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Dynamic mechanical analysis of the two glass transitions in a thermotropic polymer

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Abstract

A dynamic mechanical analysis has been performed on a thermotropic poly(ether ester) with biphenyl units as mesogens and spacers with methyl substituents. This polymer develops a smectic mesophase with a rather slow rate of formation, in such a way that the isotropic melt of this polymer can be easily quenched into the glassy amorphous state. A quenched amorphous sample and three specimens annealed above the glass transition for different times have been analysed. These annealed specimens exhibit different degrees of liquid crystal formation. The dynamic mechanical (and DSC) results show that the glass transition (α-relaxation) temperatures of the isotropic amorphous and anisotropic liquid crystalline states are clearly different, and when the mesophase transformation is not complete, as it happens in the two specimens annealed at intermediate times, the two glass transitions are simultaneously observed. The values of the storage modulus below the glass transition are dependent on the degree of liquid crystallinity, showing that the rigidity of the mesophase is significantly higher than the one for the amorphous component.

Keywords: Dynamic mechanical analysis; Amorphous glass; Liquid crystalline glass

1. Introduction

Dynamic mechanical analysis provides information about the molecular processes taking place in polymers and many studies of this kind have been devoted to amorphous and semicrystalline polymers.

Liquid crystalline polymers, LCPs, have received a considerable attention in the last years due to the favourable combination of key properties [1] and the fact that those properties can be tailored with relatively simple variations in the chemical structure.

One of the more interesting features of LCPs is the possibility of freezing the orientational order of the mesophase just by cooling the sample at temperatures lower than the glass transition, T_g, which is an attractive way to obtain anisotropic glasses with unique optical, mechanical or electrical properties [2].

Besides the technological interest, there is also a fundamental question from the solid-state physics point of view: What are the differences between the amorphous and liquid crystalline glasses of LCPs? To answer this question it is obvious that we need to obtain both the pure isotropic amorphous and the liquid crystalline phase of a given polymer. Unfortunately, it is usually rather difficult to quench the isotropic melt to an amorphous glass when liquid crystal formation is possible, and extraordinary quenching techniques may be needed [3]. For this reason, only a few studies [4–10] have been published on this subject.

In order to slow down the formation of the mesophase, the tendency of the elongated LCP chains to build the supramolecular structure must be reduced by, for example, decreasing their structural and geometrical symmetry. This can be attained, for instance, in polymer systems where the mesogens are biphenyl units, and using spacers with an odd number of methylene units and with methyl substituents [11]. It is known that main-chain polybibenzoates with linear odd spacers show a smectic mesophase of the type SmCalt, where consecutive mesogens are arranged in an alternating antiparallel fashion [12–17]. This reduction of the geometrical symmetry of the molecule diminishes the

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self-assembly tendency of the mesogens to build the supramolecular ordering. Besides that, the methyl group introduces structural irregularity not only because of the lowering of the interchain interactions [18,19], but also because of the random distribution of head-to-head and head-to-tail sequences along the polymer backbone. Evidently, if the reduction of regularity is too high, the polymer system may loose the ability to produce mesophases (or any other kind of regular structures).

With these considerations, we have recently synthesized [11] a poly(ether ester) with the biphenyl unit as mesogen and two different methyl-substituted trimethylene spacers. This polymer, named as PH31B32, has the structural unit depicted in Fig. 1. The thermal and structural results show that this polymer can be easily prepared in either the pure isotropic amorphous state or in a low-ordered smectic mesophase [11].

The aim of the present work is to perform a dynamic mechanical study on the two pure phases (amorphous and liquid crystal) of PH31B32, and to analyze the corresponding viscoelastic relaxations, in order to compare the behaviour of the two phases.

2. Experimental section

The details for the synthesis and characterization of PH31B32 have been previously reported [11]. 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 [20]. The polymer PH31B32 (see structure in Fig. 1) 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 0.681 dL/g (measured at 30 °C in chloroform by using an Ubbelohde viscometer). The peak molecular weight was $M_p = 12{,}000$, as obtained by size-exclusion chromatography [11].

A film of the polymer was obtained by compression moulding 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 Q. Two specimens were cut from this film and annealed in an oil bath at 125 °C for 40 and 55 min: Samples A40 and A55, respectively. A third specimen was annealed at that temperature for a very long time (88 h) in order to ensure complete mesophase formation: Sample LC.

