Polymers in Solid State

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The vast majority of all polymers produced in the world are utilized in their solid form—that is, as a classic material. Thus, a discussion of the solid-state properties of polymers, their morphology, and the impact of this and their properties on their applications is an essential part of this book.

Polymers in their solid state can be roughly divided into three categories, of which, in practice, only two—the *amorphous* and the *semicrystalline* states—play a role (◘ Fig. 4.1). The single-crystalline state is of academic importance only.

Many polymers cannot crystallize. They exist in an amorphous state, similar to that found, for example, in window glass. Substances with a low molar mass can also solidify to amorphous solids, particularly complex molecules, such as certain pharmaceuticals. Water can be shock-frozen to an amorphous solid. However, for substances with a low molar mass this state is very unstable. Thus, many low molar mass amorphous phases tend to re-crystallize, that is, transform into a crystalline state corresponding to the thermodynamic equilibrium.

Under certain circumstances, however, polymers can at least partially crystallize. The crystallization of polymers is a very complex process because the long chains must arrange themselves into a defined crystalline structure. Because the intertwining of the polymer coils—so-called *entanglements*—are an obstacle to crystallization, this is a relatively slow process. Additionally, crystallization of the polymer is usually imperfect, resulting in the creation of a partially crystalline or semicrystalline material in which both amorphous and crystalline domains coexist.

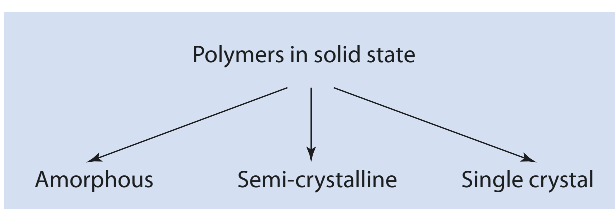
Polymeric single crystals can be obtained by performing crystallization from very dilute solutions. However, these are more of an academic interest and without importance for industrial polymer chemistry.

As is known from the analysis of substances with a low molar mass, amorphous and crystalline areas can be easily distinguished, for example, by X-ray spectroscopy. Here, one observes so-called halos from the amorphous phases, whereas the crystalline phases appear as peaks in an X-ray diffractogram. An analysis of the phase transitions upon heating a sample also provides valuable information about whether a sample is amorphous or crystalline. The morphology of a solid greatly influences the properties (e.g., the optical, mechanical, and thermal properties) of products made from polymers.

Before we discuss this in more detail, a number of fundamental physical concepts need to be introduced. The mechanical properties of a solid are measured in terms of its so-called "moduli." These include *Young's modulus* for uniaxial extension, and the *shear modulus* for shear deformation of a test piece (◘ Fig. 4.2).

According to Hooke's law, the uniaxial stress of a test piece is given by

$$\sigma = E \cdot \varepsilon \tag{4.1}$$



◘ **Fig. 4.1** Schematic representation of the morphologies of polymeric solids

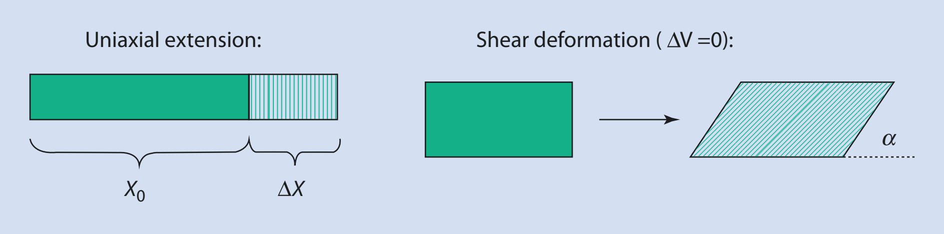


Fig. 4.2 Schematic representation of the shape change under uniaxial stress by Δx or shear stress by a shear angle α

This means that the applied stress σ (force per unit area) is proportional to the elongation of the test piece ε. The proportionality constant E is referred to as the Young's or E-modulus. Whereas, if a test piece is deformed under shear, the stress σ_s—again defined as the force applied to a given area—is proportional to the tangent of the shear angle α. In this case, the proportionality constant is again referred to as a modulus, in this case, the shear modulus G:

$$\sigma_s = G \cdot \tan \alpha \tag{4.2}$$

4.1 Phase Transitions in Polymeric Solids

As mentioned above, amorphous and crystalline solids can be differentiated by their thermal phase transitions. When crystalline substances are heated, a melting point is observed in analogy familiar from low molar mass crystals. At the melting point, an abrupt rearrangement occurs in the material. Below the melting point, there is crystalline order and this disappears during the melting process. This is the reason why the properties such as volume undergo a stepwise change at the melting point (Fig. 4.3).

