Phase transitions in liquid crystalline poly(octamethylene *p,p'*-dibenzoate)

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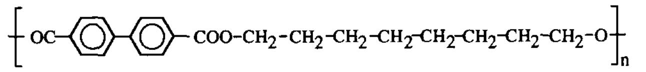
A detailed study of the phase transitions in poly(octamethylene *p,p'*-dibenzoate) (P8MB) was carried out using differential scanning calorimetry. The thermodynamic parameters of the mesophase of P8MB have been determined by maintaining this phase at high temperatures to prevent its transformation into the crystal. If the crystal is formed, however, it exhibits a monotropic transition to the isotropic melt, and consequently the mesophase is not obtained on heating. This monotropic character is reflected in the free energy diagram of P8MB, as the crystal melting point is higher than the isotropization temperature ($T_{cr\to i} > T_{lc\to i}$). From the free energy diagram it is also deduced that the crystal phase is thermodynamically the most stable one at any temperature below its melting point, although at low undercoolings the mesophase is always formed first for kinetic reasons. Moreover, the liquid crystalline (LC) glass is obtained by fast quenching from the isotropic melt, as revealed by X-ray analysis. This LC glass is stable at room temperature owing to a glass transition at 42°C, although it undergoes a relatively rapid ageing process at that temperature. Finally, the viscoelastic relaxations have been analysed for two samples of P8MB with different thermal histories.

(Keywords: phase transitions; liquid crystalline P8MB; monotropic transition)

INTRODUCTION

The study of the phase state and phase transitions of thermotropic liquid crystalline polymers (LCPs) is a field of great interest. There are five possible phase states[1] for LCPs: crystal, liquid crystal, isotropic melt, LC glass and amorphous glass. The transitions between these phases are interesting and significant for the end uses of the material. Although there have been many papers describing the phase behaviour of LCPs in recent years, the exact nature of the phase transitions involving LC phases is still not well known, and many aspects remain to be clarified.

Several papers have been published showing the thermotropic LC character of polyesters derived from dibenzoic acid[2–8]. The transition temperatures of these polydibenzoates depend on the length of the spacer, displaying the usual even–odd effect[4]. Some features of the phase behaviour of poly(octamethylene *p,p'*-dibenzoate) (P8MB) have already been reported[4,7]. The repeat unit of this polymer is



The most important result is the fact that the mesophase of P8MB is observed only on cooling from the melt state, with a rapid transformation into a three-dimensional crystal. This crystal, however, seems to exhibit a monotropic transition directly into the isotropic melt. This behaviour, which is general for the polydibenzoates with more than six methylene units in the spacer, precludes the observation of the isotropization of the mesophase under usual conditions. In these cases, however, the LC phase can be isolated by cooling from the melt and holding the temperature in a region where the transformation into the crystal is very slow, as shown for poly(heptamethylene *p,p'*-dibenzoate) (P7MB)[5]. This procedure relies on a previous analysis of the crystallization kinetics of the polymer.

The purpose of this work is to study in more detail the phase transitions in P8MB, focusing on the experimental conditions necessary to isolate the mesophase, in order to determine the thermodynamic parameters of the different transitions and to evaluate the relative stabilities of the various phases.

EXPERIMENTAL

Poly(octamethylene *p,p'*-dibenzoate) was synthesized by melt transesterification of the diethyl ester of *p,p'*-dibenzoic acid with octamethylene glycol using isopropyl titanate as the catalyst. The polymer was purified by precipitating into methanol a solution in tetrachloroethane. The intrinsic viscosity, determined at 25°C in tetrachloroethane, was 1.30 dl g^{-1}. Some details of the characterization of P8MB have been reported previously[7].

