Multiple relaxations in small-molecule solids

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The observation of three dielectric loss peaks in small molecular solids is reported for the first time. These are labelled α, β and γ, respectively. A relationship is proposed between the occurrence of multiple relaxations in these solids and in polymers.

INTRODUCTION

When dielectric loss in polar polymers is measured as a function of temperature, several relaxation peaks are usually observed[1]. In amorphous polymers a huge loss peak occurs around, and above, the glass–rubber transition temperature, T_g, and at least one more peak occurs in the glassy region. The glass–rubber transition relaxation is called the primary relaxation, while the other relaxations occurring below T_g are called secondary relaxations. Usually the peak occurring at the highest temperature is termed α. The next peaks are labelled β, γ, δ, etc., in order of decreasing temperature. In amorphous polymers the α peak is the one corresponding to the glass–rubber relaxation, while the β peak is the first loss peak in the glassy region.

Organic liquids such as benzene, *cis*-decalin, cyclohexanol, bromobenzene, chlorobenzene, etc., or their mixtures, may form glasses if cooled rapidly through their freezing points[2]. Supercooled liquids can also be obtained from non-glass forming crystallizable liquids of small molecules[3]. The small molecule glasses resemble amorphous polymers both in being of organic origin and in having a glass transition[2], whose temperature, T_g, depends upon the composition of the system.

Johari and Goldstein[2] have studied dielectric loss in a large number of glasses formed by rigid and flexible small molecules in a polar or non-polar solvent. Each of their small molecules contained one or two similar dipolar groups, such as a bromine or a chlorine atom, in a mono- or disubstituted benzene molecule. The result of their investigation was the observation that all their molecular glasses showed a strikingly similar dielectric behaviour. There is a huge α peak above T_g (at the measuring frequency used) and a β region in the glassy state, the intensity of which is 10 to 100 times smaller than that of the α peak. The Johari–Goldstein measurements show that the small molecule systems resemble polymers, not only in being organic in nature and having a T_g, but also in that the characteristics of their dielectric properties are similar to those of polymers.

However, although both the α and the β peaks are observed in small-molecule solids, no γ relaxation has so far been reported for these systems. We report the observation of the γ process in a number of specially prepared small molecule solids. An important link is then proposed concerning the possible origin of multiple relaxation in polymers and in small molecule solids.

EXPERIMENTAL

Experimental samples

A number of dipolar molecules dissolved in the non-polar *cis*-decalin were studied. These included cyclohexanol, *ortho*-chlorophenol, *meta*-nitrotoluene, a mixture of *ortho*-chlorophenol and *ortho*-nitrotoluene, and a mixture of phenol, *m*-nitrotoluene, *p*-chlorophenol, *o*-chlorophenol and *p*-nitrophenol, all dissolved in decalin.

The molecules studied by Johari and Goldstein contained only one type of dipole, e.g. bromobenzene, dibromobenzene, etc. In our work, all, except cyclohexanol, have two (or more) different types of dipole attached to the same molecule, e.g. $-NO_2$, $-OH$.

Figure 1 shows the structural formulae of the small molecules used in this study. Phenol, *p*-chlorophenol and *p*-nitrophenol are crystalline solids at room temperature. They have a temperature-dependent solubility in decalin. If the crystals are warmed above room temperature they melt into liquid, and can therefore mix more easily with decalin. As the temperature is reduced more and more of these crystals fall out of solution, forming separate phases. This presented us with a method of simulating the partially crystalline state

