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X-ray diffraction study of the influence of temperature on the structural correlations of poly(2-hydroxypropyl ether of bisphenol A)

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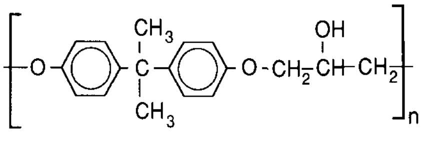
The X-ray diffraction pattern of glassy poly(2-hydroxypropyl ether of bisphenol A) is studied at room temperature on oriented samples in order to associate its different peaks to different structural correlations. On the other hand, X-ray diffraction patterns have been obtained at different temperatures from $T_g - 50$ K up to $T_g + 50$ K for the above-mentioned polymer. Attention has been paid to the evolution with temperature of the position of the wide diffraction maximum corresponding to interchain correlations in the polymer. The temperature evolution of this parameter shows a marked discontinuity just at the glass transition temperature.

(Keywords: glass transition; X-ray diffraction; structural correlations)

INTRODUCTION

Poly(2-hydroxypropyl ether of bisphenol A), a copolymer of bisphenol A and epichlorhydrin, currently known as Phenoxy (PH), is an amorphous engineering thermoplastic that has been a subject of investigation in the past years. Papers on the physicochemical properties[1,2] as well as the ability of this polymer to be blended with other homopolymers[2,3] can be found in the literature. The repeating unit in the polymer chain shows the bisphenol A residue:



This fact makes this polymer similar to polycarbonate (PC), which has been widely studied for many years by polymer scientists[4].

The local structural characteristics of PH can be studied by wide-angle X-ray scattering (WAXS) in a similar way to the one used to obtain structural information from disordered polymers[5]. WAXS patterns from amorphous polymers show marked diffraction maxima at relatively low scattering vector (s) values between 1 and 2 Å^{-1} which correspond to interchain structural correlations, and lower maxima at higher scattering vector values corresponding to intrachain structural correlations[5,6]. Diffraction maxima obtained at scattering vector values lower than those corresponding to interchain correlations are attributed to molecular organization at larger scale. In the case of PC, a small WAXS peak[6–8] appears at values of s around 0.7 Å^{-1} and is assigned to correlations in the direction of the macromolecular chain axis[7].

On the other hand, the 'glass transition' phenomenon has been well known and widely studied for glasses for many years, especially for glassy polymers: the different behaviour for the volume (or the enthalpy) of a given glassy material on the two sides of a certain temperature zone defines a temperature value characteristic for each material called the glass transition temperature (T_g). Up to now, few studies have been carried out in order to ascertain whether the structural parameters of glassy polymers vary with temperature through their glass transition. By using small-angle X-ray scattering (SAXS), Fischer and Dettenmaier[9] have measured the mean-square value of the density fluctuations ($\langle(\Delta\rho)^2\rangle$) of poly(methyl methacrylate) (PMMA), PC and poly(ethylene terephthalate) (PET), showing in the three cases that the temperature behaviour for $\langle(\Delta\rho)^2\rangle$ is linear, with a slope higher in the liquid ($T > T_g$) region

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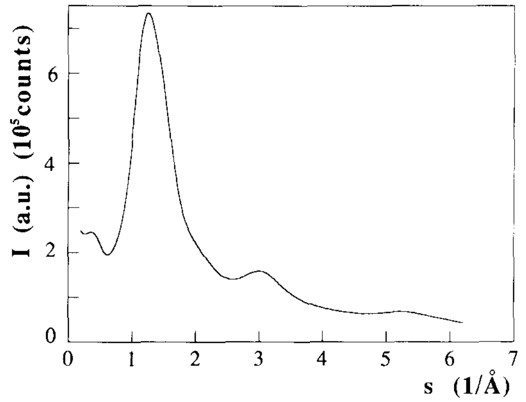

