Structural analysis of injection-moulded semicrystalline polymers by Fourier-transform infra-red spectroscopy with photoacoustic detection and differential scanning calorimetry: 2. Polyamide-6,6

L. Quintanilla, J. C. Rodríguez-Cabello and J. M. Pastor*
Departamento de Física de la Materia Condensada, Facultad de Ciencias/Escuela Técnica Superior de Ingenieros Industriales (ETSII), Universidad de Valladolid, 47011 Valladolid, Spain

(Received 22 February 1993; revised 5 August 1993)

In this paper, a study of the structural changes due to annealing of injection-moulded polyamide-6,6 has been carried out. The spectroscopic behaviour of polyamide-6,6 is quite similar to that of poly(ethylene terephthalate) (PET). Using the band at $1650\,\mathrm{cm}^{-1}$ as an internal reference band, the intensity changes of the bands situated at 1146 and $936\,\mathrm{cm}^{-1}$ were followed. The former decreases when the annealing temperature exceeds 180°C whereas the latter increases. Furthermore, the bandwidth of the band at $936\,\mathrm{cm}^{-1}$ decreases from 23 to $20\,\mathrm{cm}^{-1}$ for annealing above 180°C. These spectroscopic changes were related to *gauche/trans* isomerism induced by the thermal treatment. Moreover, polyamide-6,6 verifies a two-phase conformational model, similarly to PET. As far as the thermal behaviour is concerned, two endothermic peaks at low (LM peak) and high (HM peak) temperature were found in thermograms of samples annealed above 150°C, and these displayed similar behaviour to those found in PET. The LM peak can be attributed to melting of crystals with increasing perfection and fold-surface smoothing of the crystalline layers due to the annealing treatment, and the HM peak to melting of the recrystallized crystalline structure during heating in differential scanning calorimetry (d.s.c.). On the other hand, the influence of the fabrication process in polyamide-6,6 seems not to be as important as in PET. The correlation between Fourier-transform infra-red spectroscopy with photoacoustic detection (p.a.-*FT*i.r.) and d.s.c. measurements show that the amide group works as an important constraint that limits the mobility of the crystalline molecules, and most of the conformational changes occur in the amorphous phase for annealing temperatures above 180°C. In the ordered phase, a slight crystallinity increase beyond this temperature can be related to crystalline perfection and fold-surface smoothing.

(Keywords: polyamide-6,6; photoacoustic *FT*i.r.; structural analysis)

INTRODUCTION

Polyamides have become one of the most studied polymers in recent years. These polymers are quite interesting not only from a scientific and technological point of view, but also from an industrial and economic one. In particular, poly(hexamethylene adipamide) (polyamide-6,6) has been selected for further development because it appears to have the best balance of properties and manufacturing cost.

The structure of the crystalline portions of polyamide-6,6 has been determined from X-ray diffraction studies[1,2] of oriented fibres. The basic ingredients are extended zigzag-like chains, which zip together through linear hydrogen bonds between the amide groups to form sheets. The hydrogen-bond pattern results in a progressive relative stagger between the chains and parallel to the chain direction within the hydrogen-bonded sheets. Successive sheets close pack, and the nature of the van der Waals interactions and distribution of amide groups induce a progressive intersheet shear. The result is a triclinic unit cell. The X-ray fingerprint shows two strong equatorial diffraction signals[1,2]: the (100) reflection represents the interchain distance within the hydrogen-bonded sheet and the usually unresolved doublet {(010) +(110)} is related to intersheet distance.

Consequently, only *trans* isomer conformation can be involved in the crystalline phase of polyamide-6,6, but both *trans* and *gauche* conformations can be found in the disordered phase.

In 1942, Brill[3] reported that the two strongest peaks in the X-ray diffraction pattern, the (100) reflection and the {(010)+(110)} doublet, merge into a single peak at 160°C. The Brill transition, as it has come to be known, represents a change from a triclinic unit cell to a pseudohexagonal form[3,4]. However, this transition is

---

* To whom correspondence should be addressed

0032-3861/94/11/2321-08

reported to be reversible when the sample that suffered it is analysed at room temperature[5].

