

PREFACE

Glass is defined as a system where the structural relaxation time on lowering the temperature at a constant pressure (or vice versa) is comparable to the experimental time scale and hence, the material no longer responds to the external stresses. In other words, the material is stuck in a non-equilibrium state below this temperature T_g . As per this general definition, many materials qualify as glasses, we find that there are various types of glasses some of which are categorized as (i) structural glass (or liquid glass) formed by supercooling a liquid including organic glasses, inorganic glasses and polymers; (ii). Glassy crystals formed by supercooling the orientationally disordered crystalline phase; (iii). Glassy liquid crystals formed by supercooling the partially ordered liquid meso-phases and (iv). spin glasses which are like the above 2nd group but are related to the magnetic spins. In addition to the other glassy materials some are (some what) it is doubtful to be clubbed as glasses. Groups (i) & (iii) are industrially important from application point of view, but groups (ii) & (iv) are interesting from academic point as they are much simpler because of the involvement of only one degree of freedom. In relaxation experiments the glass transition can be seen as a major (primary or α -) relaxation which gets arrested at the glass transition temperature T_g , but often (secondary or β -) relaxations of much smaller magnitude are found below T_g the origin of which is of current interest to glass physicists. So also of interest the non-Debye nature of the primary relaxation and its connection to the deviation from Arrhenius type of temperature dependence. Present work, focuses on the critical examination of these two relaxations in glasses of group (i) & (ii) using dielectric relaxation (frequency range of $10^6 - 10^{-3}$ Hz and differential scanning calorimetry (DSC) down to liquid nitrogen temperature. In the case of the latter group of materials, use has been made of the X-ray diffraction for the study of the crystalline structures at room temperature. One half of the research work deals with the binary liquids of the group (i), and the second

half is related to the work on group (ii) materials.

The thesis as such consists of eight chapters, where chapter 1 starts with a brief survey of the developments in glass physics. It also discusses the dielectric relaxation in general as this particular technique is the most used technique for the study of glasses.

Chapter 2 is devoted to the description of the experimental techniques used in the study. A brief account is given on the DSC and dielectric techniques. The X-ray diffraction technique is also discussed very briefly as a supporting technique.

Chapter 3 deals with the study of homogeneity in some binary liquids [mostly hydrogen (H-) bonded liquids] in the supercooled liquid state. The frequency dependence of the relaxation spectra and the temperature dependence of the relaxation process have been critically examined for the α -process and hence, for the heterogeneity. Solid-liquid phase diagrams are also determined using DSC (where ever possible) to support the conclusions.

Chapter 4 deals with an exhaustive study of the relaxation in binary liquids of non-H-bonded systems, with its primary emphasis on resolving the issue of the origin of β -relaxation. It is well known that rigid dipolar solutes (in small quantities) dispersed in a nonpolar glassy matrix exhibit a sub- T_g (or β_s -) relaxation due to the solute often designated as Johari-Goldstein relaxation which is intermolecular in nature. In this chapter, we report the results of our study of such a sub- T_g process in a wide variety of dipolar solutes in different glassy systems using dielectric relaxation technique. The T_g of these solutions are determined using DSC. The solvents used in this study are *o*-terphenyl, isopropylbenzene and methylcyclohexane. The solutes chosen include both rigid and flexible molecular liquids. These results of our study emphasize the importance of the size of the cage of the host matrix and the flexibility of the solute molecule, in the sub T_g - relaxation.

Some (not all!) hexa-substituted benzenes are known to exhibit molecular rotation in their crystalline phase, but this phenomenon is not very well understood. In this con-

text, we have critically examined two materials, namely pentachloronitrobenzene and 2,3,4,5,6-pentabromotoluene over a wide range of temperatures, using dielectric spectroscopy and differential scanning calorimetry (DSC) to ascertain the nature of the above said relaxation. The results of this study are given in chapter 5. A relaxation process is found in the crystalline phase, which is slightly non-Arrhenius in its temperature dependence in the former and deviation from Debye behaviour has been found in both the samples. This behaviour is similar to that of the primary (or α -) relaxation found in glass forming materials. The sub- T_g relaxation data do not indicate any secondary (or β -) process (of measurable magnitude). However, the same materials when studied in small quantities in the liquid matrix of *o*-terphenyl (non-polar) exhibited considerable magnitude for the β -process of molecules even below the liquid T_g of these mixtures. The results are discussed in the context of the glass transition phenomena of the above materials.

Chapter 6 deals with glass transition phenomena in two-component plastic crystals most of which are hexa-substituted benzenes. In addition to the dielectric and DSC studies, we have used X-ray diffraction to study the materials. This relaxation process is similar to that of the primary (or α -) relaxation found in glass forming materials and is clearly non-Arrhenius in its temperature dependence. The sub- T_g relaxation data do not indicate any observable secondary relaxation. Because of this, the corresponding α -process can reasonably be described by a Havriliak Negami shape function throughout the frequency range. 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. The solid-liquid phase diagrams are determined to support the conclusions. It is shown that the relaxation leading to the glass transition phenomenon in these systems is a highly hindered.

Chapter 7 discusses the various relaxation processes in poly(cyclohexylmethacrylate),

a glassy polymer. Though it is slightly outside the scope of the present work, an interesting finding is the detection of a secondary (β -) process in the temperature range of 293-353 K with an activation energy of 73 kJ/mol. [This process is in addition to the α - and γ - processes found by earlier workers]. A brief report of our study on this system is given in this chapter.

Chapter 8 gives a brief summary of the results and conclusions.