Differential scanning calorimetric measurements were carried out with a Perkin–Elmer DSC7 calorimeter connected to a cooling system. Samples of 6–8 mg were used, at a heating rate of 20 °C/min. The DSC-determined glass transition temperature has been taken as that temperature where the specific heat increment is half of the total one at the transition.

Wide-angle X-ray diffraction (WAXD) patterns were recorded in the reflection mode at room temperature by using a Philips diffractometer with a Geiger counter, connected to a computer. Ni-filtered Cu Kα radiation was used. The diffraction scans were collected over a period of 20 min in the range of 2θ values from 3 to 43°, using a sampling rate of 1 Hz. The goniometer was calibrated with a silicon standard.

Dynamic mechanical relaxations were measured with a Polymer Laboratories MK II Dynamic Mechanical Thermal Analyser, working in a tensile mode. The storage modulus, E', loss modulus, E'', and the loss tangent, tan δ, of each sample were obtained as function of temperature over the range from −150 to 130 °C, at fixed frequencies of 1, 3, 10 and 30 Hz, and at a heating rate of 1.5 °C/min. Strips around 2.2 mm wide and 15 mm length were cut from the moulded sheets. The apparent activation energy values were calculated on the basis of E'' according to an Arrhenius-type equation, considering an accuracy of ±1 °C in the temperature assignment from the maxima. The frequency dependence with temperature of the α-relaxation (glass transition) has been also considered to follow an Arrhenius behaviour, although it is due to cooperative motions, as well known. This approximation can be made without significant error since the analyzed range of frequencies is low enough to be fitted to such a linear behaviour.

3. Results and discussion

As it was shown before [11], the isotropic phase of PH31B32 can be easily quenched from the melt. In fact, the mesophase of this polymer is formed at rather low rates, in such a way that it is not observed at the usual cooling rates in the calorimeter, and relatively long annealing times at temperatures above the glass transition (and below the isotropisation) are needed to produce the low-ordered smectic mesophase. Therefore, the DSC heating curve of a sample of quenched PH31B32 shows only the glass transition (see lower curve of Fig. 2), centred at 97.6 °C. However, the samples annealed at 125 °C exhibit a clear endotherm corresponding to the isotropisation of the mesophase, whose enthalpy depends on the annealing time, as observed in Fig. 2. Thus, the sample annealed for a long time (sample LC) presents an isotropisation

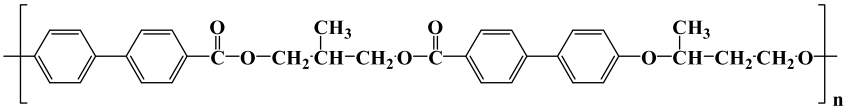

Fig. 1. Structural unit of PH31B32.

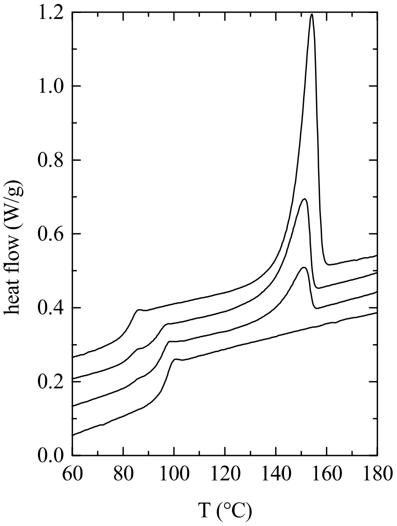

Fig. 2. DSC melting curves corresponding to the different specimens of PH31B32. From bottom to top: Q, A40, A55 and LC specimens. Scanning rate: 20 °C/min.

endotherm with a peak temperature of 154.2 °C and an enthalpy of 18.1 J/g (a value typical of low-ordered smectic mesophases). Moreover, the glass transition appears now in this sample centred at 83.7 °C, i.e. at a temperature significantly smaller than that for the amorphous quenched sample.

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. The glass transition temperature of polymers is closely related to the flexibility of the chains in the sense that a high value of T_g is generally assumed to be connected with relatively high barriers of bond rotations. These barriers depend not only on the type of bond, but also on the intermolecular constraint and, therefore, on the supramolecular arrangement of the chains. For this reason the glass transition temperature of the anisotropic liquid crystalline phase can differ from that of the isotropic amorphous phase. Conformational analysis and X-ray diffraction indicate that conformers with mostly *trans* conformations predominate in the LC phase [14–16]. Segmental movements above the glass transition in the LC phase shall not modify this orientation significantly, being, therefore, more restricted than in the amorphous state. 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 [7,8].