Previous density and X-ray diffraction studies carried out at room temperature have shown that annealing above 170°C raises the degree of crystallinity of polyamide-6,6[6]. Moreover, annealing of quenched samples shows a slight increase in the distance between chains within a sheet and a more important closer packing among hydrogen-bonded planar sheets, when the annealing temperature rises[6].

Infra-red studies have also been performed to analyse the influence of the annealing process on the crystallinity variation[7]. The two bands situated at 936 and 1146 $\mathrm{cm^{-1}}$ have long been attributed to 'crystalline' and 'amorphous' phases of polyamide-6,6, respectively[7-11]. The origin of these bands has been tentatively assigned to a C–CO stretching and a CO twisting movement[11]. In a strongly self-associated polymer, such as polyamides or polyurethanes, the development of order is reflected in both the distribution of conformation along the chains and strong molecular interactions due to hydrogen bonds[12]. Nevertheless, the above bands have been used for analytical determination of crystallinity levels. Garcia and Starkweather[13] have proved that the band at 936 $\mathrm{cm^{-1}}$ is not a true crystalline band owing to its behaviour with increasing temperature of the sample. Large changes can be observed at temperatures lower than that at which the onset of melting occurs, and even the presence of residual absorbances above the melting point can be detected. Therefore, this band is not truly crystalline in nature and a substantial amorphous contribution has been proposed[13]. In addition, they suggest that the assignment of the band to a C–CO motion provides information about skeletal vibration and, therefore, it can be used to follow conformational changes.

Owing to the strong polar groups present, polyamide-6,6 absorbs strongly in the infra-red. Therefore, in order to obtain the usual Fourier-transform infra-red (*FT*i.r.) spectra in transmission with a correct level of absorption, it would be necessary to use very thin microtomed samples. However, it would also have to be borne in mind that the microtoming procedure could induce structural changes in the sample under examination. Thus, the infra-red vibrational *FT*i.r. study reported here was carried out by using photoacoustic detection (p.a.-*FT*i.r.), since it has been proved that this technique is a very useful tool to characterize the surface of highly scattering and strongly absorbing samples, and does not require special sample preparation[14,15]. Glass-fibre-reinforced polyamide-6,6 will be the subject of our following paper, and the p.a.-*FT*i.r. technique becomes essential to its study[15].

In spite of the importance of vibrational spectroscopy for the characterization of macromolecular structure, only a limited number of problems may be solved by its exclusive application. A more complete picture of polymer structure can be obtained by an appropriate choice and combination of chemical and physical methods: in this work, differential scanning calorimetric (d.s.c.) will be used as a complementary technique.

More than one endothermic peak appears in the thermograms of polymers such as polyamide-6,6 or poly(ethylene terephthalate) (PET)[16,17]. It is generally recognized that such endotherms can arise from several different causes, which are dependent on the sample thermal history. In part 1[18], we have reported a detailed study of the thermal behaviour of injection moulded semicrystalline PET on annealing treatment.

The melting behaviour of annealed semicrystalline polyamide-6,6 has been widely studied during the past 25 years[5,16,19-22]; however, this has given rise to contradictory interpretations. A number of proposals have been made regarding the origin of the multiple-fusion endotherms: two crystal distributions, effects due to orientation, the presence of more than one crystalline phase (such as the triclinic and pseudohexagonal form previously reported in polyamide-6,6[1]). Bell *et al.*[16,20] proposed that the two peaks are due to the melting of two morphological species, form I and II. Form I (higher-temperature form) consists of crystals in which the chains are folded, and form II (lower-temperature form) contains crystals in which the chains within the crystal are extended.

Conversely to the X-ray diffraction technique, the Brill transition cannot be followed clearly by a thermal parameter in melt-crystallized polyamide-6,6 samples[5,22]. This transition gives rise to a quite broad endotherm extending over the whole region from the glass transition temperature (about 50°C) to the melting temperature (around 265°C)[5].

The main subject of this paper is to study the evolution of the conformations in polyamide-6,6 as a function of thermal treatment by the correlation between spectroscopic (p.a.-*FT*i.r.) and thermal (d.s.c.) techniques.