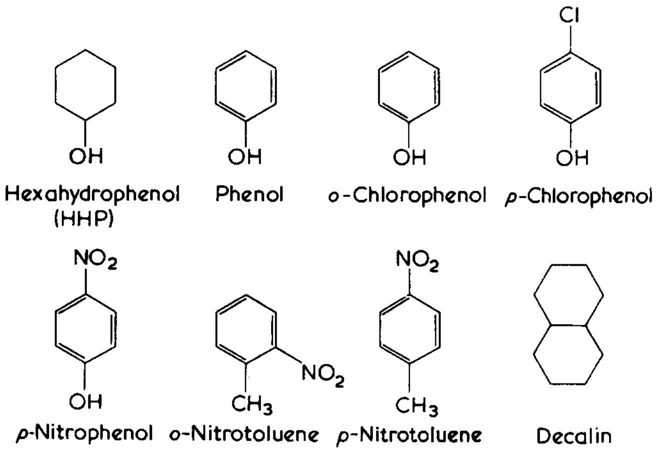

Figure 1 Structural formulae of the small molecules used in this study

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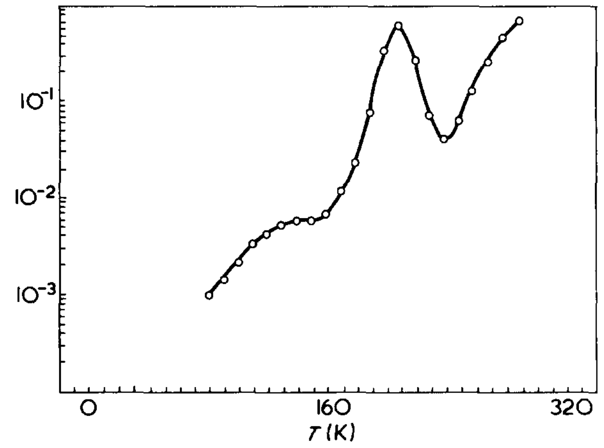

Figure 2 Plot of tan δ against temperature T (K) at 1 kHz: 50 vol % HHP

that is often obtained in polymeric solids, which often exhibit the γ relaxation. In studying the frozen solutions of these solids in decalin we were interested in finding out whether the crystals that fell out of solution would exhibit separate loss peaks.

After preparing the mixtures, the following visual observations were carried out: each liquid, or mixture of liquids, was put in a test tube and placed in a flask of liquid nitrogen to cool it. In glass forming systems, the liquid was found to become more and more viscous, as the test-tube was gently shaken under liquid nitrogen, until it gradually became a clear (glassy) solid. On taking it out of the liquid nitrogen, the solid became softer and softer, as its temperature increased, until it gradually became liquid again, without showing a melting point. A non-glass forming mixture showed a distinct freezing point, the whole mixture turning white as crystals fell out of solution to form separate crystalline phases. The results of the low temperature tests were:

(i) decalin itself is glass forming;

(ii) cyclohexanol is glass forming. Its mixtures, in all proportion, with decalin are also glass forming;

(iii) a 25 vol % *o*-chlorophenol in decalin mixture can be cooled down to the solid state with a small phase separation;

(iv) a 25 vol % mixture of *o*-chlorophenol and *o*-nitrotoluene (12½% of each) in decalin phase-separates;

(v) a mixture of equal volumes of phenol, *m*-nitrotoluene, *p*-chlorophenol, *o*-chlorophenol and *p*-nitrophenol which were mixed with a 50 vol % of *cis*-decalin, also phase-separates. We shall refer to this mixture as the 'concoction'.

All the molecules with two dipoles, shown in *Figure 1*, are very powerful solvents, which must be handled with care. They also give off poisonous vapours.

Apparatus and procedure

The apparatus used, consisting of a General Radio type 1615A transformer ratio-arm bridge and a 3-terminal dielectric cell, has been described elsewhere[4]. In our work the cell was modified into a tank in order to take liquids. Two holes were drilled through the top electrode, and a pipe, through which the liquid mixtures were poured into the tank, was soldered on to one of the holes. The other hole permitted excess fluid to flow out of the cell, ensuring that the tank was completely filled, and electrode contact with the dielectric material to be measured was good, even in the solid state. The top and the bottom electrodes were, in the mounted form, separated by a rubber 'O' ring, which provided the outer walls of the tank. To ensure that it did not interfere with the proper working of the cell, the 'O' ring was chosen wide enough to enclose the guard electrode.