The two specimens of PH31B32 annealed at intermediate times show considerably smaller isotropisation peaks (Fig. 2) and also two glass transitions are observed, indicating that the mesophase formation is not complete for intermediate annealing times and the two phases (amorphous and mesophase) coexist. The degree of transformation can be deduced either from the relative specific heat increments at the glass transitions or, better, from the enthalpy of isotropisation, assuming that the sample annealed for a very long time presents a total mesophase formation (in fact, this sample does not show the glass transition corresponding to the amorphous isotropic sample). The values of the estimated degree of mesophase formation (%LC) are presented in Table 1, deduced from the corresponding values of the isotropisation enthalpy.

The peak isotropisation temperature values are also presented in Table 1, showing a slight, but appreciable, increase with the annealing time, as it was reported before [11].

The first derivatives of the specific heat curves allow to identify more clearly the two glass transitions. These derivatives, in the region of the glass transitions are shown in Fig. 3, where two maxima, centred at around 84 and 97 °C, are clearly observed, corresponding to the inflection points in the specific heat increment at the glass transition. The maximum at 97 °C (the isotropic amorphous component) decreases in intensity with increasing annealing times, while the one at 84 °C (the anisotropic mesophase component) increases.

An additional feature in the derivatives of Fig. 3 is the observation of a region in the high-temperature part of both glass transitions where the derivatives take negative values. The origin of this feature is the enthalpy relaxation (aging process) of the material. The aging process is well documented in the amorphous regions of polymers [21–23], but we have also observed and analyzed it in liquid crystalline phases [24,25].

The X-ray diffractograms corresponding to specimens Q and LC of PH31B32 are displayed in Fig. 4. The lower diffractogram (Q sample) shows only a wide peak typical of amorphous polymers, with a maximum corresponding to 0.47 nm. The diagram for sample LC is not very different in the region of higher angles: It is only slightly narrower and centred at a somewhat higher angle, with a corresponding

Table 1
Sample characteristics: Enthalpy of isotropisation, percentage of mesophase and peak temperature

Sample	Preparation conditions	ΔH (J/g)	%LC	Peak (°C)
Q	Quenched	0	0	–
A40	Annealed 40 min at 125 °C	3.6	19.9	151.1
A55	Annealed 55 min at 125 °C	8.1	44.8	151.4
LC	Annealed 88 h at 125 °C	18.1	100	154.2

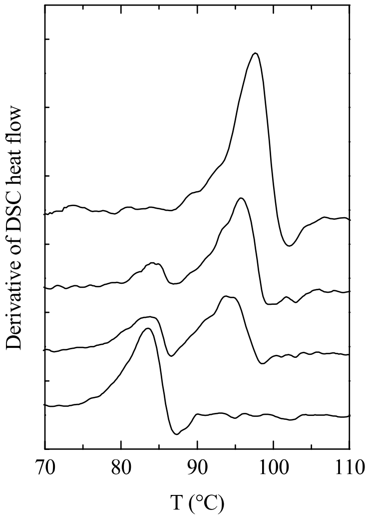

Fig. 3. First derivative, in the glass transition region, of the DSC melting curves in Fig. 2. From bottom to top: LC, A55, A40 and Q specimens.

smaller Bragg distance: 0.46 nm. However, the diffractogram for sample LC shows a narrow diffraction peak in the region of lower angles: It is centred at 6.96°, i.e. it represents a Bragg distance of 1.27 nm. These features are characteristic of a low-ordered smectic mesophase, with smectic layers spaced 1.27 nm, regularly piled, and the broad peak at high angles indicates lateral disorder: The molecules are packing in an unstructured way into the layer. As shown before [11], the analysis on stretched samples indicates that the mesophase of PH31B32 is of the type SmCalt: The mesogens are tilted with respect to the layer planes and the tilt direction alternates in successive layers.

The diffractograms for samples annealed at intermediate times show a low-angle diffraction peak with a correspondingly lower intensity.

The dynamic mechanical behaviour of the PH31B32 samples has been analysed at four different frequencies. The results, at 3 Hz, for the storage modulus, E', the loss modulus, E'', and tan δ are shown in Figs. 5–7, respectively. At least three relaxations, which will be named as α, β and γ, in order of decreasing temperature, are observed in the four samples.

