

Chapter 8

Summary and Conclusions

The sub- T_g or secondary relaxations have important applications as they determine the usable temperature range of a glassy material. Below the kinetic freezing temperature of the sub- T_g process, the material in question becomes very brittle. As already discussed in the introduction, the existence of β - process is thought (prior to this work) by many researchers as a general feature of glass forming systems. The deviation on the higher frequency tail of the α - process is also thought to be a characteristic feature of the glass forming systems. What was also not clear is the relation between non-Debye and non-Arrhenius characteristics of the α - process. In order to clarify the above said points, dielectric relaxation measurements above 77 K in a number of glass forming material over a frequency range of $10^6 - 10^{-3}$ Hz were performed. The Differential Scanning Calorimetry (DSC) measurements have been made above 100 K. X-ray diffraction study has also been done on some of the plastic crystalline systems to support the conclusions. All the measurements reported here, are at atmospheric pressure. While dealing with the present report, it should be borne in mind that the measurements correspond to supercooled state, and there is always a danger of collapse of the material to the corresponding ground state. Hence, experimental data may not always be available over the entire temperature range. (this is partly because of non-availability of experimental facility for frequencies above 1 MHz). It was also found that it was not always possible to work with a particular series of chemicals of slightly differing structures, as the na-

ture of supercooling alters completely with slight differences in structure. For example, pentachlorobenzene is a non-plastic crystal, but pentachloronitrobenzene is a plastic crystalline material, that can be supercooled for the necessary information about the glass transition behaviour.

From dielectric study we have obtained the information about the spectral shape, relaxation rate, magnitude of relaxation and their temperature dependence for the α - and β - processes. We have also obtained information about the phase changes by monitoring the dielectric behaviour during the slow heating of the sample over the transition zone. From DSC study, we have obtained the transition temperatures including the T_g s, the associated thermodynamic parameters like enthalpy of transition ΔH and the necessary information regarding the stability of the supercooled phase. Apart from that, we have also obtained (where ever possible) the necessary information regarding the solid to liquid phase diagrams in the case of binary liquids.

Because the β - process is very weak, the range of f_m values usually is limited to 200 Hz-200 KHz (above which it may merge with the α - process). This range of three orders of magnitude is quite narrow compared to that of α - process which spans over at least 10 decades. In addition, the magnitude of the β - process as seen in dielectric measurements decreases with decrease of the temperature. If we look at all the previous reports, most of the reports deal with β - process in binary liquids with Van der Waals interaction, and no information is available on binary hydrogen bonded liquids. Moreover, any amount of incompatibility between the component liquids of the binary may lead to another α - process due to a separated liquid phase. This can always be mistaken for a β - process. Therefore, we thought it necessary to get some information about the homogeneity of binary liquids in their supercooled state. Our results clearly show that two Hydrogen (H)-bonded liquids or two non H-bonded liquids may be treated as compatible if the molecular structures and sizes are not too dissimilar. Some evidence of heterogeneity was found in mixtures consisting of one H-bonded and one non H-bonded liquids. Most

of the H-bonded binary liquids did not show very prominent β - process as opposed to the non-H-bonded mixtures.

To find out the origin of the β - process, we have critically examined the relaxation spectra of rigid dipolar solutes (in smaller quantity) dispersed in a nonpolar glassy matrix. In the case of rigid molecular solutes, such as mono-halogen benzenes, the activation energy (ΔE_β) of the β_s -process is found to increase with decreasing T_g of the solvent, with a corresponding decrease in the magnitude of the β_s -process. In the case of more symmetrical molecular solute viz. *tert*-butylchloride, the change in ΔE_β is not very appreciable. These results emphasize the importance of the size of the cage of the host matrix in the relaxation of the solute molecules. We have also studied the sub- T_g relaxation(s) due to some flexible molecular solutes, viz. 1butylbromide, 1hexylbromide, 1butylacetate and benzylacetate. These observations lead us to the conclusion that the β - process observed in the glassy states of these pure solutes are predominantly intramolecular in nature.

As compared to the structural glasses studied above, the glassy crystalline substances such as the hexa-substituted benzenes (which are composed of rigid molecules) do not show any secondary (or β -) process of observable magnitude. However, the same materials when studied in small quantities in the liquid matrix of *o*-terphenyl (non-polar) indicated a considerable magnitude for the β - process of molecules even below the liquid T_g of these mixtures. This indicates clearly that any contribution to the sub- T_g region from intermolecular process is bound to be negligibly small in these substances, which is a reflection of the (little) free volume available in these systems. Interestingly, our study indicates that a small doping of the crystal of PCNB with PCB increases the hindrance to the rotation of PCNB molecules, indicating that a few defects on the lattice can alter the relaxation strength drastically.

Because of lack of β - process, the corresponding α -process can reasonably be described by a Havriliak Negami (HN) shape function throughout the frequency range. The

absence of any deviation from HN equation on the high frequency side clearly shows that the much advocated high frequency tail as characteristic of glasses is questionable. The relaxation is much broader than that observed in many other plastic crystals, and does not fit into the general scheme of the 'strong and fragile' classification of Angell. This group of substances are also interesting as the α - process is non-Arrhenius especially in the higher members (by molecular weight) of the series. A similar behaviour is noticed in binary systems of hexa- and penta- substituted benzenes. Another very striking feature of these substances is that the relaxation observed (i.e. the α - process) is highly hindered.

Thus, these studies on both structural glasses and glassy crystals clearly show that the β - process due to intermolecular process is observable in structural glasses, and is probably responsible for deviations of the α - process from the Havriliak Negami equation. Encouraged by this observation, one glassy polymer namely poly(cyclohexylmethacrylate) was critically examined for a β - process which had eluded the researchers for a long time. Our results clearly reveal a secondary (β -) process in the temperature range of 293-353 K with an activation energy of 73 kJ/mol., which may be interpreted as due to segmental motion of the main chain.

Scope for further work:

(i). The main problem that we faced during our measurements is the lack of $\Delta\epsilon$ values for the time domain measurements. This is because we are using a linear amplifier for sampling of the data, whereas a logarithmic amplifier will serve the purpose much better, as the loss currents vary by several decades of current.

(ii). Measurements on the higher frequency side above 1 MHz., will improve the quality of the data.

(iii). There are many other systems which can be brought under glasses and there is a lot of scope for further work in these areas.

(iv). Temperature variation of the X-ray pattern of the hexa-substituted benzenes will give a much wider scope for understanding these materials, especially if one can make measurements on single crystals grown instead of the powder samples used in the present study.