Figure 1 WAXS pattern for isotropic PH at room temperature

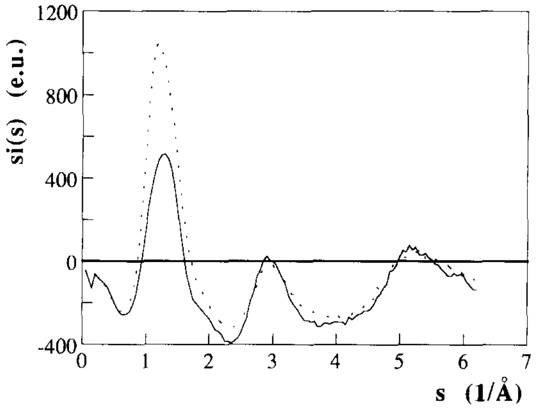

Figure 2 Reduced intensity function *si(s)* at room temperature for an oriented sample of glassy PH: meridional (—) and equatorial (···) sections

than in the glassy ($T < T_g$) one; the change in the slope was located at the respective T_g values. More recently, Curro and Roe[10,11] have obtained very similar results for poly(styrene) (PS), PMMA and PC by using the same technique. Moreover, they measured the isothermal relaxation of the density fluctuations frozen at temperatures below T_g in each polymer. Nevertheless, to date, no systematic studies have been developed by means of WAXS in order to study how the medium-range order of polymeric glasses changes with temperature, specially around T_g: Killian and Boueke[12] and Song and Roe[13] for PS and Saffell and Windle[8] and Mitchell and Windle[7] for PC have tried to study by means of WAXS patterns the structural changes *versus* the temperature in amorphous polymers.

This paper reports a structural study of glassy PH as well as a study of the evolution of the diffraction pattern with temperature below and above T_g.

EXPERIMENTAL

The material used in this work was PKHH from Union Carbide with a number-average molecular weight of 25000. The calorimetric T_g is located at 373 K. Prior to any measurement, the polymer was purified by solution in tetrahydrofuran and subsequent precipitation in hexane.

WAXS experiments were carried out in a symmetrical transmission diffractometer equipped with a graphite crystal incident beam monochromator, pinhole collimation, temperature control and step scan procedures using Cu radiation (1.54 Å). Diffraction data were collected at values of the scattering vector between $s = 0.2$ and 6 Å^{-1} in steps of 0.02 Å^{-1}. Scattering measurements on an oriented sample were obtained by rotating the sample in a plane containing the scattering vector in steps of 9° between $\alpha = 0°$ and $\alpha = 90°$, where α is the angle from the extension axis of the sample to the θ–2θ axis ($s = 4\pi \sin \theta/\lambda$).

The oriented sample for X-ray analysis was prepared by extrusion of the polymer previously headed at $T > T_g$ in a channel die to an extension ratio of about 2.

WAXS measurements around T_g were performed at temperatures between 423 and 323 K by first cooling the sample by 10 K min^{-1} from 453 K to the temperature of the measurement in order to assure the same thermal history for the sample in all the measurements.

Diffraction data were smoothed, corrected and normalized to electronic units following the procedures previously described[4,14–16].

RESULTS AND DISCUSSION

Figure 1 shows the non-corrected scattering pattern for an isotropic PH sample at room temperature. The shape of this curve is the typical one observed for a glassy polymer like PC[7] with a great interchain peak (at 1.24 Å^{-1} in our case) and intrachain structural correlation peaks (at 3.03 and 5.17 Å^{-1} in this case) with lower intensity. As a polymer based on bisphenol A in its structural unit, PH shows a small interchain peak at around 0.4 Å^{-1} in the same sense as PC does around 0.7 Å^{-1}. This weak peak for PC was observed by WAXS[7] and wide-angle neutron scattering[17].

