

## Structural relaxation in the amorphous and liquid-crystalline phases of a thermotropic polymer

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### Summary

The analysis of the structural relaxation in specimens of a thermotropic polymer that are either in the glassy amorphous or in the liquid crystalline state (or in a mixture of them) has been carried out. The results indicate that the two phases behave independently, exhibiting two independent (and well different) glass transitions and with their own structural relaxations. Moreover, the physical aging has a profound influence on the ability to develop the liquid-crystalline phase. It seems that the changes in local order associated with a densification of the liquid-like packing lead to the development of some kind of local alignment, which favors the subsequent liquid-crystallization.

### Introduction

If a glass-forming material is cooled from the liquid state through the glass transition, its structure begins to depart from the equilibrium one as a result of the decreasing molecular mobility, since the molecules are not able to reach their equilibrium conformations in the time scale of the cooling. The non-equilibrium state tends to relax below the glass transition temperature approaching the corresponding stable state. This time dependent structural change towards equilibrium, that is known as physical aging or structural relaxation, is accompanied with measurable property changes, and the properties evolution during aging displays a very rich phenomenology.

Therefore, the study of glass-forming materials is a research area of interest because its theoretical and technological consequences. On the one hand, some questions about the physics of the glass transition and the nature of the glassy state are open. On the other hand, glassy materials performance and reliability must be predicted during the design process. Consequently, a rather extensive body of literature has been developed, from the initial free-volume and configurational entropy concepts to more elaborated models recognizing both the cooperativity of the rearranging regions and the non-linearity and non-exponentially of the process, by introducing different kinds of distributions of relaxation times [1-6].

Two of the more important open questions are, first, the correlation between the fundamental thermodynamic quantities (volume, enthalpy, entropy) with the final

mechanical properties, and, second, the particular structural changes and molecular reorganizations taking place during the process [6].

Although the study of the structural relaxation has been principally made on amorphous polymers, physical aging is not restricted to such systems. Thus, several reports deal with the structural relaxation in semicrystalline polymers, where the amorphous phase, confined in between the crystallites, shows a  $T_g$  distribution and a distribution of mobilities, with the corresponding effects on physical aging [7].

On the other hand, the enthalpic relaxation has been also studied in liquid-crystalline polymers, LCPs, and although these systems possess two-dimensional order, the observed rates and magnitudes of the enthalpic relaxation are comparable to those of conventional amorphous polymers [8].

We have also studied the structural relaxation of a smectic LCP by means of enthalpy and microhardness measurements [9-12] by applying both the AES model [13], and the KAHR model [14], showing that the enthalpy relaxation can be described in terms of the KWW equation [15]. The reported activation energy of the process seems to be smaller than that for other amorphous polymers, what may be related to the liquid crystalline nature.

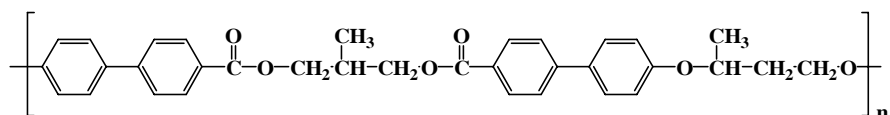
However, these comparisons may not be reliable, considering the different methodologies employed and also, very importantly, the possible influence of molecular weight. Therefore, if one wants to have a reliable comparison of the structural relaxation between amorphous and liquid crystalline systems, the obvious choice is to find a polymer that can be studied in both the glassy amorphous and glassy liquid-crystalline state. Unfortunately, this is not an easy task: although, in principle, glassy amorphous states of mesophase-forming polymers can be obtained by supercooling the isotropic melt, avoiding the formation of the mesophase, however, for most LCPs the quenching of the melt is not possible even at very fast cooling rates because of the rapid kinetics of the liquid crystallization process.

We have succeeded, however, in obtaining such system: a thermotropic poly(etherester), PH31B32, with substituted odd spacers. This polymer develops a smectic mesophase with a rather slow rate of formation, in such a way that the isotropic melt of PH31B32 can be easily quenched into the glassy amorphous state and, by appropriate annealing, the liquid crystalline phase can be developed, and the corresponding glassy mesophase can be also obtained [16,17].