To transfer the mixtures into the dielectric tank, hypodermic syringes were used. All volumetric measurements were done using syringes and burettes.

RESULTS

Figures 2–6 show plots of tan δ against temperature, all at 1 kHz. Cyclohexanol (50 vol %, *Figure 2*), shows both an α relaxation in the temperature range 160 to 240K, and a β relaxation below 160K. This mixture did not phase-separate.

Figure 3 for a 25 vol % *o*-chlorophenol in decalin mixture also shows two loss peaks in the solid state: an α peak between 180 and 240K, and a β process below 180K.

The 50 vol % *m*-nitrotoluene/*cis*-decalin mixture also shows two loss peaks (*Figure 4*).

Figure 5 for 12½ vol % *o*-chlorophenol and 12½ vol % of *o*-nitrotoluene in *cis*-decalin, and *Figure 6* for the 'concoction', are more interesting. They show three loss processes below

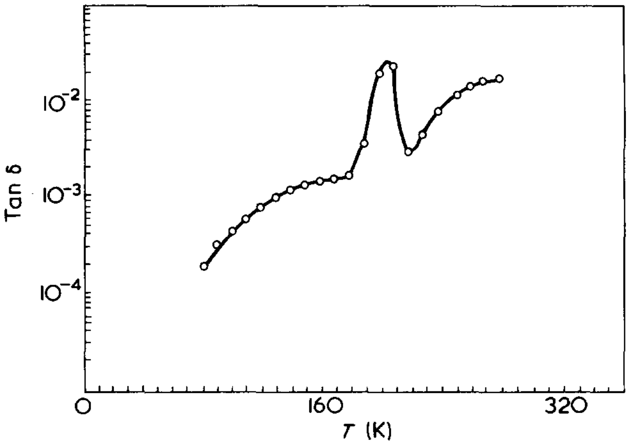

Figure 3 Plot of tan δ against temperature T (K) at 1 kHz: 25 vol % *o*-chlorophenol

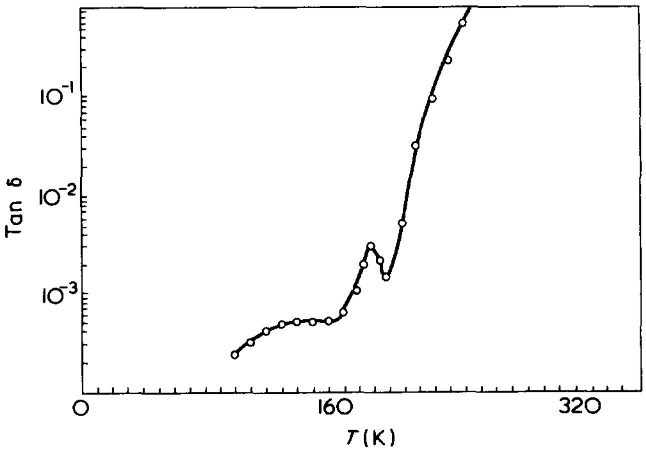

Figure 4 Plot of tan δ against temperature T (K) at 1 kHz: 50 vol % *m*-nitrotoluene

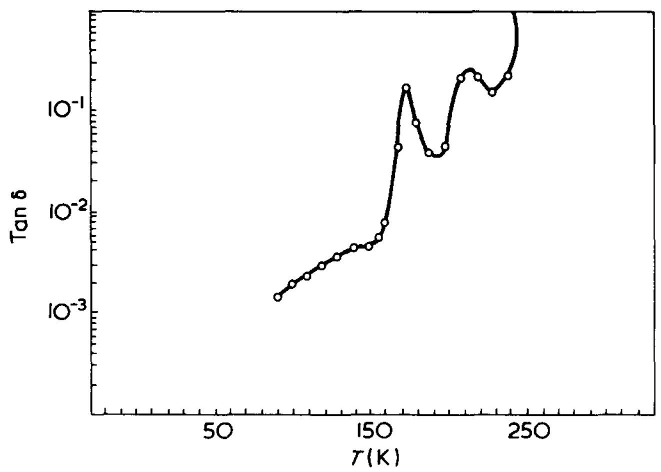

Figure 5 Plot of tan δ against temperature T (K) at 1 kHz: 12.5 vol % *o*-chlorophenol, 12.5 vol % *o*-nitrotoluene