Thermal transitions of this type are referred to as *first-order phase transitions*; they can be assigned an enthalpy, in this case, the enthalpy of melting. Because of the structural change on melting, the entropy of the melted phase is greater than that of the crystalline phase so that a ΔS can be defined for this transition as well as a corresponding free enthalpy ΔG.

In contrast to this, amorphous solids are as disordered in the solid phase as they are in their melts.[1] Vitreously solidified amorphous states are supercooled, disordered melts or glasses. This means that they undergo no structural change when heated and transitioning to the liquid phase. This process, which corresponds to the melting process of crystalline compounds, is referred to as the *glass transition*, and the associated temperature T_G as the *glass transition temperature*. If we now consider the dependence of, for example, the volume on the temperature (Fig. 4.4), we can see that indeed the thermal expansion, i.e., the slope of this line, is different above and below T_G, but that no abrupt change of volume occurs at the glass transition.

This is because the structure of the material is identical—i.e., disordered—above and below T_G.

1 On closer inspection, there are subtle differences here as well, which are, however, not further discussed in the present book.

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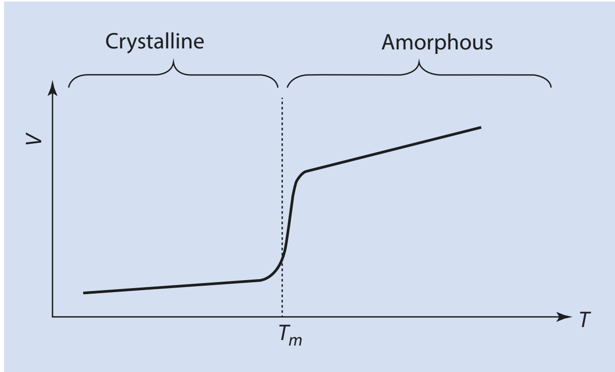

Fig. 4.3 Sketch showing the change of volume with melting. T_m melting temperature

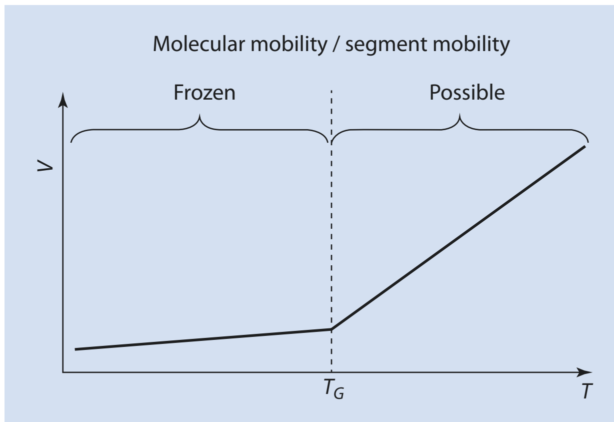

Fig. 4.4 Sketch showing the volume change at a glass transition. T_G glass transition temperature

Transitions of this type are referred to as *second-order transitions*. In contrast to first-order phase transitions, there is no transition enthalpy required here because no enthalpy needs to be invested to break a crystal lattice. Nor is there any substantial change in entropy, because both states are approximately equivalent in structure. As a consequence, no ΔG can be assigned to a second-order transition. However, abrupt changes in other properties, such as heat capacity, are observed. Because the melt generally has more translational degrees of freedom above T_G, stimulation requires more enthalpy and the addition of a larger amount of heat is required to raise the temperature by one degree. Hence, a sharp rise in heat capacity occurs across a glass transition, which can be measured as Δc_p.

Semicrystalline polymers consist, as already mentioned, both of crystalline and amorphous areas. In principle, polymers are, aside from the above-mentioned exceptions, never crystalline to 100 %, so there is a co-existence of crystalline and amorphous domains. Thus, when heating of a semicrystalline or partially crystalline polymer, both a glass transition at a temperature T_G and a melting process at a temperature T_m can be observed (Fig. 4.5).

It is always the case that T_G is lower than T_m. This should be obvious. If it were not so, a substance would, when cooling from the melt, solidify to a glassy solid at the higher T_G and would then have to crystallize below T_G. However, below T_G the molecules are insufficiently mobile to allow the reorientation necessary for crystallization.