The α-relaxation is considered the glass transition due to the high intensity of the relaxation, and to the correspondingly strong decrease in the storage modulus. Moreover, its temperature location corresponds to the DSC determined values for the glass transition. In fact, the inset in Fig. 6 shows that it is composed of two peaks, centred around 90 and 78 °C. The intensity of the former one is decreasing as the annealing time increases, as corresponds to the glass transition of the amorphous polymer. The lower-temperature component, however, increases its intensity with the annealing time, as corresponding to the glass transition of the liquid crystalline phase.

The two components are more clearly observed in the derivative of the storage modulus, as shown in Fig. 8 for the glass transition region. Again, two peaks are evident, at around 90 and 78 °C.

Focussing the attention on the specimens with pure phases (Q and LC), it can be deduced from both Fig. 8 and the inset in Fig. 6 that the peak of the LC component is appreciably wider than that of the isotropic sample (Q sample). Thus, the width at half maximum for E'' and at half minimum for the derivative of E' is around 11–12 °C for the LC component while it is only around 7–8 °C for the isotropic amorphous one. The smaller width of the isotropic component is accompanied by a correspondingly higher intensity of the α-peak in E'' (or the derivative of E', meaning a higher decrease of the storage modulus at the transition for this isotropic component).

Nevertheless, these differences are not as big as when comparing an amorphous polymer and its corresponding semicrystalline counterpart.

On the contrary, the tan δ results (Fig. 7) in the region of the α-relaxation are much more different among the four

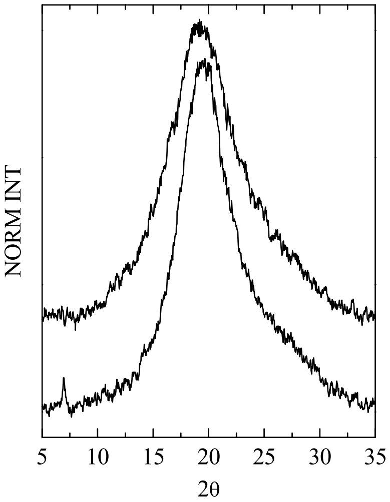

Fig. 4. X-ray diffractograms of the two specimens of PH31B32 with pure phases: Q sample (upper) and LC sample (lower diffractogram).

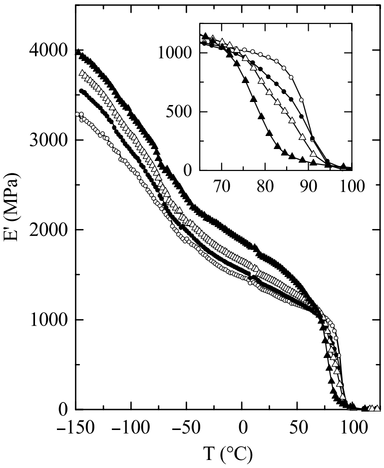

Fig. 5. Variation with temperature of the storage modulus, at 3 Hz, of the different PH31B32 specimens: Q (open circles), A40 (full circles), A55 (open triangles), LC (full triangles).

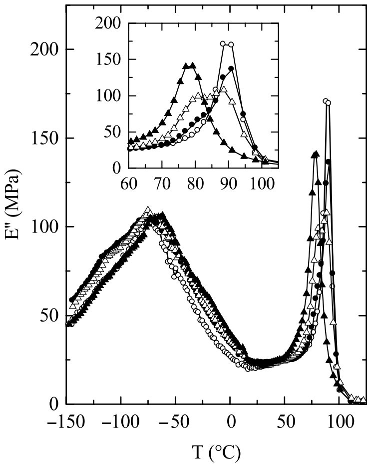

Fig. 6. Variation with temperature of the loss modulus, at 3 Hz, of the different PH31B32 specimens: Q (open circles), A40 (full circles), A55 (open triangles), LC (full triangles).

studied specimens, since the tan δ values are much higher for the isotropic sample. In fact, extremely high values are obtained for tan δ maximum of quenched PH31B32, as observed in Fig. 7: Although the absolute values are not completely reliable near the maximum, it appears that tan δ is around 6 for the α-relaxation of the amorphous sample, and only 0.45 for the pure mesophase. As a comparison, a study on polybibenzoates with oxymethylene spacers [26] showed that tan δ maximum for the α-relaxation is near unity for the polymers exhibiting a smectic mesophase, and it goes to around 1.8 for an amorphous polybibenzoate. On the contrary, when the sample crystallizes the tan δ maximum at the α-relaxation decreases very much to a value of only around 0.15 [27].