The aim of this work is to carry out a preliminary analysis of the structural relaxation in specimens of PH31B32, aged at several temperatures, that are either in the glassy amorphous or in the liquid crystalline state (or in a mixture of them).

### Experimental Part

The synthesis and characterization of PH31B32 have been performed as previously reported [16]. In short, the monomer 1,3-bis(4-diethyloxycarbonyl-4'-biphenyloxy)-1-methylpropane was obtained from ethyl 4'-hydroxy-4-biphenylcarboxylate and (R,S)-1,3-butanediol, under Mitsunobu conditions [18]. The polymer PH31B32, with the following structural unit:



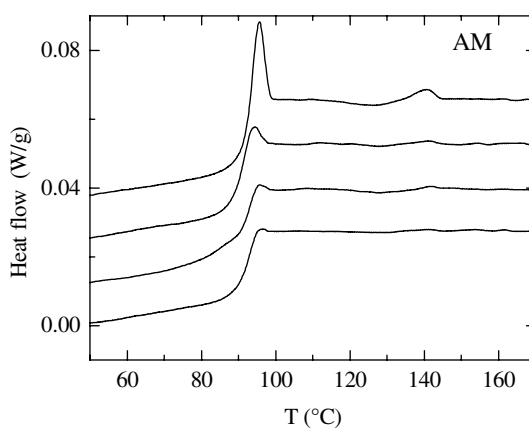
was obtained by melt transesterification of the monomer with 2-methyl-1,3-propanediol using tetraisopropyl titanate as catalyst. The purified polymer was found to have an intrinsic viscosity of 0.68 dL/g (measured at 30°C in chloroform by using an Ubbelohde viscometer). The peak molecular weight was  $M_p=12000$ , as obtained by size-exclusion chromatography [16].

A film of the polymer was obtained by compression molding in a Collin press between hot plates (180°C) at a pressure of 1.5 MPa, and subsequently cooling down to room temperature between water-cooled plates in the press. This sample is named as AM. Two specimens were cut from this film and annealed in an oil bath at 125°C for 55 min (sample MIX) and 88 hours (sample LC). As reported before [16,17], sample AM corresponds to a totally amorphous specimen, sample LC involves a complete mesophase formation, and sample MIX corresponds to a specimen where the mesophase formation has attained a 45 %.

The DSC measurements were performed with a TA Instruments Q100 calorimeter equipped with a refrigerated cooling system. The temperature and the enthalpy were calibrated using indium as a standard. All the experiments were carried out in an aluminum pan with around 6 mg of sample, using a heating rate of 4°C/min.

## Results and Discussion

The three samples of PH31B32, the totally amorphous one, the pure mesophase, and a mixture of the two phases, have been aged at three different temperatures, (66, 76 and 86°C) for two hours, in order to analyze the enthalpy relaxation of the two phases. The DSC curves for sample AM are shown in figure 1, compared with the results for a non-aged specimen.



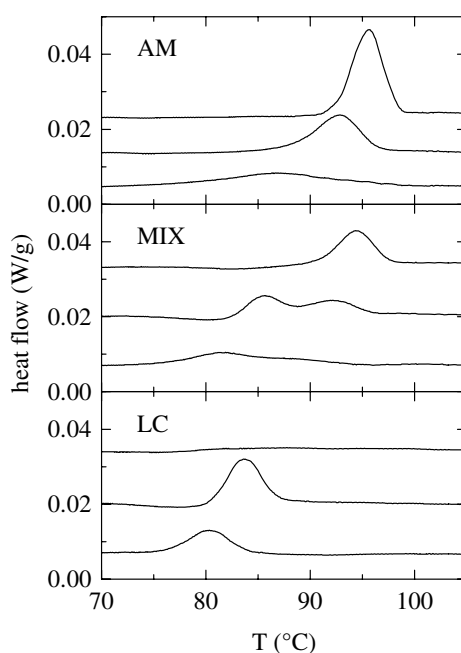
**Figure 1.** DSC curves corresponding to sample PH31B32-AM. From bottom to top: non-aged specimen and aged at 66, 76 and 86°C, respectively.