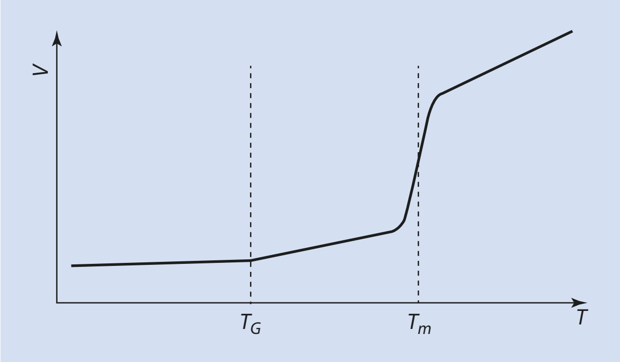

Fig. 4.5 Sketch showing the volume change at the glass transition and the melting temperature of partially crystalline polymers. T_G glass transition temperature, T_m melting temperature

4.2 Methods for the Determination of T_G and T_m

Below, the most important methods for determining the glass transition temperature and the melting temperature are presented. These can be classified according to static and dynamic procedures.

4.2.1 Static Procedures

Static procedures are based on the measurement of a material property, such as density, volume, heat capacity, or refractive index, as a function of temperature. In these procedures, the sample is slowly heated to maintain equilibrium, and the change of the respective intrinsic property is measured. Examples are dilatometry (▶ see Sect. 5.3) and the measurement of the refractive index, where discontinuities in the curves of the volume or refractive index can be observed as a function of temperature at the glass transition temperature (Figs. 4.5 and 4.6, respectively).

However, in general, the preferred method is *differential scanning calorimetry* (DSC). The principle of DSC is that a sample is heated at a constant rate and the heat flow required to maintain this defined rate is measured. The heat flow correlates with the heat capacity c_p of the sample, i.e., the amount of heat necessary to produce a given change in temperature. As mentioned above, we observe an abrupt increase in heat capacity c_p at the glass transition temperature, whereas, at the melting point the latent heat ΔH_m (the heat of melting) is required. Thus, the temperature of the sample does not change during the melting process, even though heat is absorbed. This is valid until the moment when the crystal lattice is completely "broken" and the transition to an isotropic melt has occurred. Formally, the heat capacity tends to infinity during the melting process so that a peak results in the DSC (Fig. 4.7). From the area under this peak the heat of melting for the sample can be calculated. Alternatively, if ΔH_m is known, the degree of crystallization can be determined.

DSC is a method frequently used both in industrial and academic laboratories. Its advantages lie in the very small amount of sample material required (approximately 5 mg). Furthermore, the technology is well established and the available devices are quite robust and easy to use. In particular, sample preparation is also relatively simple. The sample has to be placed in a measuring vessel—usually a disposable aluminum pan.

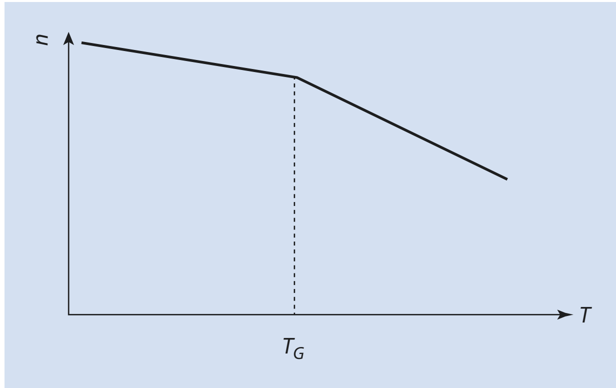

Fig. 4.6 Refractive index of a polymer as a function of temperature. T_G glass transition temperature

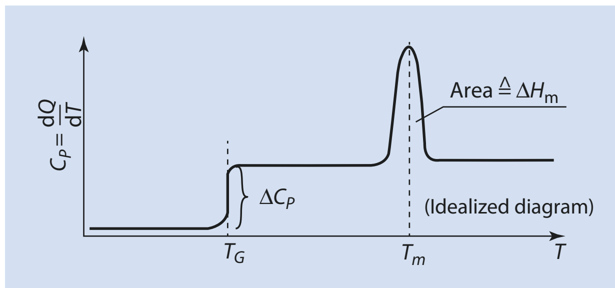

Fig. 4.7 Heat capacity as a function of temperature on heating for semicrystalline polymers as observed with DSC

The disadvantages of DSC lie in its limited sensitivity. Not every phase transition is resolved. Moreover, the measuring curve is sometimes difficult to interpret. Thus, the curve in Fig. 4.7 is an idealized DSC curve rarely generated by real polymers. Measured DSC curves are often not parallel to the axes, but arched or curved, so that it is sometimes hard to discern the individual transitions correctly.