EXPERIMENTAL

Materials

The sample used in this work was furnished by SNPE (France) as 3 mm thick plate obtained by injection moulding of a commercial polyamide-6,6 (tradename PA6,6 Technyl A218); it has formic acid viscosity ≈ 140, $M_w \approx 33\,000$ and $M_n \approx 16\,500$. The polyamide-6,6 was injected into the mould at a temperature of 269°C with a pressure of 100 bar. The temperature of the mould was fixed at 70°C and the injected sample was maintained in it for 5 s at a pressure of 95 bar.

For the annealing treatments, samples of $3 \times 2 \times 3\ \mathrm{mm^3}$ were cut from the plates and introduced into a stabilized oven at different annealing temperatures (T_{ann}) ranging from 45 to 250°C, kept there for 1 h and then cooled to room temperature.

Photoacoustic Fourier-transform infra-red measurements

Photoacoustic Fourier-transform infra-red (p.a.-*FT*i.r.) spectra of polyamide-6,6 samples were obtained at room temperature on a Mattson Cygnus 100 FTIR spectrometer equipped with a MTEC 200 PA cell.

We have obtained a set of spectra at 8 $\mathrm{cm^{-1}}$ resolution and averaged over 312 scans with a mirror speed of 0.12 $\mathrm{cm\,s^{-1}}$, as the best signal-noise ratio was obtained at this speed.

Powdered carbon was used as a photoacoustically saturated (black) reference material.

Differential scanning calorimetric measurements

The thermal analysis was carried out in an air atmosphere with specimens whose weight ranged between 7 and 10 mg; the calibration of both temperature and melting enthalpy was made with a standard sample of indium.

The d.s.c. experiments were performed on a Mettler TA4000 (DSC 30) equipment at a heating rate of 10°C min^{-1}; each thermogram was recorded from 20 to 320°C.

From the measured heat of fusion (ΔH_{exp}), an apparent degree of crystallinity C_{dsc}(%) was determined according to the equation:

$$C_{\mathrm{dsc}}(\%) = \Delta H_{\mathrm{exp}} / \Delta \mathrm{H}^0$$

where ΔH^0 is the heat of fusion of an ideal polyamide-6,6 crystal. A value of 46 cal g^{-1} (ref. 19) was adopted for this parameter.

RESULTS AND DISCUSSION

Vibrational analysis

In *Figure 1*, general p.a.-*FT*i.r. spectra of unannealed polyamide-6,6 and samples annealed at 90, 180 and 230°C are shown. The expanded p.a.-*FT*i.r. spectra of the annealed samples (*Figure 2*) are limited to the 860–1200 cm^{-1} range, since the bands situated at 936 and 1146 cm^{-1} are to be used to monitor spectral changes promoted by the thermal treatment.

In p.a.-*FT*i.r. experiments, we have found, similarly to other authors[23], that the integrated intensity of the band