It can be observed that the non-aged specimen shows only the glass transition, centered at around 94°C and with a value of  $\Delta C_p$  at the transition of 0.34 J/gK.

However, the aged samples exhibit two noticeable aspects: first, an exothermic peak at the top of the glass transition is observed, attributed to the enthalpic relaxation, whose intensity depends rather clearly on the aging temperature. Secondly, a small but

appreciable endotherm is observed at around 140°C, which is the region of the isotropization temperature of PH31B32 [16]. This endotherm is better observed in the sample aged at 86°C, but it is preceded by an exothermic peak. We will discuss this aspect below.

If we focus the attention on the curve corresponding to the AM sample aged at 66°C, the enthalpic relaxation is not very evident, as expected when considering that the aging took place a temperature considerably below  $T_g$  (94°C) and for only two hours. However, if the non-aged profile is subtracted, a significant, but rather wide, endothermic peak is left, as observed in the upper frame of figure 2. It is centered at around 87°C, comprising an enthalpy of 0.6 J/g.



**Figure 2.** DSC curves for the different PH31B32 specimens (AM sample: upper frame; MIX sample: middle frame; LC sample: lower frame) after subtraction of the profile for the corresponding non-aged specimens. From bottom to top in each frame: specimens aged at 66, 76 and 86°C, respectively.

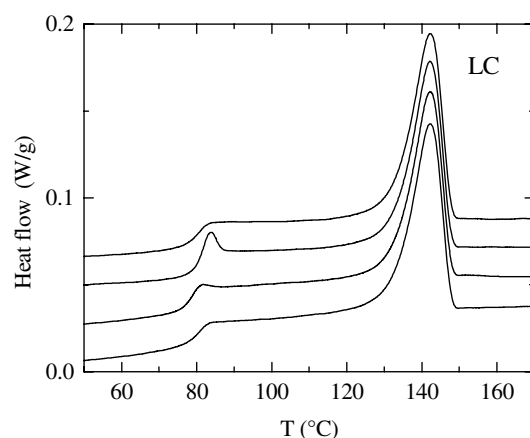
The specimen aged at 76°C exhibits a more intense aging peak, that it is also better observed when subtracting the non-aged curve (see upper part of figure 2). It appears centered at around 93°C, with an enthalpy of 0.9 J/g.

Finally, the specimen aged at 86°C presents the highest enthalpy relaxation: after subtraction of the non-aged profile a narrow and rather intense endothermic peak is observed, centered now at around 96°C, with an enthalpy of 1.3 J/g.

Therefore, both the location and intensity of the enthalpy relaxation peak (as well as its width) depend, as expected, on the aging temperature.

Regarding sample PH31B32-LC, i.e. the sample which is totally liquid-crystalline, the corresponding DSC curves are shown in figure 3. The heat flow shows, evidently, the isotropization of the mesophase, centered at 142°C, and now the glass transition

appears at a considerably lower temperature: at around 82°C, compared with the 94°C obtained in the case of the amorphous sample. As shown before [16,17], since the glass transition is related to the freezing of segmental motions, and the liquid crystalline phases retain some mobility around the longitudinal axes of the mesogen, it seems reasonable to expect a glass transition of the liquid crystalline phase at the temperature at which the minimum free volume required for the rotations is approached. Segmental movements above the glass transition are possible in the LC phase, which will not modify the inherent orientational anisotropy significantly. However, these movements are more restricted than those in the amorphous phase, and thus the free volume necessary to perform these rotations is considerably smaller than the volume for segmental motion in the isotropic melt. Consequently, according to the free volume theory, the glass transition of the LC phase is reached at lower temperatures than the glass transition of the isotropic state.