Figure 2 shows the reduced intensity curve *si*(*s*) for the oriented PH sample disposed in two different positions with respect to the θ–2θ axis ($\alpha = 0°$ and $\alpha = 90°$). The curves obtained at values of α between 0° and 90° are in between these two. The most prominent peak is enhanced towards the equator. It indicates that it arises from interference among polymeric chains[5–7]. The peaks at higher scattering vectors are not changed with orientation, so they are not particularly anisotropic as one could expect from their origin in intrachain correlations[5]. The weak peak obtained at around 0.4 Å^{-1} shows extremely small differences when the WAXS experiment is carried out in different directions with respect to the oriented PH sample. Although very small, these differences always show that the diffracted intensity for this peak is higher in the meridional direction. However, as will be shown in this paper, this wide and low intensity maximum overlaps significantly with the main interchain diffraction peak and, because of this fact, it is not easy at this stage to point out its non-isotropic character. Nevertheless, in order to go deeply into the different origin of the two peaks, we present in *Figure 3* the anisotropic component of the diffraction intensity, obtained by subtraction of the isotropic scattering, for two sections of the scattering of the anisotropic PH sample, showing that the main interchain peak is clearly equatorial in character. The one appearing at low angle is mainly meridional, though it can be associated to interference along the axis of the macromolecular chain with characteristic distances longer than the typical ones of both interchain and intrachain structural correlations that have been discussed above. These types of weak structural correlations have been widely discussed in terms of molecular models based on energy calculations and diffraction analysis of PC[7,18-20], which is very similar in the monomeric structure to PH. Since the PC chain is spatially corrugated, some correlations among the phenylene groups of neighbouring chains have been proposed to be responsible for the weak peak located at around 0.7 Å^{-1} in PC; this fact would be valid for other polymers containing phenylene groups, as indicated in refs 7 and 21. In our case, the same type of correlations would be responsible for the peak at 0.4 Å^{-1} in PH. From the position of the maximum of the peak s_m one can calculate an average value of the structural interchain correlation length d by using Bragg's law[5]:

$$d = 2\pi / s_m \qquad (1)$$

The characteristic correlation length associated to this weak peak is around 16 Å. Nevertheless, when we compare this distance to the one that is associated to the same weak peak obtained in PC in the same angular region (around 9Å), one could think that the above-mentioned comment, explaining that this peak in PH could arise from correlations among phenylene groups as suggested for PC, would not be right. However, we must take into account the chemical structure of the repeating units of polymeric chains of PC and PH respectively. The monomer of PC is formed by the bisphenol A group and a carbonyl group, whereas the monomer in PH is formed by the bisphenol A group and a 2-hydroxypropyl group instead of the carbonyl one. The fact that the 2-hydroxypropyl group is much more bulky than the carbonyl one could explain the difference between the characteristic correlation lengths in the two polymers.

At this point, we will now focus our attention on the changes of the diffraction pattern of PH induced by temperature above and below T_g. These WAXS measurements were carried out at different temperatures on a transmission diffractometer, with the same characteristics as the one used above, equipped with a sample cell allowing a temperature variation of the material controlled with an accuracy of ±0.5 K. Diffraction patterns were obtained at 18 different temperatures between 323 and 423 K in order to cover a wide temperature range in both liquid and glassy states, at $T > T_g$ and $T < T_g$, respectively, of the material. Prior to each WAXS measurement in the glassy state ($T < T_g$), the sample was heated up to around 400 K and then cooled down to the temperature of measurement at 10 K min^{-1} in order to have material with the same previous thermal history. This is important in the glassy region ($T < T_g$) where the metastable structure resulting for the material depends strongly on the cooling conditions, as has been described in a wide number of papers in the literature[22-25].

Figure 4 shows diffraction patterns for PH at two different temperatures in the glassy and liquid state of the material. The other patterns obtained at temperatures between 323 and 423 K are in between these two. We can clearly observe that the diffracted intensities at scattering vectors lower than 2 Å^{-1} show appreciable differences, whereas at values of s higher than 2 Å^{-1} no differences are detected among curves corresponding to different temperatures. One cannot expect changes in the intrachain structural correlations region because the temperature (in our case, the glass–liquid transition) will not change the monomeric structure of the macromolecular chain, that is, for instance, the lengths of the bonds between the constituent atoms of the material. However, the lower s-values region, corresponding to the interchain structural correlations of higher distances, is expected to show changes with the temperature through the liquid–glass transition because of the characteristic crossover of the specific volume or the density of the material in this temperature zone which occurs not only in polymers but also in a very wide variety of non-crystalline materials like organic liquids, biomaterials, inorganic melts and certain metallic elements and alloys that can exist in the glassy state[26,27].

