa and **b**, an isothermal experiment at 100°C. As mentioned in the 'Methods' section, the scattered

intensity is proportional to the difference in specific volume between the crystalline and amorphous phase in the semi-crystalline polymer. The variation in specific volume difference in isobaric and isothermal conditions, with decreasing temperature and increasing pressure respectively, is shown in the inlay of the figures. The solid part of the line corresponds to the data presented in the figure; the dashed part of the line refers to data obtained from another set of experiments. From these figures two $\Delta V = 0$ points, one in the lower pressure region and the other in the higher pressure region, can be determined, along with a ΔV maximum positioned between the two $\Delta V = 0$ points. The scattering vector *q* refers to the scattering angle. The z-axis refers to the Lorentz corrected intensity.

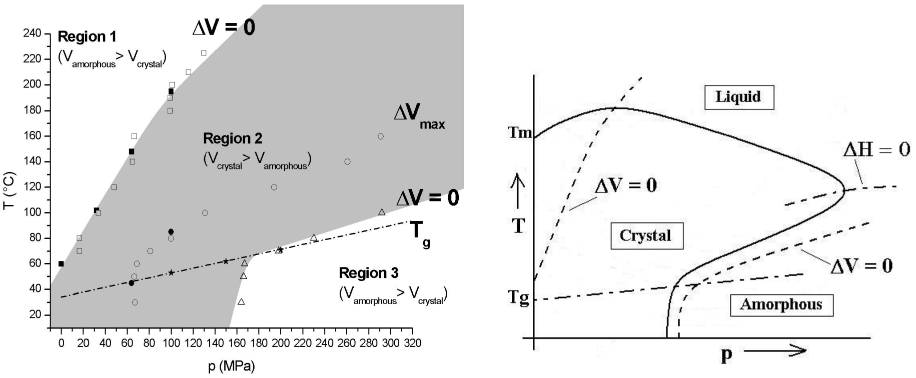

Figure 2 From a series of experiments similar to those shown in figure 1, **a** summarises the obtained $\Delta V = 0$ and ΔV maximum points in a *p*-*T* diagram. Open symbols refer to isothermal measurements, closed symbols to isobaric measurements, the stars are measured glass transition temperatures.The two resultant $\Delta V = 0$ lines divide the *p*-*T* diagram into three regions; regions 1 and 3 correspond to the normal specific volume difference relationship where $V_{amorphous}$ is greater than $V_{crystal}$, the shaded region 2 corresponds to the unusual specific volume difference relationship where $V_{crystal}$ is greater than $V_{amorphous}$. Within region 2, which is bounded by the two $\Delta V = 0$ lines, the ΔV_{max} line is located. The T_g line, obtained from PVT measurements, is shown in this figure. The influence of the glass transition on the trajectory of the second $\Delta V = 0$ line and the ΔV_{max} line is evident. A schematic *p*-*T* phase diagram is presented in **b**; the two obtained $\Delta V = 0$ lines, shown as the dashed lines, govern the trajectory of the phase transition line, shown as a continuous line, in both the normal and re-entrant region of the phase diagram. At the re-entrant point the phase transition line intersects with the anticipated $\Delta H = 0$ line, shown as a dash-dot line.

For details please see published work on these experiments ‘Non-linear changes in specific volume; a route to resolve entropy crisis’ Nico van Ruth and Sanjay Rastogi; *Macromolecules* 2004; *37*(22) pp 8191 - 8194

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