The two contributions for the α-relaxation are also clearly observed in Fig. 7 in the specimens annealed at intermediate times (the big difference in intensity between the amorphous and liquid crystalline components of tan δ makes difficult to observe these contributions in a normal scale, so that the ordinate in Fig. 7 is presented in logarithmic scale).

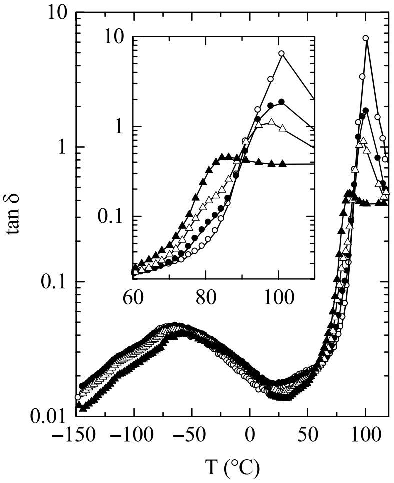

Fig. 7. Variation with temperature of tan δ, at 3 Hz, of the different PH31B32 specimens: Q (open circles), A40 (full circles), A55 (open triangles), LC (full triangles).

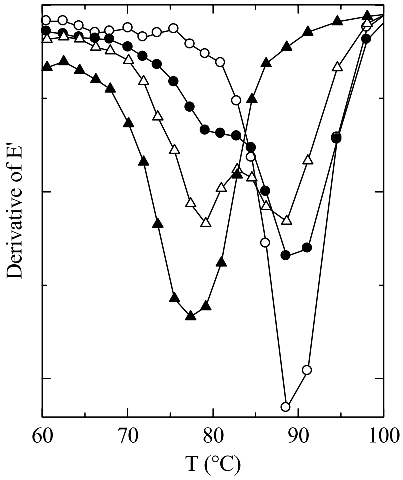

Fig. 8. Derivative of the storage modulus, at 3 Hz, in the region of the α-relaxation (glass transition) of the different PH31B32 specimens: Q (open circles), A40 (full circles), A55 (open triangles), LC (full triangles).

As a final comment for the α-relaxation (the glass transition), Table 2 shows the temperature values obtained in the different determinations (DSC, derivative of E', E'' and tan δ) for the Q and LC samples (the pure phases). As usual, tan δ values are around 10 degrees higher than the E'' (and E') determinations, while the DSC values are more or less intermediate.

Concerning to the relaxations at lower temperatures, the β-relaxation in polyesters has been studied extensively by DMTA and dielectric measurements. It takes place in both cases in the temperature interval between −80 and −50 °C. This relaxation in polyesters is believed to be a complex mechanism arising from movements of several groups [26–33]. In fact, this relaxation in aromatic polyesters has been reported to be composed of two overlapped peaks [34,35] named as β_1 and β_2.

In the present results (Figs. 6 and 7), the region below room temperature seems to be composed of three overlapped peaks. E'' and tan δ curves are usually described as composed by contribution of different Gaussian curves, one for each observed relaxation process. Such a convolution does not have a theoretical basis that can explain satisfactorily the shape of the dependence of both magnitudes on temperature, though some factors that can influence them are known. A method of curve convolution

Table 2
Values obtained in the different estimations of the glass transition (α-relaxation) for the two specimens with pure components

Sample	T_g or α-relaxation (°C)			
	DSC	E'	E''	tan δ
Q	97.6	89.4	89.6	101
LC	83.7	77.5	78.0	85

to analyze the dynamic mechanical loss curves in the region of the glass transition of several polymers has been proposed [36], confirming the validity of this empirical approximation. This convolution is, in principle, a very useful tool for the estimation of relative areas of the different relaxation mechanisms and for the assessment of the relaxation locations when the overlapping of the different processes is very important.

Such kind of deconvolution is shown in Fig. 9 for the LC and Q samples. Three Gaussian peaks provide a rather good fitting of the modulus values. However, it is evident from the figure that there is a great uncertainty on the position, width and intensity of the peaks: In fact, only the position of the central peak is obtained with good accuracy. Nevertheless, it seems clear that at least three contributions are present.