One observes in *Figure 4* that the position and the intensity of the main peak are appreciably changed and, for the weak and low-intensity peak at $s \approx 0.4$ Å^{-1}, it seems that temperature only produces changes in the intensity, not in the position. We will first pay attention to the evolution with temperature of the main equatorial peak and, afterwards, we will study the variations for the

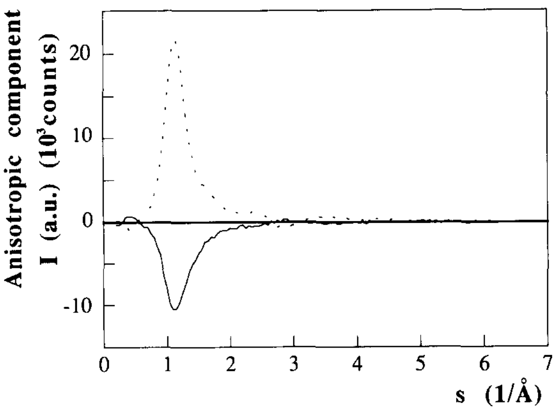

Figure 3 Anisotropic component of the scattered intensity at room temperature for oriented PH: meridional (—) and equatorial (···)

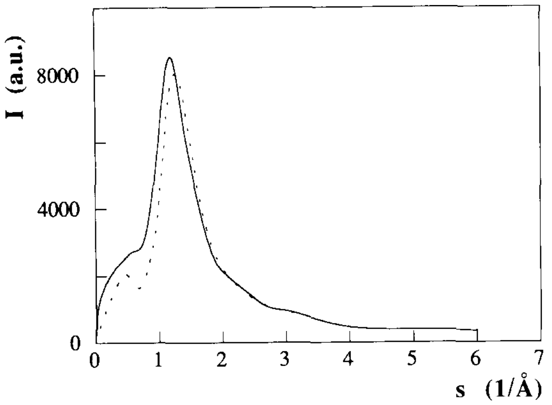

Figure 4 Background-corrected WAXS patterns for PH obtained at 423 K (—) (above T_g) and 323 K (···) (below T_g)

meridional peak associated to longer correlation distances.

Figure 5 shows the evolution of the average distance (obtained by means of expression (1)) corresponding to the main diffraction peak, which has been signalled above to arise from interchain correlations, *versus* the temperature of the sample. We can observe that the variations with temperature are very small: the total change that one observes from $T_g - 50$ K up to $T_g + 50$ K is around 10%. Within the experimental dispersion, it is clear that around 380 K (temperature very close to T_g) there is a marked crossover in the temperature behaviour between two linear variations of d against temperature, with a low value for the slope in the glassy zone ($T < T_g$) and a higher one in the liquid region ($T > T_g$) in the same sense that has been signalled for the volume or the enthalpy of amorphous materials[26,27] around its glass transition. The breakdown for these two temperature behaviours occurs very close to the calorimetric T_g of PH. The evolution in the glassy state d_g (T) follows a linear relation with temperature given by:

$$d_g(T)/d_0 = 1 + \alpha_g T \qquad (2)$$

where d_0 represents a reference value of the correlation length (in this case $d_0 = 4.95$ Å obtained at room temperature) and α_g, resulting in a value of $2.6 \times 10^{-4}\,\mathrm{K}^{-1}$, would be understood as a dilatation coefficient for structural correlation length in the glassy state of the material. On the other hand, in the liquid zone, a linear relation for the correlation length d_l is also obtained and is given by:

$$d_l(T)/d_0 = 1 + \alpha_l T \qquad (3)$$

where $\alpha_l = 17.6 \times 10^{-4}\,\mathrm{K}^{-1}$ can be interpreted for the liquid state of the material in the same sense as α_g.