the liquid state. In *Figure 5* the α process occurs around 230K and the β process around 185K; and we observe an additional process below 160K. This third loss process, following standard nomenclature, was termed γ.

Similarly for the 'concoction': an α process occurs above 250K as a shoulder to the liquid state relaxation. A small β peak occurs between 240 and 200K, while a huge γ peak occurs between about 205 and 140K.

In all the above measurements no additional loss peaks were observed down to 4.2K.

DISCUSSION

We discuss the above results by first noting the following:

(i) The standard nomenclature α, β, γ, etc. for loss peaks makes no reference to the molecular process(es) giving rise to the peaks. For example, the highest temperature loss peak in the amorphous polysulphones is the one associated with the glass–rubber relaxation. This peak is termed α. On the other hand, partially crystalline polymers exhibit a loss peak (associated with the crystalline phase) in the temperature range between the T_g region and the melting region. In this case the highest temperature peak is termed α, while the glass–rubber relaxation becomes the β relaxation and the glassy state relaxation becomes the γ relaxation. Thus 'α peak' simply means the peak that occurs at the highest temperature, the 'β peak', that which occurs at the next lower temperature, and so on.

(ii) The positions and magnitudes of dielectric loss peaks observed in small molecule solids are affected by plasticization in exactly the same way as peaks in polymers[2,5]. The mixing of different small molecules which are described above is, in effect, plasticization.

(iii) Since we wish to correlate our results for monomeric solids with those found for polymers, it is instructive to note that some purely amorphous polymers, e.g. the higher methacrylates, exhibit a γ process.

(iv) A note about the experimental samples: the samples are liquids above and just below room temperature. They are solids in the low temperature range covered in the present study. Now it is a well known fact that in any one substance liquid state relaxations give rise to loss peaks of much higher magnitude than those occurring in the solid state. This is one possible explanation of the huge losses measured in the liquid state near and above room temperature (see above).

Now coming to the results presented above, it is interesting to observe that, while all the glass forming samples exhibit only two loss processes, the multiphase systems exhibit a third loss process (*Figures 5* and *6*). Since the γ process appears only in those solids which exist in more than one phase, it is logical to attribute the appearance of more than two loss processes to the multiphase nature of the dielectric mixture-solids.

The dielectric behaviour described in the foregoing is seen clearly to parallel that of polymers. A possible relationship is therefore strongly suggested between the occurrence of multiple relaxation peaks in partially crystalline and amorphous polymers on one hand, and in glassy and multiphase monomeric solids on the other: it is apparent that 'additional phases contribute additional environments, in which (permanent) electric dipoles relax, giving rise to additional loss peaks'. The liquid state, the rubbery state, the glassy state and the crystalline phase are such environments. Thus the 'environment' hypothesis, as stated above, applies to both the Johari–Goldstein type of glasses (including the glasses studied in this work) and the multiphase solids of *Figures 5* and *6*. It also covers all types of polymers, amorphous or partially crystalline.

The last statement requires further qualification. There are certain purely amorphous polymers which exhibit three loss peaks, and which therefore do not appear to conform to the hypothesis. The higher methacrylates are mentioned above. Other very interesting examples which were recently investigated by the present author[5] are polysulphone and polyethersulphone. These two polymers have two transition temperatures[6], and a γ peak is found around the lower transition temperature.