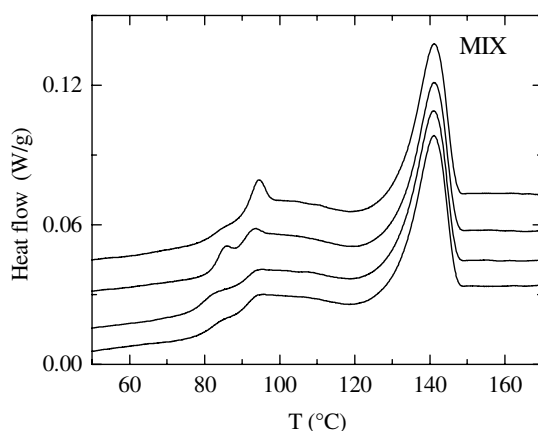
**Figure 3.** DSC curves corresponding to sample PH31B32-LC. From bottom to top: non-aged specimen and aged at 66, 76 and 86°C, respectively.

It is also evident from figure 3 that the LC phase of PH31B32 experiences a structural relaxation, as deduced from the corresponding enthalpy relaxation peaks. The same temperatures and times of aging (two hours at 66, 76 and 86°C) have been employed for the PH31B32-LC sample. Similarly to the case of the AM sample, the non-aged specimen shows only the glass transition, but now the value of  $\Delta C_p$  at the glass transition for the LC phase is much lower: 0.22 J/gK, compared with the 0.34 J/gK for the amorphous phase.

Regarding the experiment aged at 86°C, since this temperature is higher than the  $T_g$  for the mesophase (around 82°C) the curve is identical to that for the non-aged specimen.

In the case of the other two aging temperatures (66 and 76°C) the behavior is rather similar to that of the amorphous sample (having into account the difference in  $T_g$  of the two phases). Thus, the subtracted curves in the lower frame of figure 2 show a displacement of the enthalpic peak to higher temperatures and an increase of the enthalpy involved as the aging temperatures increases. Thus, the specimen aged at 66°C exhibits an aging peak centered at around 80°C, with an enthalpy of 0.5 J/g, while that aged at 76°C is centered at around 84°C, with an enthalpy of 0.9 J/g.

The DSC curves corresponding to the different specimens of sample PH31B32-MIX (the one with a 45 % mesophase formation) are presented in figure 4. The same aging temperatures (66, 76 and 86°C), plus the non-aged experiment, have been analyzed. A close inspection of the results indicates that this MIX sample behaves practically as a weighted addition of the AM and LC samples. Thus, the non-aged specimen shows the two glass transitions of the two pure phases. Evidently, the specimen aged at 86°C shows only the aging of the amorphous part, since this aging temperature is higher than the glass transition temperature of the LC component. Moreover, the width and position of the glass transition, observed in the middle part of figure 2, are also practically a weighted summation.



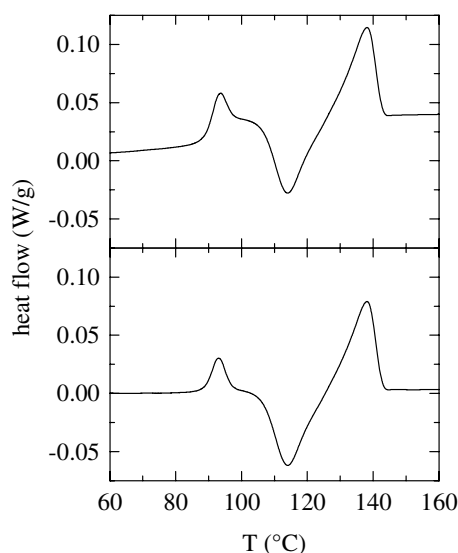
**Figure 4.** DSC curves corresponding to sample PH31B32-MIX. From bottom to top: non-aged specimen and aged at 66, 76 and 86°C, respectively.

In conclusion, the results obtained for this PH31B32-MIX sample, composed of 45 % of mesophase and 55 % of amorphous phase (as reported before [16,17]), indicate that the two phases behave independently, exhibiting the two independent glass transitions and with their own structural relaxations. It means, therefore, that the sample is formed by two well-separated regions, or with domains big enough to show that independent behavior.