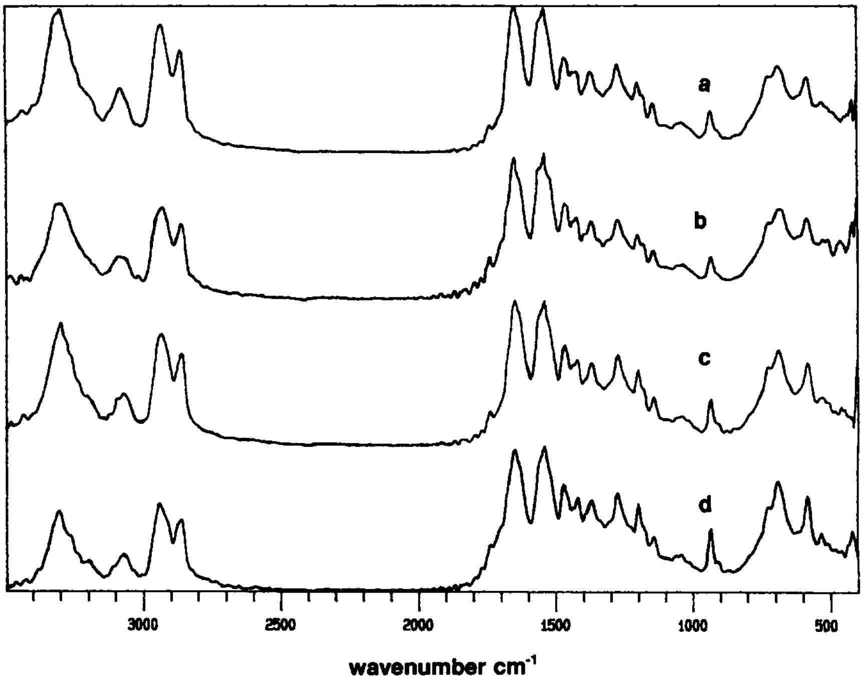

Figure 1 P.a.-*FT*i.r. spectra of (a) unannealed polyamide-6,6 and samples annealed at (b) 90, (c) 180 and (d) 230°C in the spectral range 400–3500 cm^{-1}

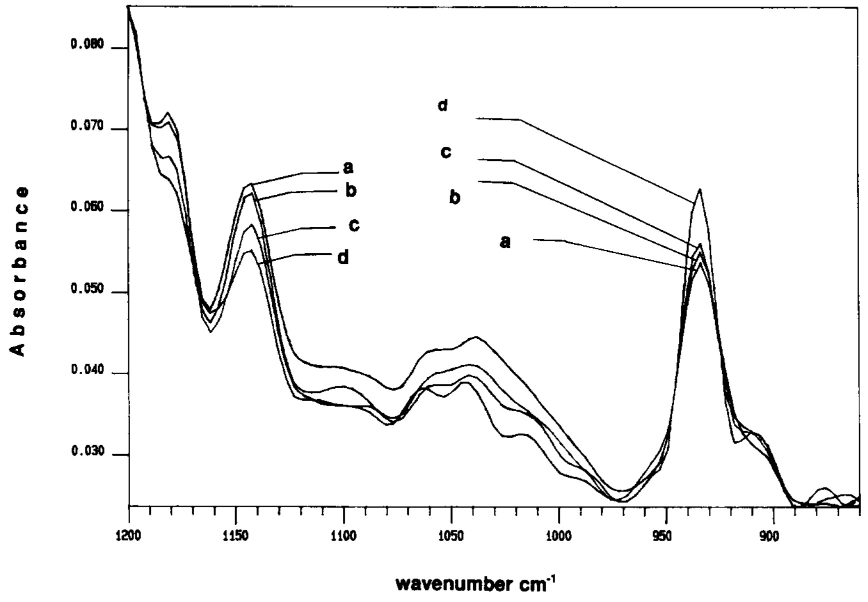

Figure 2 P.a.-*FT*i.r. spectra of (a) unannealed polyamide-6,6 and samples annealed at (b) 90, (c) 180 and (d) 230°C in the spectral range 860–1200 cm^{-1}

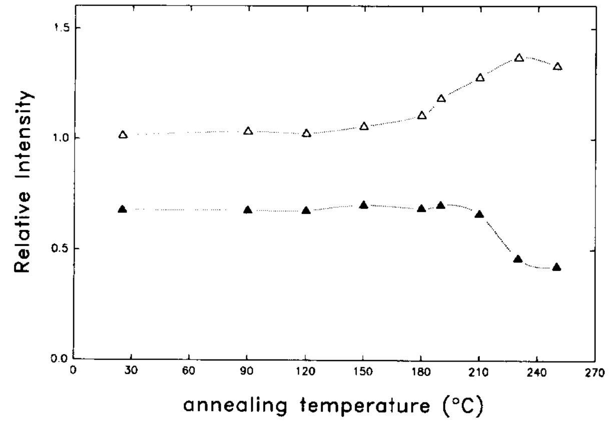

Figure 3 Relative intensity of bands at 1146 (▲) and 936 cm^{-1} (△) *versus* annealing temperature

situated at 1650 cm^{-1} (amide I) appears not to be affected by annealing. We were therefore able to use this band as an internal reference band in order to follow the intensity evolution of the bands at 936 and 1146 cm^{-1} with annealing treatment.