DSC provides the possibility of varying the heating rate and *hysteresis* can be observed for first-order phase transitions. Particularly large hysteresis is observed for the crystallization peak, associated with the transition from a melt to a crystalline phase. This is because crystallization requires the formation of crystal-nuclei. This process requires a certain time so that, at a very high cooling rate, the crystallization temperature can be significantly undershot.

4.2.2 Dynamic Procedures

In *dynamic mechanical thermal analysis* (DMTA), a sample is subjected to periodic sinusoidal, mechanical stress, for example, by a periodic tensile or torsional movement. This is accomplished at a frequency f and with a stress σ. During such measurements it is often observed that the deformation of the material is delayed in time with respect to the applied stress, so that the periodic oscillation of the material and the mechanical excitation are phase-shifted (Fig. 4.8).

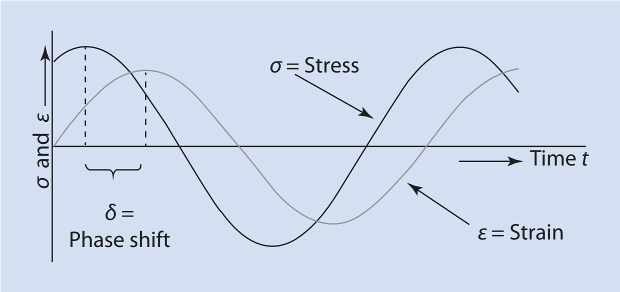

Fig. 4.8 Periodic progression of stress σ and strain ε

The angle of the phase shift is referred to as δ. Such a periodic oscillation can be—as known from mathematics—represented in the form of complex numbers. Thus, we can define the strain ε as

$$\varepsilon = \varepsilon_0 e^{-i\omega t} \tag{4.3}$$

and the stress σ as

$$\sigma = \sigma_0 e^{-i\omega t + \delta} \tag{4.4}$$

In doing so, ε_0 or σ_0 signify the respective amplitudes, ω the angular frequency ($\omega = 2\pi f$), and t the time.

Although Young's modulus represents the ratio of stress and strain for simple systems which obey Hooke's law, a complex E-modulus (E^*) can be defined for these complex cases. The rule is

$$E^* = \frac{\sigma}{\varepsilon} = \frac{\sigma_0}{\varepsilon_0}(\cos\delta + i\sin\delta) \tag{4.5}$$

The complex modulus E^* thus consists of a real part and an imaginary part, which are referred to as E_1 and E_2 (sometimes also as E' and E''):

$$E^* = E_1 + iE_2 \tag{4.6}$$

E_1 is referred to as the *storage modulus* and E_2 as the *loss modulus*. E_1 is a measure of the energy that can be stored in the system and E_2 a measure of the energy that is lost in the system. The quotient of the moduli E_2/E_1 therefore is given by $\sin\delta/\cos\delta$, i.e., $\tan\delta$—this is designated the *loss factor*, and describes the ratio of dissipated to stored energy.

Without proof, it can be shown that the loss factor can be written as

$$\tan\delta = \frac{E_2}{E_1} = \frac{1}{\omega\tau} \tag{4.7}$$

Here, τ denotes the relaxation time of the system.

If E_1 and E_2 are plotted as a function of temperature for materials going through the glass transition, the typical graph shown in Fig. 4.9 is obtained.

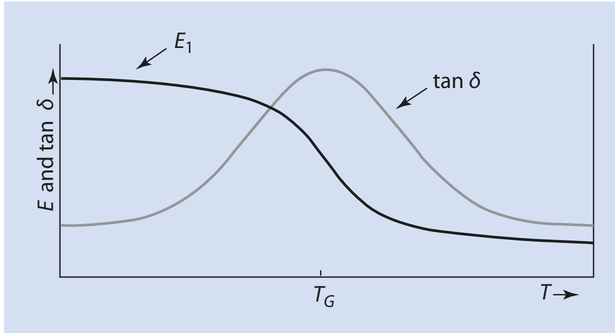

Fig. 4.9 Graph of the storage modulus and the loss factor as a function of temperature

It can be seen that the storage modulus drops abruptly across the glass transition. This becomes obvious by considering that the melt after the glass transition is a liquid and as such is generally not able to store energy. By contrast, the loss factor passes through a maximum at temperatures around the glass transition temperature. A maximum of the loss factor is equivalent to the material being a damping element. This can easily be explained graphically.