Now, we will try to relate our results to others obtained by means of more classical techniques used in the study of glass transition processes in polymers, e.g. dilatometry. In a recent work[28], Alegría *et al.* present the relative variation of the volume of PH around T_g, fitting it with the equation:

$$(V - V_0)/V_0 = 1 + \alpha T \qquad (4)$$

α being the dilatation coefficient in the glassy or in the liquid state and V_0 a reference volume of the sample, e.g. the volume at room temperature. The obtained slope values are $2.4 \times 10^{-4}\,\mathrm{K}^{-1}$ and $11.1 \times 10^{-4}\,\mathrm{K}^{-1}$ for the glassy and the liquid state, respectively. Our value for the expansion coefficient in the glassy state coincides with the one obtained from dilatometric experiments, but in the case of the liquid state the value presented in our work is noticeably higher than the one from dilatometry in ref. 28, as well as from the more complete volumetric data from ref. 1. This disagreement becomes more important when one thinks that α values calculated here are linear while the ones from refs 1 and 28 are volumetric. Nevertheless, our values agree very well with the dilatation coefficient of the free volume that is deduced from dilatometric data in refs 28 supposing that the glass transition process is driven by free volume. Very similar results occurred when the structural interchain correlations were investigated by means of neutron diffraction experiments for polybutadiene around T_g (ref. 29). The abnormally high values of the expansion coefficients deduced in this work can be understood by the fact that the temperature only affects the interchain equatorial peak (as described later in this paper, the mainly meridional in character weak peak at around 0.4 Å^{-1} is not appreciably changed by the temperature). This fact proves that the expansion of the polymer mainly occurs along the equatorial direction. In any case, the result of *Figure 5* shows that the structural interchain correlations in amorphous polymers are strongly sensitive to the glass transition process.

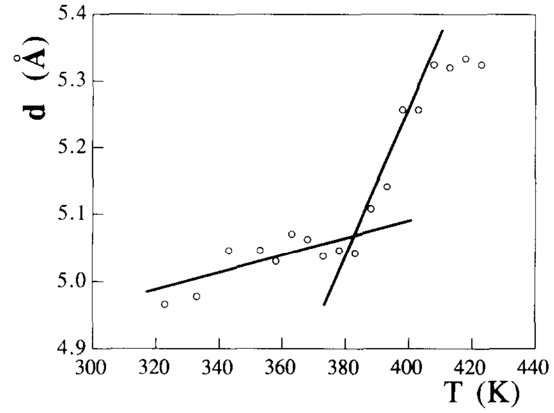

Figure 5 Evolution of the average interchain distance d *versus* temperature of the PH sample for the main peak

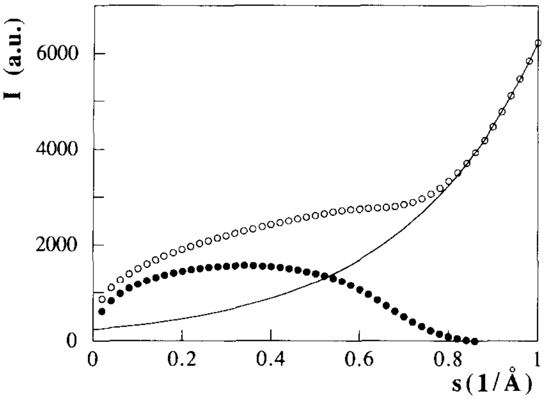

Figure 6 Example of the subtraction of the contribution of the main equatorial peak from the intensity of the meridional in character weak peak in the diffraction diagram of PH obtained at 423 K: (○) experimental points; (——) the fitting to the intensity of the low-angle part of the main peak; and (●) the result of the subtraction of full line from open circles