The thermal analysis was carried out in a Perkin–Elmer DSC7 calorimeter calibrated with different standards and

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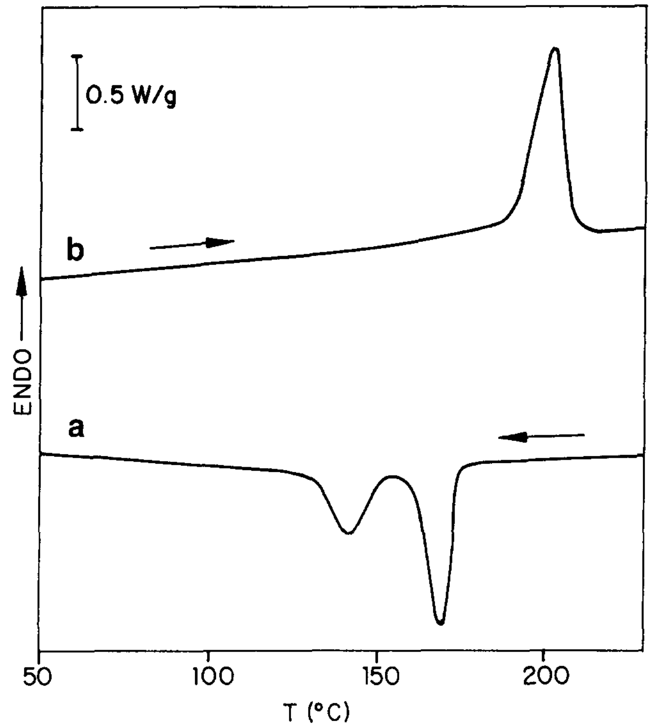

Figure 1 D.s.c. curves (scanning rate 20°C min^{-1}) for P8MB: (a) cooling from the melt; (b) subsequent melting

connected to a cooling system. X-ray diffraction patterns were obtained with a Geiger counter X-ray diffractometer from Philips employing nickel-filtered CuKα radiation.

A polymer film of P8MB was prepared by moulding the material in a Collin press at 240°C for 5 min. Two pieces of this film were used after the appropriate thermal treatment using a Mettler FP82HT hot stage connected to a Mettler FP80HT temperature controller. Starting from the melt (240°C), the first sample was slowly cooled at 2°C min^{-1}, while the second one was quenched into liquid nitrogen.

Viscoelastic relaxations were measured with a Polymer Laboratories Mk II dynamic mechanical thermal analyser working in the tensile mode.

RESULTS AND DISCUSSION

Figure 1 shows typical differential scanning calorimetry (d.s.c.) cooling and heating ramps for P8MB. On cooling from the melt (230°C), two exotherms are found at 168°C and 142°C, corresponding respectively to the liquid crystallization from the isotropic melt and the mesophase–crystal transformation[4,7]. On heating, however, only one endotherm at 202°C is obtained, suggesting a monotropic character similar to the case of P7MB[5]. Whether this endotherm represents actual monotropic behaviour or whether it is composed of two peaks in a narrow range of temperatures is not completely evident. Several isothermal and non-isothermal d.s.c. experiments were performed to solve this problem, as reported below.

The analysis of the crystallization kinetics of P8MB shows that, starting from the melt, the formation of the mesophase at 182°C is a very rapid process (it is complete before the temperature equilibration of the calorimeter), while the subsequent transformation of the LC phase into the crystal displays a time-scale appropriate for d.s.c. determinations. The degree of transformation, evaluated from the corresponding isotherm at 182°C, is shown in *Figure 2*. It can be seen that only the mesophase exists when the isothermal time is less than 10 min, while the transformation into the crystal is complete after 80 min. At intermediate times, the two phases coexist.