In order to carry out the quantitative analysis, peak heights were measured with respect to baselines drawn between the valleys on either side. The dependence of the intensity ratios I_{936}/I_{1650} and I_{1146}/I_{1650} on annealing temperature has been plotted in *Figure 3*. This picture shows that the first increases in intensity when the annealing temperature rises above 180°C, while the second decreases. Moreover, the bandwidth of the band centred at 936 cm^{-1} decreases from 23 cm^{-1} for the unannealed sample and for that annealed below 180°C to 20 cm^{-1} for the samples annealed beyond 180°C (*Figure 2*).

In addition to the above peaks, Köenig *et al.*[7,9] have assigned the bands at 1329 and 1224 cm^{-1} to the unique regular fold conformation in polyamide-6,6 crystals. They have also suggested that these bands arise from vibrations of the N-vicinal CH_2 group coupled with the amide III mode of the CONH group (wagging and twisting modes)[9,24]. In our spectra, two shoulders can be observed situated at 1335 and 1224 cm^{-1}, which can be related to the above chain-folding bands. The p.a.-*FT*i.r. spectra show that both bands only appear at the highest annealing temperatures and the band at 1224 cm^{-1} is quite difficult to detect. This phenomenon arises from the fact that the highest annealing treatments are supposed to remove crystal imperfections and to improve chain packing at the amorphous–crystalline interphase.

At this stage of the spectroscopic study, the similarity with the experimental behaviour of PET reported in a previous paper[18] on the thermal treatment is pointed out: intensity changes and decrease of bandwidth occur when the annealing temperature rises, and chain-folding bands at the highest thermal treatments appear in both PET and polyamide-6,6. In PET, the band situated at 898 cm^{-1} (CH_2 rocking, *gauche* conformation) decreases with annealing temperature, whereas the 973 cm^{-1} band (O–CH_2 stretching, *trans* conformation) increases due to conformational changes that take place on annealing[18,25,26].

From these experimental results and a previous report[13] in the literature, we suggest that the spectral changes occurring in the bands situated at 1146 and 936 cm^{-1} can be attributed to *gauche*/*trans* isomerism induced by annealing, since this thermal treatment provides sufficient energy to the molecules to promote conformational changes. On the other hand, the spectra of the *trans* isomer in the crystalline and disordered phases must be sufficiently similar so as not to be resolvable under these experimental conditions; thus, the band at 936 cm^{-1} provides information about total *trans* conformation.

We proved[18] that PET satisfies a two-phase conformational model. Owing to the experimental similarity found between this polymer and polyamide-6,6, it can be thought that the latter would have to satisfy an analogous model, which must verify the relation[18]:

$$1 = p_1 \frac{I_{936}}{I_{1650}} + p_2 \frac{I_{1146}}{I_{1650}}$$

where p_1 and p_2 are the band weights, which are related to the radiation–matter interaction. Thus:

$$\frac{I_{1650}}{I_{1146}} = p_1 \frac{I_{936}}{I_{1146}} + p_2$$

This linear relation between the intensity ratios is required to verify the model for polyamide-6,6. *Figure 4* shows a good fitting from this expression with the experimental values from the p.a.-*FT*i.r. measurements and, consequently, evolution of the conformations with thermal treatments on polyamides-6,6 can be followed by this technique.

On the other hand, the products $p_1(I_{936}/I_{1650})$ and $p_2(I_{1146}/I_{1650})$ represent the individual isomer distribution at different annealing temperatures (*Figure 5*). This

