Survey of Multiple Mechanical Transitions in Polymers in Relation to Thermal Transitions

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Abstract

Dynamic mechanical, dielectric loss and broadline NMR studies carried out in recent years by many investigators between 4.2 and 600 K. reveal that most polymers exhibit a small number of broad but discrete loss peaks which presumably arise from different modes of molecular motion in the side groups or subgroups of the backbone polymer chain. While the two main transitions, melting, \( T_M \), and glass transitions, \( T_G \), are readily found by all types of thermal analysis, the weaker secondary transitions and relaxations are not always so apparent. This survey is concerned in part with the dependence of multiple relaxations on polymer structure and in part on the apparent failure of thermal methods to reveal weaker transitions. These secondary transitions exhibit discontinuities in thermal expansion, \( \Delta \alpha \), and compressibility, \( \Delta \chi \), and have positive pressure coefficients, \( d T/DP \), but do not exhibit a discontinuity in specific heat, \( \Delta C_p \), as would be expected from the Ehrenfest equations. We present evidence for a third-order transition, \( T_3 \), (near the \( \beta \) transitions in atactic polystyrene and polyvinylchloride) from heat content measurements. Dynamic mechanical transitions for some polymers above \( T_G \), especially styrene-butadiene rubbers and polytetrafluoroethylene, are also reflected by a third-order transition in heat content. We have not found a correlation between the intensity of the thermal \( T_3 \), namely, \( \Delta C'_p \), and the intensity, \( G'' \), of the corresponding mechanical loss peak. Finally, we suggest tentatively that weaker secondary transitions may show up in thermal conductivity measurements. There remains the unresolvable paradox that some secondary mechanical relaxations appear as second-order transitions in V-T or V-P plots but as third-order transitions judged by H-T determinations.

I. Introduction

Schmieder and Wolf (1) found that most polymers exhibit a small number of discrete but relatively broad dynamic mechanical energy loss peaks when measured with a torsion pendulum at a frequency of 1 Hz over a broad range of temperatures. They showed that each polymer has a fairly characteristic mechanical spectrum which can be changed by chemical alteration, copolymerization or thermal history. Figure 1a is a composite schematic plot for polystyrene based on various literature sources (2). This curve will shift to higher temperatures as the frequency is increased but at a different rate for each loss peak. Figure 1b is a so-called relaxation map for the four glassy loss peaks in atactic polystyrene.

Dielectric loss data, if obtained over a wide enough frequency range, will also reveal different energy loss peaks, especially for the more polar polymers. Likewise NMR techniques are used: both the broadline line-
width and the spin lattice relaxation methods. There are a number of excellent review articles for dynamic mechanical (3-9), dielectric (7) and NMR (10-11) data illustrating the wealth of information currently available on polymers.

If a relaxation map, such as indicated in Figure 1b, is prepared using dynamic and dielectric loss data as well as NMR relaxation times, the points for all three methods tend to fall on a common line for a given relaxation. This suggests that the same subgroup molecular motion is involved to greater or lesser extents in all three methods. McCall (12) has compiled a number of such relaxation maps.

General Considerations: It is possible to make a few generalizations about multiple relaxation phenomenon:

1. With temperatures expressed in °K., \( T_M \approx 1.5 T_G \) for a wide variety of polymers (13), although there are many deviations from this average (14). One possible interpretation is that the same kinds of subgroup molecular motion occur at \( T_M \) and \( T_G \) but \( T_G \) is lower because the range of order is much shorter in the glass than in the crystal (15). This implies that the structure of the amorphous glass is an imperfect replica of the crystal structures.

2. There is generally a secondary transition commonly designated as the \( \beta \) process, lying just below \( T_G \) such that \( T^\beta = 0.75 T_G \) (16). This implies that the \( \beta \) relaxation is a precursor for the glass transition and involves the same kinds of motion.

3. Eby has shown (17) that the frequency dependence of relaxation for many polymers follows an equation of the type

\[
f = (kT/2\pi h) \exp\left( -\frac{\Delta H^\ddagger}{R T} \right) \exp\left( \frac{\Delta S^\ddagger}{R} \right)
\]

where \( \Delta H \) and \( \Delta S \) are the activation enthalpies and entropies. He further shows that \( \Delta S^\ddagger/\Delta H^\ddagger = 4\alpha \) where \( \alpha \) is the coefficient of cubic expansion. This relation is found to hold for a number of polymers. Next, by using the relation \( \Delta V^\ddagger = 4\alpha \Delta H^\ddagger \), where \( \alpha \) is the compressibility, he calculates activation volumes. From this he deduces that 16 to 29 monomer units are involved in the glass transition and 2 to 5 monomers in secondary relaxations. Hence Equation 1 provides a connection between dynamic mechanical loss and thermal properties.

4. Starkweather (18) has shown for a number of semi-crystalline polymers with extended chain crystals that the relaxation map (similar to Fig. 1b) is such that all lines intersect at a common point, which is the melting point of the polymer at a frequency of \( kT/2\pi h \approx 1.2 \times 10^{12} \text{ Hz} \). He finds that helical chain polymers deviate from this rule which may account for the frequency of intersection in Fig. 1b occurring at \( 10^9 \text{ Hz} \).

5. Another convenient generalization is that of Simha and Boyer (19), namely,

\[
\Delta \alpha T_G = 0.113
\]

where \( \Delta \alpha = \alpha_L - \alpha_G \), the change in coefficient of cubic expansion at \( T_G \). The constant may be thought of as the amount of free volume at \( T_G \). A more precise expression has been derived by Simha and Weil (20).

6. Finally, we wish to show for later use several common forms of the Ehrenfest relationship which are commonly applied to glass trans-