With this information, several d.s.c. experiments were performed in the following way. Starting from the isotropic melt, P8MB was isothermally crystallized at 182°C for different periods of time, and subsequently the melting curves were registered. The results are shown in *Figure 3*, where two different endotherms can be seen. The first one, centred at 190°C, corresponds to

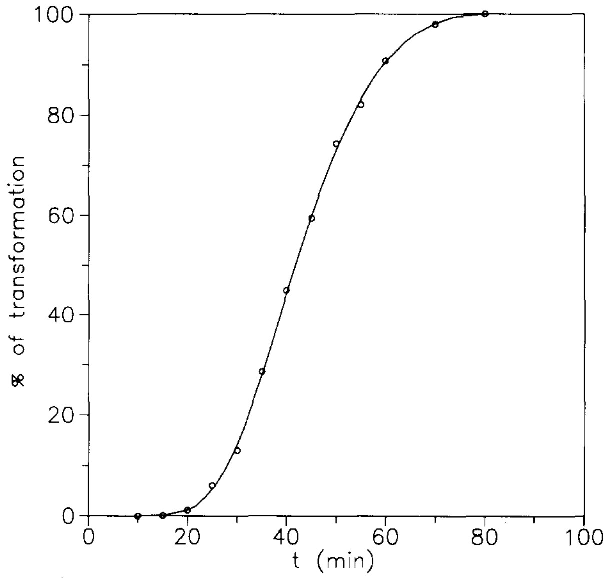

Figure 2 Degree of mesophase–crystal transformation at 182°C for P8MB as a function of time

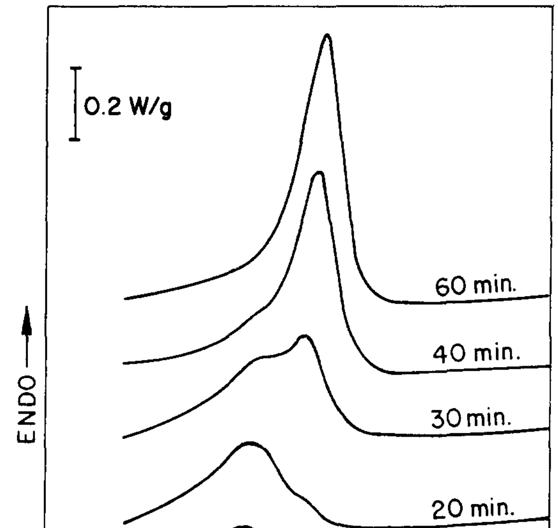

Figure 3 D.s.c. melting endotherms for P8MB after isothermal crystallization for the indicated times at 182°C, starting from the isotropic melt (heating rate 5°C min^{-1})

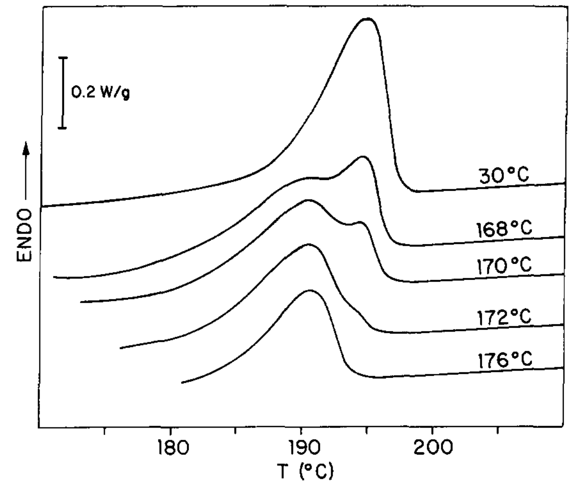

Figure 4 D.s.c. melting endotherms for P8MB after cooling to the indicated temperatures, starting from the isotropic melt (scanning rate 5°C min^{-1})

Table 1 Apparent^a thermodynamic parameters of the transitions in P8MB

	Transition				
	cr→i	lc→i	i→lc	lc→cr	cr→lc
T(°C)	195	190	178	160	197^b
ΔH (kcal mol^{-1})	3.9	2.3	2.3	1.6	1.6
ΔS (cal mol^{-1} K^{-1})	8.3	5.0			3.4

a Heating rate 5°C min^{-1}. Error margins: temperatures ±2°C; enthalpies ±0.3 kcal mol^{-1}

^{b}Extrapolated from *Figure 6*

the isotropization of the mesophase and its intensity diminishes at longer times, while the second peak appears as the mesophase is being transformed into the crystal phase. This second endotherm at 195°C represents, therefore, the melting of the crystal phase directly into the isotropic melt; that is, P8MB really exhibits monotropic behaviour, as the clearing of the mesophase occurs at a temperature lower than the melting point of the crystals.