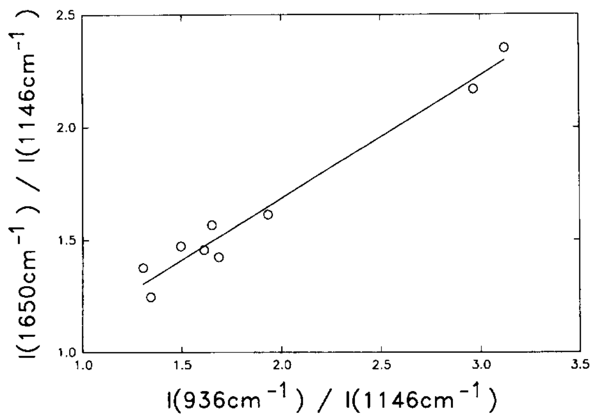

Figure 4 Intensity ratios I_{1650}/I_{1146} *versus* I_{936}/I_{1146}. Verification of the two-phase conformational model in polyamide-6,6

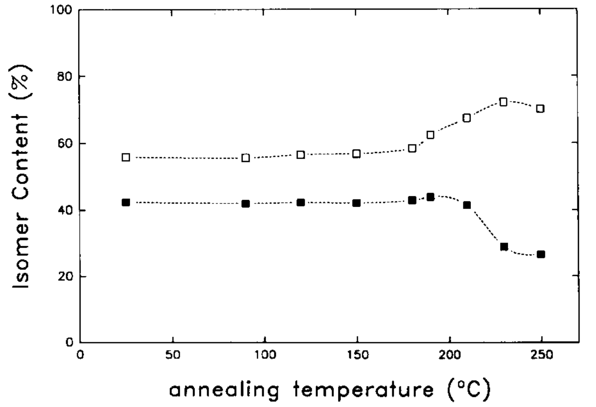

Figure 5 Distribution of total *trans* (□) and *gauche* (■) rotational isomers in polyamide-6,6 as a function of annealing temperature

evolution, similarly to that reported by Köenig and Itoga[7], shows two different regions. Below $T_{\mathrm{ann}}=180°\mathrm{C}$, no appreciable conformational change can be detected in our experimental conditions; beyond this temperature, an approximately linear increase in *trans* isomer content with annealing temperature with equation:

$$\%\mathit{trans}=0.27T_{\mathrm{ann}}+11$$

at expense of the decrease of *gauche* isomer content, can be detected.

Consequently, it can be thought that the H bonds work as pins and prevent the mobility of groups in the skeletal chain until the thermal energy supplied by annealing is capable of overcoming this constraint (above 180°C).

Thermal behaviour

D.s.c. thermograms of unannealed sample and samples annealed at 205, 220 and 230°C are reported in *Figure 6*. The glass transition (around 50°C) is barely perceptible, but a quite broad endotherm from glass transition temperature to melting range related to the Brill transition and two clear endothermic peaks that depend on the thermal history of the sample can be observed.

Substantial changes occur in the thermogram of the samples with previous annealing process. For unannealed sample and that annealed below 150°C, only an endothermic peak at 266°C is observed, indicating the melting of polyamide-6,6. An endothermic low melting peak (LM peak) appears in the d.s.c. thermograms of samples annealed above 150°C followed by another endothermic high melting peak (HM peak) at the melting range.

The LM peak continually shifts towards higher temperatures and grows in size with increasing T_{ann} and, eventually, only one endothermic peak can be detected in the thermogram.

Since the HM peak temperature remains almost constant over a large range of T_{ann}, the melting temperature of the LM peak (T_{m}) can be used to study the effect of annealing on the sample. A plot of the two melting temperatures *versus* T_{ann} is given in *Figure 7*. It can be observed that T_{m} increases linearly approximately 20–35°C above the annealing temperature. From these results, the best fitting is given by the relation:

$$T_{\mathrm{m}}=1.2T_{\mathrm{ann}}-8$$

Furthermore, the area under the LM peak increases when the annealing temperature rises, whereas the area under the HM peak decreases; however, the sum of both areas remains almost the same.