On the other hand, we can observe in *Figure 5* that the position of the maximum of this main diffraction peak seems to remain constant at temperatures higher than 410 K. This fact indicates that the main interchain correlation length is not changed at these temperatures and could be interpreted by the idea that interchain structural correlations could be hindered by some crosslinking among polymeric chains. In this framework we find in the literature evidence of hydrogen bonding above 420 K in PH and in its blends with poly(ethylene oxide)[30]. Furthermore, studies made in our laboratory

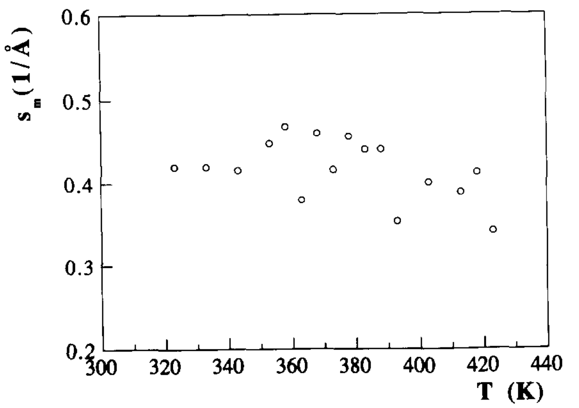

Figure 7 Evolution of the position of the meridional in character diffraction maximum s_m *versus* temperature of the PH sample

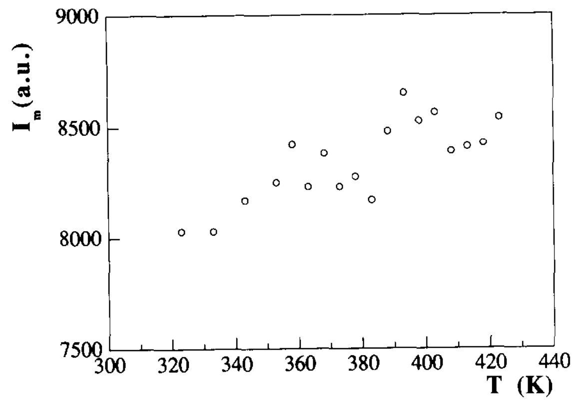

Figure 8 Variation of the intensity in the maximum I_m for the main interchain peak of PH *versus* temperature

show that PH maintained for a long time (as is the case in our WAXS experiments) above 420 K is not able to be dissolved by its usual solvents (e.g. tetrahydrofuran or dioxane) as it is before this type of thermal treatment. This fact can also be understood as experimental evidence of some crosslinking or reticulating of polymeric chains in PH.

At temperatures lower than T_g, the variation of d, although small, is noticeable and this fact is in accordance with the idea that molecular motions of glassy materials below T_g are not completely hindered and, in this temperature region, some possibility of molecular motion exists like, for instance, β or β-like relaxation processes that have been widely discussed in the literature[25,31–33].

At this point, we will now study the influence of temperature on the position of the weak peak, which has been assumed above to be mainly meridional in character. *Figure 4* does not suggest changes in the location of this peak; nevertheless, one can observe that, at higher temperatures, this peak is enlarged or overlapped with the main one, which is shifted towards lower scattering vector values, and shows higher intensities with increasing temperature. At this stage, the contribution of the main peak to the intensity of the low-angle peak has been evaluated by fitting the points of the main peak between 0.8 and 1 $Å^{-1}$ to an exponential law and subtracted from the experimental points in the weak diffraction peak region. Then, we have studied the remanent intensity in this region. An example of this subtraction is shown in *Figure 6*. We must notice the odd shape of this remaining peak obtained in the medium-angle region, that is in the limit between small- and wide-angle regimes. It is important to take into account that this width implies that there is a strong distribution of correlation lengths among phenylene groups of neighbouring chains around a mean value of some 16 Å. After repeating this operation for all the diffraction diagrams obtained for PH at different temperatures, we have plotted the position of the maxima of these low-angle peaks *versus* temperature (see *Figure 7*). There is a high dispersion in the experimental points, most of all in the high-temperature zone. However, we are not able to observe any change, and hence any influence, of the glass transition process in the position of the peak. In this sense, this result is in agreement with other works developed in PC[7,8] studying the influence of temperature and thermal history on the weak peak, meridional in character, obtained at 0.7 $Å^{-1}$, which is very similar to this peak at around 0.4 $Å^{-1}$ in PH. In refs 7 and 8 no changes in the position of these peaks are found; only variations in the intensity or in the shape have been reported.