Another way to isolate the mesophase is to cool down the sample from the melt at a given rate until a certain temperature is reached, and then immediately register the melting curve. The range of appropriate temperatures for these experiments can be estimated from the cooling curve in *Figure 1*. The results are displayed in *Figure 4*, and they show that only the mesophase is present when the temperature is lowered to 176°C, while the crystal melting peak appears at lower temperatures. In fact, the upper curve in this figure is similar to the upper curve in *Figure 1*, with the difference in heating rates reflected in the peak temperature values. We did not attempt to extrapolate all the transition temperatures to zero heating rate, and the peak values obtained from the experiments at 5°C min^{-1} have been considered. The reason is that we found that peak temperatures at this rate are practically equal to those obtained by extrapolating to zero heating rate the temperature at which the last trace of crystallinity disappears, which is often considered as the most representative value. With these considerations, the thermodynamic parameters for the different transitions in P8MB are listed in *Table 1*.

It can be seen that the transition temperatures for P8MB are considerably higher than those for P7MB[5,8], despite the fact that the spacer is one methylene unit longer in P8MB. The reason is the well-known even–odd effect that leads to phases more highly ordered in the even members[4]. Thus, P8MB also exhibits higher transition enthalpies than P7MB. Moreover, the transformation of the mesophase into the crystal is a more rapid process in P8MB: on cooling at 20°C min^{-1}, crystal formation occurs 26°C below mesophase formation in P8MB, while this difference is 40°C for P7MB[5,8].

The relative stabilities of the different phases can be illustrated in a phase diagram representing the free energies of the various phases. These free energies should be calculated from the specific heats as a function of temperature. In the absence of these values, the phase diagrams can be obtained in relation to the isotropic state by determining the corresponding free energy differences. If the temperature range is not very broad or the difference in heat capacity between the supercooled liquid and the ordered phase is not considerably temperature dependent, the free energy of fusion ΔF_u of a polymer melting at T_m with an enthalpy of fusion ΔH_u is given by[9,10]

$$\Delta F_u = \Delta H_u (T_m - T)\frac{T}{T_m^2} \tag{1}$$

This equation can be used to estimate the free energies of the mesophase and crystal in relation to the isotropic state using the values in *Table 1*. It has to be considered, however, that these numbers represent actual values and not equilibrium ones. This is especially important for the crystalline phase, because very small differences, if any, are expected from the isotropization parameters of the mesophase. Another restriction for the use of equation (1) is that the orientational order of the LC phase may change as a function of temperature. Therefore, the free energy diagrams deduced from equation (1) can be used only for semiquantitative purposes.

Regarding the enthalpy of melting $\Delta H_{cr\rightarrow i}$ shown in *Table 1*, this represents the apparent value for a sample of P8MB crystallized to completion by slowly cooling from the melt, which evidently does not give material that is 100% crystalline. In order to determine the degree of crystallinity, X-ray diffraction experiments were carried out on two samples of P8MB. The first one was slowly crystallized from the melt and the second was rapidly quenched from the melt into liquid nitrogen. The crystallization at room temperature of this quenched sample is prevented because the glass transition temperature of P8MB is 42°C (see below). The diffractograms of the two P8MB samples are shown in *Figure 5*. The profiles are similar to those for the crystal and the pure mesophase of P7MB[5], with the difference that the smectic peak at about $2\theta = 5°$ is very broad in the quenched P8MB sample. The LC glass is obtained in the quenched sample because it is very difficult to quench the isotropic melt into an amorphous glass when the formation of the liquid crystal is possible, owing to a strong drive towards equilibrium[1].