As an experimental conclusion, the thermal behaviour of polyamide-6,6 is quite similar to that of PET[18]. In the latter, although the partially extended-chain and folded-chain endotherm hypotheses were also initially proposed to explain the multiple-fusion peaks, nowadays there is a trend favouring the following interpretation[17]: annealing treatment of PET above the glass transition temperature (75–80°C) produces small crystallites whose degree of perfection depends on thermal treatment. During the d.s.c. scan, some of these crystals melt and recrystallize with a higher perfection. This explanation does not necessarily imply that the crystallites melt completely, and there may exist some type of internal reorganization process that leads to a higher perfection[27]. The LM peak

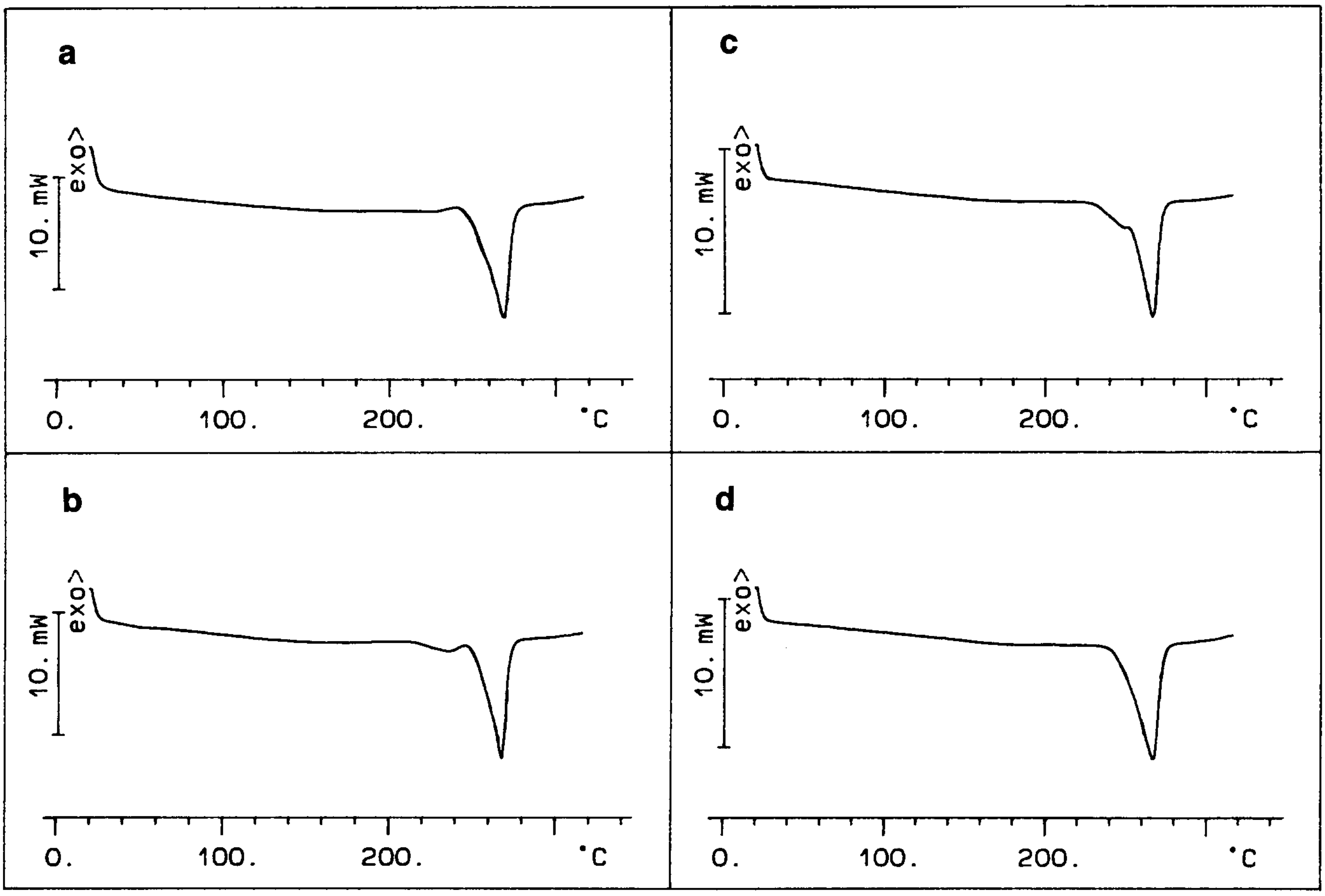

Figure 6 D.s.c. thermograms of (a) unannealed polyamide-6,6 and samples annealed at (b) 205, (c) 220 and (d) 230°C