In a thought experiment, one imagines a polymer at low temperature as a hard metal spring. At low temperature the polymer chains are in a glassy solid state, they are not very mobile, and relatively large forces are required for small elongations. In other words, the material can be represented by a hard spring with a relatively high modulus.

As this system passes through its glass transition, the chains become more flexible, the material becomes softer, and the modulus of a spring representing the material is low. A polymer above its glass transition temperature can be represented by a soft metal spring.

Both hard and soft springs have their own resonance frequency. As is known from physics, a spring can store a lot of energy in the region of its resonance frequency, and it can be easily excited. With a hard spring, this resonance frequency is relatively high and for a soft spring the frequency is low. However, at their respective resonance frequencies, large oscillations can easily be induced in both springs.

What happens when a material passes through its glass transition? Because polymers always have a certain molar mass distribution, and, in particular, amorphous phases are heterogeneous with respect to their local order, there are both soft and hard springs present in the material close to the glass temperature. Thus, the system no longer finds its resonance frequency and any attempt to store energy in these materials results in a much larger energy dissipation. As a consequence, energy dissipation is observed at temperatures close to the glass transition, and thus a high damping of input energy. In an experiment, one would find that a weight hanging on a hard and a soft spring, arranged in series, cannot be excited to a greater, persistent oscillation.

DMTA measurements are designed to measure the storage and loss moduli of the sample as a function of temperature whereby the glass transition can then be identified from the position of the maximum in the loss modulus curve.

This can be achieved by heating a sample with a constant frequency and measuring the phase shift between the stress and strain curves. However, in practice it is simpler to vary the frequency rather than the temperature. This leads us to the so-called *time-temperature superposition principle*. How are frequency and temperature related?

Let us imagine that we are observing a sample at high temperature. If we put a load on the sample, for example by denting it or pulling on it, then at high temperature the polymer chains have sufficient mobility to respond to the strain by changing their conformation; the material appears soft. The same thing happens when we put a strain on a material at low frequency. The duration of the strain is relatively long and the polymeric material has a relatively long time to counteract the strain. Again, it appears soft. At low temperatures or high strain frequencies the opposite is the case. At low temperatures, the mobility of the material is not sufficient to react to the strain by changing its coil conformation. The material appears hard. At high measuring frequencies, the material does not have enough time to react to the strain and it appears hard.

This behavior—the dependence of the mechanical properties on the duration of the applied strain—is by no means limited to polymers. Compare stepping into a water-filled bathtub with a belly flop from a 5-m springboard. You can probably notice dramatically the dependence of the mechanical effect on your body on the speed of your plunge. Similarly, water behaves differently at a bathtub temperature of 37 °C than at −10 °C. Here, low temperatures cause a similar effect to that of short strain durations.

Thus, there is an analogy between measurements at high frequencies and measurements at low temperatures—and vice versa. Therefore DMTA measurements can either be carried out at a constant measuring frequency when varying the temperature, or—which is more often done technically—the temperature is kept constant and the measuring frequency varied. The data are then converted into a temperature curve.

Figure 4.10 shows the dependence of the storage and loss moduli on the measuring frequency, or more specifically on $\log(1/\omega\tau)$. The maximum of the loss modulus is achieved when this logarithm becomes zero, i.e., when the relaxation time τ is identical to the reciprocal of the measuring frequency. Thus, when the time in which the material can relax is approximately similar to the observation time, the sample is in an intermediate state where the material cannot yet fully relax but the first movements have already started. This state corresponds to the gradual transition from a hard to a soft spring. Exactly here, analogous to the above thought experiment, high damping is observed.

The DMTA suits itself ideally for the detection of very fine phase transitions. This can be shown by the example of polystyrene (Fig. 4.11).