The crystallinity of the slowly crystallized sample can be estimated by subtracting the corresponding amount of non-crystalline component, the profile of which can be approximated by the profile of the mesophase[5,11]. A value of 50±5% is obtained for the crystallinity of the slowly crystallized P8MB, and therefore the enthalpy

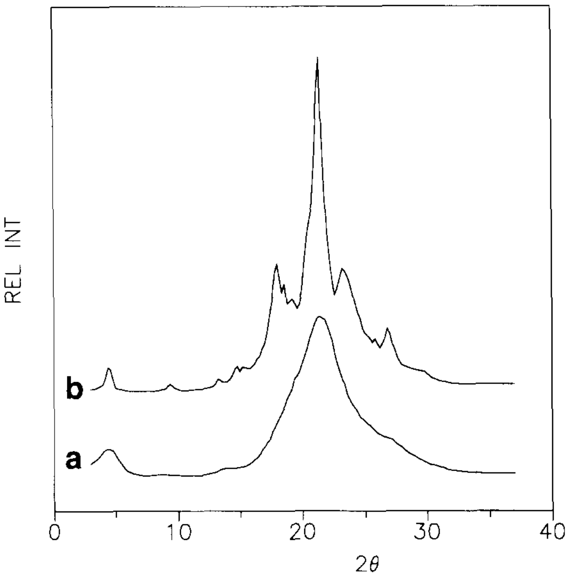

Figure 5 X-ray diffractograms for P8MB samples with different thermal treatments: (a) quenched from the melt; (b) slowly cooled from the melt

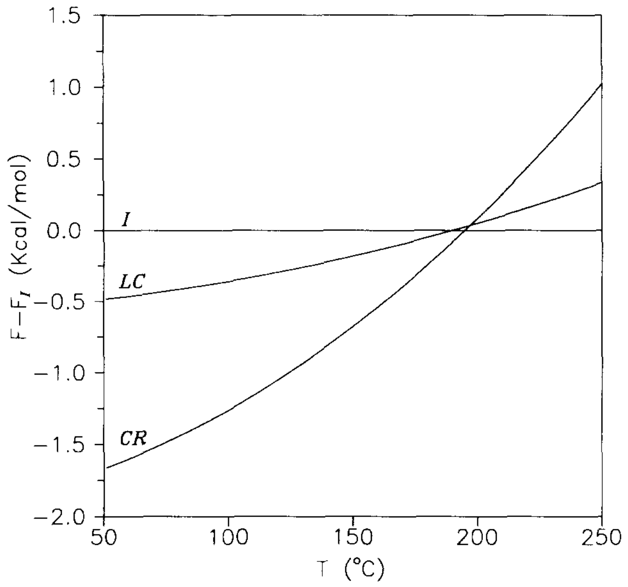

Figure 6 Free energy diagram for P8MB

of melting of the 100% crystal is estimated to be 7.8 kcal mol^{-1} (92 J g^{-1}).

With this value and the other parameters in *Table 1*, the free energy plots shown in *Figure 6* have been determined with the use of equation (1). The monotropic character of P8MB is evident from *Figure 6*, as the crossing of the curves corresponding to the crystal and the isotropic melt occurs at a temperature higher than the isotropization point. Moreover, the theoretical temperature for the crystal–mesophase transition is 197°C, higher than the isotropization temperature of 190°C, which is also a characteristic of monotropic behaviour.

The relative stabilities of the different phases depend on the free energies per repeat unit. The phase having the lowest free energy or the highest free energy of fusion should be thermodynamically the most stable one. Thus, *Figure 6* shows that the crystal phase is the most stable one at any temperature below its melting point. However, kinetic considerations will also affect the formation of a certain phase and the liquid crystal is formed at much lower undercoolings than the crystal. Therefore, it has been shown in this work that the mesophase of P8MB can be isolated at high temperatures, where its transformation to the crystal is very slow. Moreover, the LC glass can be obtained by rapidly quenching from the isotropic melt.