Going back to *Figure 4*, one observes that, in addition to the shifting of the main peak towards lower angles when the temperature becomes higher, the height of the two interchain peaks is clearly increased with temperature. We will now pay attention to this fact. It is clear that the intensity of the main peak changes appreciably with temperature (see *Figure 8*) within the great dispersion existing in the experimental points. Nevertheless, we cannot find any influence or crossover due to the glass transition in the temperature variation of the intensity of the maximum. The fact that the intensity of the main peak clearly increases with temperature is in contradiction with the idea that the intensity might decrease when the temperature increases due to the increasing thermal disorder or decreasing electron density. Unfortunately, we are not able to explain it and, moreover, we find in the literature works that report the same feature of higher diffracted intensities at higher temperatures in polystyrene[12,13] and in polybutadiene[29] without comments about this particular point. We have evaluated the half-height width for this peak at each temperature of measurement but no variation has been

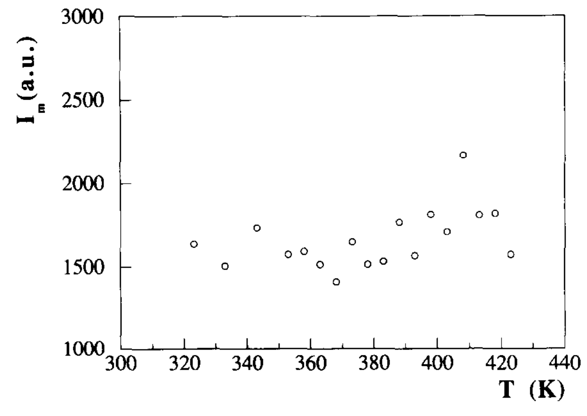

Figure 9 Variation of the intensity in the maximum I_m for the meridional in character weak peak *versus* temperature

found. Moreover the shape of the peak remains unchanged with temperature. On the other hand, both the area and the intensity in the maximum of the weak meridional peak at around 0.4 Å^{-1} have been studied but no variations are found with temperature (see in *Figure 9* a plot of the intensity of the maximum corrected from the influence of the main peak as explained above). From the results, we cannot obtain a definite conclusion about the influence of the glass transition on the intensity of the maxima associated to the two types of interchain structural correlations. In the case of interchain equatorial correlations, the dispersion in the experimental points does not allow one to extract any definite conclusion although a variation with temperature is observed. On the other hand, it seems that the temperature does not affect the correlations between phenylene groups of neighbouring chains. In refs 7 and 8 some intensity or area variations have been observed in this peak for PC with a breakdown in the overall behaviour through the two temperature sides of T_g. If we represent our raw data, we can find this kind of breakdown in the temperature behaviour. Nevertheless, it seems that this discontinuity in the temperature variation of the intensity of the maximum must be assigned not to the meridional weak peak but to the influence of the equatorial peak, the position of which is strongly shifted towards lower angles when the temperature increases. In any case, the fact that there is no significant effect of temperature on the remainder of the scattering and, in particular, on the shapes or widths of the peaks, indicates that the polymer expands without any general structural reorganization. In order to understand the particular temperature sensitivity of the main interchain peak, it is useful to consider the factors that relate the intensity of the diffraction peak to temperature. In all types of materials, crystalline and non-crystalline, the changes in the diffraction peak intensity with varying temperature will result from variations in both the thermal disorder and the electron density. We think that this last factor, the electron density of the material, might be severely affected by the glass transition process because of the usual dilatometric results in non-crystalline materials. Nevertheless, in our case, no appreciable change of the variation of the maximum intensity of the main peak at the two sides of T_g (glassy and liquid states, respectively) is observed. The effect of the thermal disorder that is superimposed onto the electron density changes could override the influence of the glass transition process on the intensity of the diffraction pattern. At this point, more accurate WAXS experiments in the measurement of the intensity, which might be carried out in a diffractometer with better statistics, could allow us to go deeper into this question.