In the upper part of the figure, the dependence of the storage modulus, in this case the shear modulus, on the temperature is shown for polystyrene. One can see a large transition at a temperature of about 100 °C, which corresponds to the glass transition of polystyrene. The curve at lower temperatures is, however, more difficult to interpret. This region is easier to analyze if the logarithm of the loss factor $\tan\delta$ is plotted as a function of the

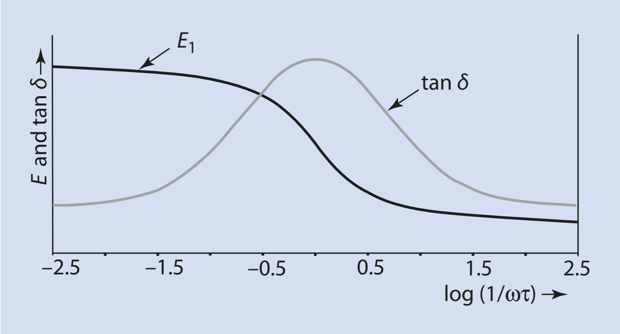

Fig. 4.10 Graph of storage and loss moduli as a function of frequency

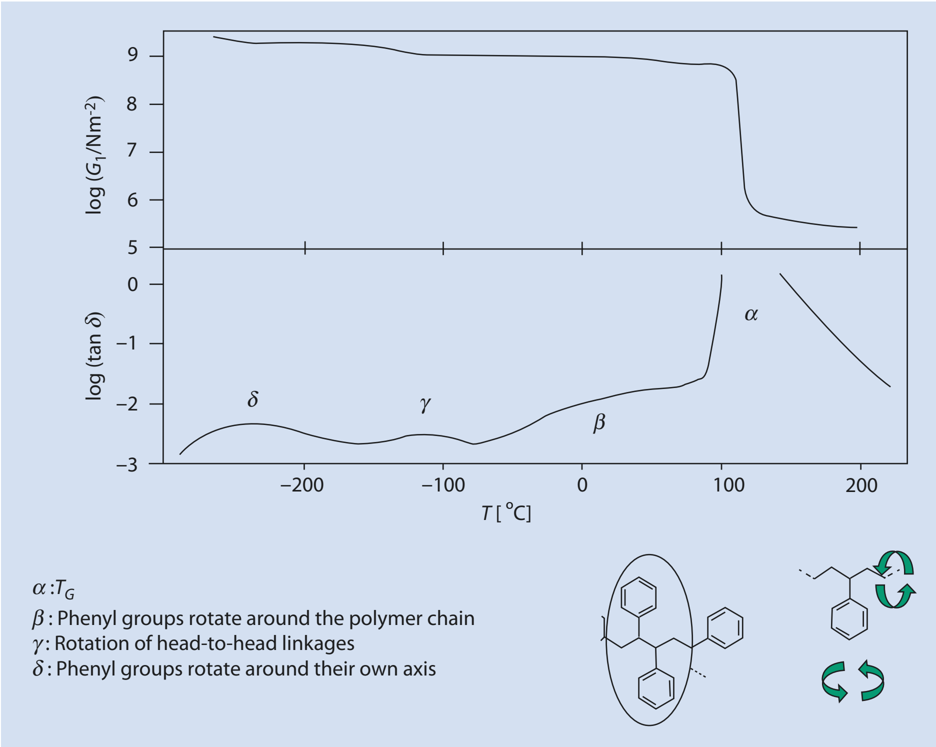

Fig. 4.11 DMTA measurement of polystyrene (Arridge 1975)

temperature (lower part of the diagram). Here we also see a very distinctive maximum at about 100 °C, which can be assigned to the glass transition. However, three additional transitions at lower temperatures can also be identified. These are referred to as the β, γ, and δ transitions. It has been shown that, at the β transition, the phenyl groups stop rotating around the polymer chain. If the sample is cooled below the γ transition, the rotations of head-to-head linkages also become frozen. At the δ transition, the rotation of the phenyl groups around their own axes also ceases. Thus, interestingly, we find further thermal transitions in the material below the main glass transition temperature T_G.

Dielectric thermal analysis (DETA) functions according to principles similar to DMTA. Analogous to DMTA, in DETA an alternating electric field is applied to the sample rather than an oscillating mechanical field. The polarization of the material is measured. Analogous to the DMTA measurements, a phase shift between the polarization and the applied alternating field is observed. At low frequencies or high temperatures, for example, an entire dipolar moiety can orient itself in the electric field. At high frequencies/lower temperatures, only the electrons within the group are displaced. At temperatures around the glass transition temperature there is a non-uniform reaction and high damping results.

In principle, DETA can be used in the same way as DMTA; however, it can only be applied to polymers with dipolar groups. Thus, in combination with DMTA, DETA allows conclusions as to whether dipolar groups are involved in a particular transition. If they are, the transition is observed using both techniques. If not, the transition is only identified using DMTA.

Reference

Arridge RGC (1975) Mechanics of polymers. Clarendon Press, Oxford University Press