The glass transition temperature of P8MB was determined using both d.s.c. and dynamic mechanical measurements. As happens for many semicrystalline polymers, the slowly crystallized sample does not exhibit a clear transition in the d.s.c. traces. In contrast, the quenched specimen leads to the d.s.c. curve presented in *Figure 7*, where a glass transition at about 42°C is obtained (defined as the temperature where the increment in heat capacity is one half of the total at the transition). In addition, the endotherm at the top of this transition corresponds to the enthalpy relaxation of the ageing process undergone by the sample while standing at room temperature for 4 days. This endotherm is centred at 49°C and represents an enthalpy of about 0.1 kcal mol^{-1}, which is of the same order as that for poly(diethylene glycol *p,p'*-dibenzoate) (PDEB)[12]. This ageing phenomenon, which seems to be general in the LC glasses of polydibenzoates, can be clearly observed in samples held at temperatures around 10–20°C below the glass transition temperature. This temperature interval is similar to the case of amorphous polymers[13,14], although the process is significantly faster for polydibenzoates[12].

Dynamic mechanical measurements were performed on both quenched and slowly crystallized P8MB samples. The corresponding plots of the storage modulus E' and loss tangent $\tan\delta$ are shown in *Figures 8* and *9*, respectively. As for other polydibenzoates[15,16], three transitions, named α, β and γ in order of decreasing temperature, are observed for the two samples. The α relaxation is characterized by a sharp decrease in the storage modulus and has an apparent activation energy

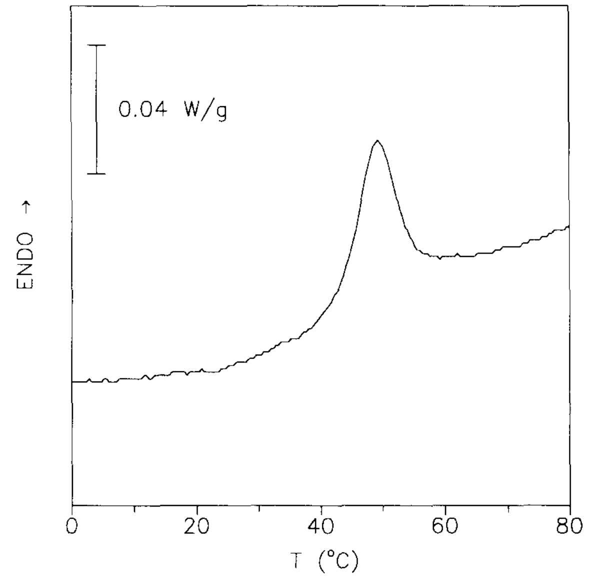

Figure 7 D.s.c. heating curve (20°C min^{-1}) for a quenched sample of P8MB, subsequently aged at room temperature for 4 days. The glass transition and the enthalpy relaxation of the ageing process are observed

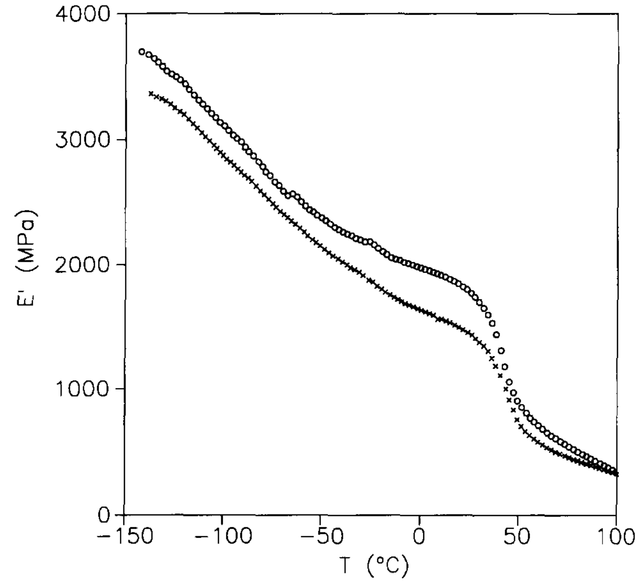

Figure 8 Plots of the storage modulus (at 3 Hz) as a function of temperature for the two samples of P8MB: (×) quenched from the melt; (○) slowly cooled from the melt