Finally, we must point out that the radial distribution function (*RDF*) of the material has been obtained (by means of the method described in ref. 34) for all the temperatures from the diffraction patterns fully corrected (from background, polarization, absorption and multiple scattering effects) and normalized to electronic units, in order to know if *RDF* was altered by the temperature. *RDF* is a function describing the atomic density around an arbitrary reference atom[5,14]; it is used to describe the short-range order in an amorphous material. In this type of material, it usually gives valuable information up to some 8 Å. It means that only the first two peaks, corresponding to first and second neighbours of a reference atom, respectively, are exploitable. No significant changes have been found in the first peak, located at around 2 Å. It corresponds to the intrachain structural correlation distances that remain unchanged by temperature as can be seen in *Figure 4*. The second peak of the *RDF*, located between 5 and 6 Å, shows changes towards higher distances as the temperature increases. This fact is in accordance with the values (and their temperature evolution) obtained for the characteristic interchain structural correlations that are shown in *Figure 5*. Nevertheless, due to the poor precision in the building of the *RDF* because of the short angular range of our scattering data, we are not able to find a break associated to T_g in the position of this second peak of the *RDF*. In any case, better experimental studies of scattering patterns of PH involving larger diffraction angle values and more accurate calculations seem to be necessary to investigate with good precision the temperature evolution of the *RDF* in its second maximum.

Another important point that has been investigated in this polymer is whether interchain correlations change with time at isothermal conditions below T_g, that is, whether interchain structural correlations are also affected by a physical ageing process in the same sense that volume or enthalpy are in glassy polymers, due to the crossover shown by the position of the peak around T_g (ref. 35). Some tests have been carried out at different temperatures below T_g by collecting diffraction patterns for PH stored during times ranging from 0.5 to 200 h. No changes in the position of the maximum of the main peak have been observed, within the precision of the points of *Figure 5*, in relation to the ones that have been reported above for the non-aged sample at the same temperature values. Moreover, no systematic variations have been detected for the intensity of the maximum when PH is aged at these temperatures $T < T_g$. In contrast to calorimetry, which is the most powerful technique used to study physical ageing processes below T_g (ref. 28), the interchain structural correlations measured by WAXS are not sensitive to these mechanisms.

CONCLUSIONS

From the structural study of the oriented sample of PH, one finds different origins of the two peaks corresponding to interchain structural correlations: the main peak is equatorial in character and the weak peak at low angles is meridional in character and could correspond, as it was assigned in polycarbonate (very similar in the monomer structure to PH), to structural correlations among phenylene rings of different chains.

The first peak is strongly influenced in intensity and position by temperature. The most important result comes out from the study of its position *versus* temperature. We found that the behaviour of the corresponding interchain correlation length is strongly altered by the glass transition: the variation of the position of the maximum with the temperature shows very different slopes in the glassy and liquid regions. Moreover, the values of these slopes, normalized to a reference temperature, are very similar to the ones obtained by dilatometry for the dilatation coefficients of PH below and above T_g, respectively. Thus, we can conclude that the structure of glassy polymers, that is the structural correlations between polymeric chains, vary noticeably with temperature. The study of these changes would allow us to learn more about the physical behaviour of these interchain correlations.

In order to confirm the results in this work it seems convenient to carry out these experiments in other types of polymeric systems showing chemical structure similar to PH or PC, that is, polymers containing the bisphenol A group (which is common to the last two polymers mentioned) in their repeat unit: actually, we think that polysulfone or polyarylate are good candidates in this framework.

ACKNOWLEDGEMENTS

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