The peak positions displayed in the components of Fig. 9 are −115, −65 and −20 °C for the LC sample, and −116, −72 and −36 °C for the Q sample. The lowest temperature peak appears in the two cases at temperatures rather similar to those assigned to the well known γ-relaxation. The γ-relaxation in polyethylene was firstly attributed to crankshaft movements of polymethylenic chains [37]. Though a lot of work concerning this relaxation in polyethylene has been done, there remains no clear consensus regarding the details of the underlying motional process [38,39]. There is, however, a body of opinions which support one or more of the various models for restricted conformational transitions as kink formation, inversion and migration [37,40–42]. Molecular dynamics simulations have been a powerful tool to corroborate the just mentioned nature of these conformational motions underlying this relaxation [43,44]. This type of motion requires chains containing sequences of three or more methylenic units. However, previous works [26–29,33] reported that the ether group can cooperate with this restricted motion of the main chain when one of the methylene units is substituted by an oxygen atom.

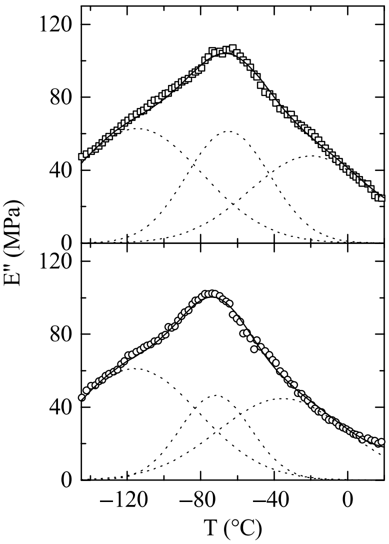

Fig. 9. Gaussian deconvolution of the low temperature region of the loss modulus, at 3 Hz, of two PH31B32 specimens: Q (lower) and LC (upper).

In the present case of PH31B32, including only trimethylene spacers in between the biphenyl units, this relaxation is expected to have a low intensity, in accordance with the experimental results: The γ-relaxation appears only as a shoulder in the lower temperature side of the β-relaxation.

The other two peaks of the deconvolutions in Fig. 9 should represent the composite β-relaxation. As pointed out above, only the central peak can be determined with adequate accuracy. It appears at −65 °C in the LC sample and at −72 °C for the Q specimen (intermediate values are obtained for samples A40 and A55). These values are rather similar to those obtained for other polyesters of the polybibenzoates series [26–29,33], with temperatures in the interval from −55 to −81 °C, depending somewhat on the chemical and solid-state structure of the polymer.

The activation energy of the mentioned central peak is obtained to be 70±7 kJ/mol for the Q sample and 66±7 kJ/mol for the LC specimens. These values are of the same order of those reported for other similar polyesters [26,27].

Concerning the activation energy of the α-relaxation, very high values (higher than 400 kJ/mol) are obtained for the two phases, so that it is not possible to establish possible differences between the two phases. We are planning to perform DETA measurements on these samples in order to get further knowledge.

From all the preceding results, it follows that there are clear differences between the isotropic amorphous and the liquid crystalline state of PH31B32, although those differences are much smaller than the ones found between a classical amorphous polymer and its semicrystalline counterpart.

As a final result, the magnitude of those differences can be quantified from the storage modulus, which is a measure of the rigidity of the material. Thus, Fig. 10 shows the variation of the storage modulus with the percentage of LC phase for two cases: At very low temperatures (−140 °C) and at room temperature (25 °C). The results show clear increases in the two cases: Around 21% at −140 °C and around 28% increase at room temperature. The rigidity of the mesophase is, therefore, significantly higher than the one for the amorphous sample.

4. Conclusions

The dynamic mechanical (and DSC) results on several specimens of the poly(ether ester) PH31B32 show that the glass transition (α-relaxation) temperatures of the isotropic amorphous and the anisotropic liquid crystalline states are clearly different, and when the mesophase transformation is not complete, as it happens in the two specimens annealed at intermediate times, the two glass transitions are

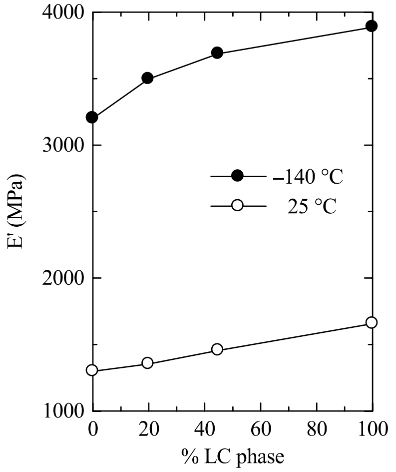

Fig. 10. Variation of the storage modulus with the mesophase content, at the indicated temperatures.

simultaneously observed. The values of the storage modulus below the glass transition are dependent on the degree of liquid crystallinity, showing that the rigidity of the mesophase is significantly higher than the one for the amorphous component.

Acknowledgements

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