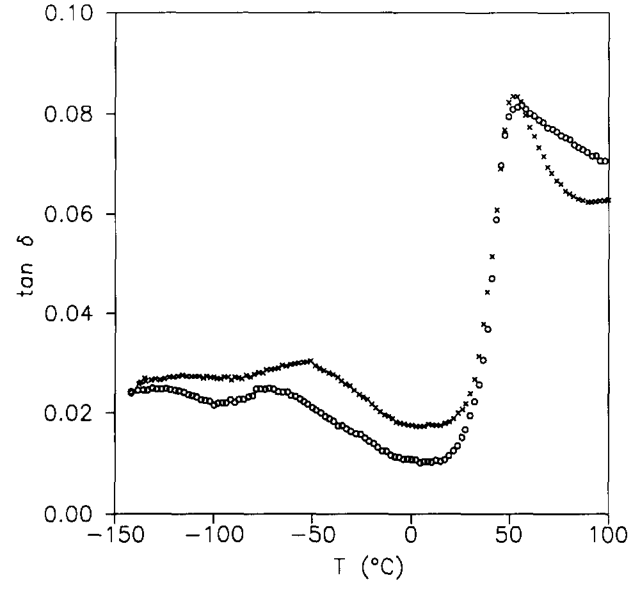

Figure 9 Plots of the loss tangent (at 3 Hz) as a function of temperature for the two samples of P8MB: (×) quenched from the melt; (○) slowly cooled from the melt

of 160 kcal mol^{-1}. These two facts lead us to the conclusion that the α relaxation is the glass transition of P8MB. It is located at 52°C (3 Hz, tan δ basis), or at 47°C when considering the loss modulus plots. These results are consistent with the d.s.c.-determined value of the glass transition temperature (42°C). As expected, the slowly crystallized sample presents higher values of E' (see *Figure 8*) owing to the presence of crystallinity (the concurring effect of ageing in the modulus of P8MB is under study). The crystallinity diminishes slightly the intensity of the α peak and broadens its shape, although its position is practically unaffected.

The β relaxation is very broad for the two P8MB specimens and appears at around −60°C (*Figure 9*). It has a complex origin and is characteristic of polyesters[15–18].

Finally, the γ relaxation can be clearly seen in *Figure 9*. It appears at −126°C (3 Hz, tan δ basis) for the slowly crystallized sample. Its location and activation energy (8.5 kcal mol^{-1}) agree with the values of the relaxations associated with crankshaft movements of polymethylene[15,17–19] and polyoxyethylene[16] sequences.

In conclusion, the thermodynamic parameters of the mesophase of P8MB have been determined by maintaining this phase at high temperatures to prevent its transformation into the crystal. If the crystal is formed, however, it exhibits a monotropic transition to the isotropic melt, and then the mesophase is not obtained on heating. This monotropic character is reflected in the free energy diagram of P8MB, as the crystal melting point is higher than the isotropization temperature ($T_{cr\rightarrow i} > T_{lc\rightarrow i}$). From the free energy diagram it is also deduced that the crystal phase is thermodynamically the most stable one at any temperature below its melting point, although for kinetic reasons the mesophase is always formed first, at low undercoolings. Moreover, the LC glass is obtained by rapidly quenching from the isotropic melt, as revealed by the X-ray analysis. This LC glass is fairly stable at room temperature, owing to its glass transition temperature of 42°C (47–52°C from the dynamic mechanical analysis), showing a relatively rapid ageing process.

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