There is only one aspect of sample MIX that is not the weight summation of the behavior of the two component phases. That aspect is the isotropization endotherm. As previously reported [16], the mesophase formation in PH31B32 is a rather slow process, which takes several hours at any temperature above  $T_g$  (and below the isotropization temperature). However, before the isotropization endotherm a clear exotherm is observed in the DSC melting curves of figure 4, which seems to be bigger in the case of the specimen aged at 86°C. Its origin should be related to the fact that the MIX sample is 45 % mesophase, i.e., already with a considerable amount of "nucleation", so that some additional mesophase formation is attained during melting. Further experiments have been performed in order to investigate the possible influence of aging on this behavior. In fact, the first clear evidence of this effect can be observed in the results for sample AM in figure 1: the magnitude of the exotherm increases with the aging enthalpy, and no such process, nor the isotropization endotherm is observed for the non-aged sample.

Another specimen of this PH31B32-AM sample has been aged for a long time (three days), in a thermostatic bath at a temperature of  $86 \pm 1^\circ\text{C}$ . The corresponding DSC curve is presented in figure 5, where a rather intense exotherm is observed. This behavior is similar to the well known cold crystallization process of quenched semicrystalline polymers, although now the formation of a liquid crystalline phase is involved. Therefore, we will use here the term "cold liquid-crystallization".

On the other hand, the value of  $T_g$  for the specimen in figure 5 is around  $94^\circ\text{C}$ , indicating that no appreciable mesophase is formed in the aging process, as it is also deduced from the enthalpy obtained by integration of the heat flow from just after the aging peak to the end of the isotropization, which gives a value practically null. However, the apparent enthalpy involved in the cold liquid-crystallization exotherm is of the order of  $10.5 \text{ J/g}$ , which has to be considered a lower limit, considering that this cold liquid-crystallization overlaps severely with the isotropization endotherm.



**Figure 5.** DSC curves for sample PH31B32-AM aged for a long time (three days) at  $86^\circ\text{C}$ : original curve (upper frame) and after subtraction of the non-aged profile (lower frame).

The isotropization enthalpy obtained for the pure LC sample is  $16.6 \text{ J/g}$ , so that considering that the value of  $10.5 \text{ J/g}$  is a lower limit, it seems that the majority (or 100 %) of the mesophase has been obtained in the few minutes of the heating of the sample in the calorimeter when obtaining the DSC curve.

Similar "nucleation" effects of the physical aging have been reported for semicrystalline polymers [19].

The structural relaxation peak obtained after subtraction of the non-aged curve, as shown in the lower part of figure 5, exhibits an enthalpy of around  $2.7 \text{ J/g}$ . It has been suggested [20] that an approximate linear relationship exists between the asymptotic value of the structural relaxation enthalpy at a given aging temperature,  $\Delta H(\infty, T_a)$  and the difference  $(T_g - T_a)$ , that reads:

$$\Delta H(\infty, T_a) = \Delta C_p (T_g - T_a) \quad (1)$$

which will be valid for temperatures not very far away from  $T_g$ . Considering the values of  $\Delta C_p$  and  $T_g$  for the amorphous sample (0.34 J/gK and 94°C, respectively), a value of 2.72 J/g is obtained with that approximation for  $\Delta H$  ( $\infty$ , 86). We can consider, therefore, that after three days of aging, the asymptotic value has been practically reached.

If we consider now the enthalpy of aging obtained for sample AM aged for two hours at 86°C, around 50 % of the asymptotic value determined by approximation (1) is deduced. However, the magnitude of the cold liquid-crystallization obtained by integrating the exotherm in the upper curve of figure 1 is only around 0.3 J/g. It seems, therefore, that the last stages of aging have a higher relative importance for the cold liquid-crystallization phenomena.

In conclusion, the physical aging has a profound influence on the ability to develop the liquid-crystalline phase. It seems that the changes in local order associated with a densification of the liquid-like packing [21] lead to the development of some kind of local alignment, which favors the subsequent liquid-crystallization once the  $T_g$  is overpassed. However, it appears that this process is essentially effective in the last stages of the enthalpy evolution. As it has been recognized [22], the dependence of a specific property with a particular aspect of the physical aging (volume or enthalpy recovery, structural order) does not follow a general rule.

A more detailed study of the effect of aging temperature and time in the structural relaxation of the two phases (amorphous and liquid-crystalline) of PH31B32 is being planned, as well as its influence on the rate of the mesophase formation.

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