The occurrence of the γ peak in an amorphous higher methacrylate can be explained as follows: the side chains behave physically as though they were independent polymer chains. It is a well known experimental fact that such side chains have a plasticizing effect on the polymer: if the side chain length is increased, T_g is lowered. The same effect is produced by increasing the amount of plasticizer in an amorphous polymer. Thus we may take the view that the 'quasi-independent' side chains provide an additional environment, in which a certain assembly of electric dipoles can relax, giving rise to additional loss peaks.

The hypothesis can be extended to the polysulphones. The author has demonstrated in ref 5 that, by increasing the crystallinity of polysulphone by heat treatment, the magni-

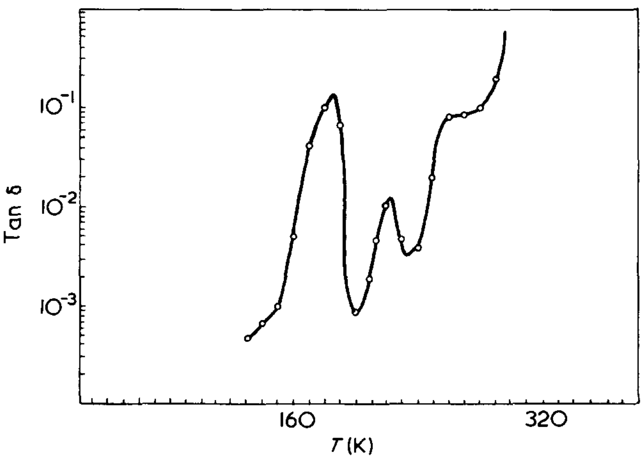

Figure 6 Plot of tan δ against temperature T (K) at 1 kHz: 50 vol % 'concoction'

tude of the γ losses also increases. This seems to suggest that both the existence of a second transition at lower temperatures and the occurrence of a γ peak around that transition region could be associated in some way with the presence of a small degree of crystallinity in the polymer.

COMMENTS

Although we have seen that the occurrence of a γ peak in the monomeric solids stems from the multiphase nature of the solids, nothing suggests that the γ peak itself arises from the additional crystalline phase. All we can say, by comparison with the Johari–Goldstein type of solids and the partially crystalline polymers, is that two of the three peaks originate from relaxations that take place in the amorphous component of the multiphase solid, but which two, we cannot tell without further experimentation. However, the task of discovering the peak which arises from the crystalline phase should be fairly simple: by repeating the experiments and systematically varying the crystalline component, one can observe which of the three peaks has its magnitude (and/or position) affected most.

As a final remark we wish to point out that certain two phase systems are capable of showing dielectric loss peaks arising from the Maxwell–Wagner interfacial polarization. This loss is not usually observed in pure partially crystalline polymers, such as poly(ethylene terephthalate) (PET). Since our own samples were of high purity, free especially from metallic contaminants, we believe that our measurements did not suffer from Maxwell–Wagner effects.

CONCLUSIONS

In the important works of Johari and Goldstein, Williams and Hains, and others, none of the samples studied showed more than two loss peaks. To the best of our knowledge no γ process has as yet been reported for monomeric solids. The purpose of this paper is therefore two-fold: to announce the first observation of γ losses in small molecule solids, and to propose a unified theory which attempts to correlate the occurrence of multiple relaxations in polymers and in monomeric solids. It is also important to note the fact that the theory presented here de-emphasizes the role played by the 'chain' nature of polymers. What emerges from our comparison of polymeric and monomeric solids as of fundamental importance to the relaxation problem is the presence of different environments in which electric dipoles relax.

In conclusion it should be pointed out that one other significance of our findings is that it is now strongly suggestive that the molecular mechanism(s) giving rise to dielectric loss are the same for monomeric as for polymeric solids. The author is presently in the process of working out a detailed mathematical theory designed to account for dielectric relaxation in both polymers and monomeric solids. The main formula of the theory, which has already been published[7], has been applied successfully to both α and β peaks of both polymers and monomers.

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