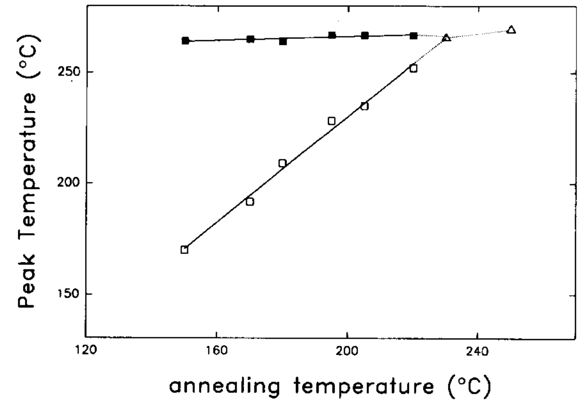

Figure 7 Low melting (□) and high melting (■) peak temperatures *versus* annealing temperature; (△) the peak resulting from the incorporation of above peaks

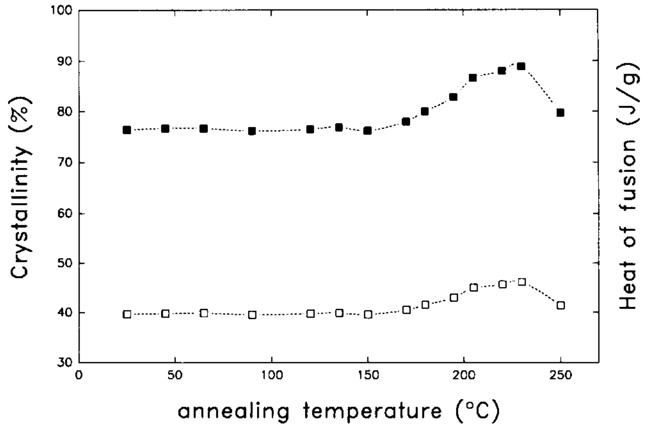

Figure 8 Latent heat of fusion (■) and crystallinity (□) as functions of annealing temperature

shift may indicate that the original crystalline structure transforms to a more stable one due to the annealing process.

The comparison of the results of this work and those obtained in PET[17,18,27] allows one to suggest that, in polyamide-6,6, the low endothermic peak can be attributed to melting or reorganization of crystals with increasing perfection and fold-surface smoothing of the crystalline layers due to the previous annealing treatment, and the high endothermic peak to melting of reorganized crystalline structure during d.s.c. heating.

In order to obtain the apparent degree of crystallinity, the baseline was constructed from the beginning of the LM peak to the end of the HM peak. In *Figure 8*, the evolution of the latent heat of fusion and its proportional parameter (C_{dsc}) are plotted. Two different regions can be distinguished. Below $T_{ann} = 180°C$, no crystallinity change can be detected; and above this temperature, until 230°C, an approximately linear increase with equation:

$$C_{dsc}(\%) = 0.1T_{ann} + 24$$

is detected. The decrease of crystallinity at $T_{ann} = 250°C$ can be related to premelting or degradation.

Attention should be paid to the influence of the fabrication process on the plates of polyamide-6,6. The injection-moulding process involves two factors that are of great importance[28,29]. First, mould walls operate as a nucleant agent; and secondly, as the material comes into contact with the cold mould, a rapid cooling occurs in the surface whereas in the bulk the molecules can crystallize better. In this sense, it has already been shown in plates of PET[18] that the industrial process gives rise to a thin skin layer, mainly 'amorphous', and a 'crystalline' core.

In order to verify if a similar layer structure appears in injection-moulded semicrystalline polyamide-6,6, the d.s.c. measurements were repeated on films cut from the surface of samples. In *Figure 9*, endothermic melting peaks of unannealed bulk sample (full curve) and surface sample (broken curve) have been drawn. First, the half-width of the former (bulk) is slightly less than that of the latter (surface) and, consequently, a more homogeneous crystal size distribution is observed in the bulk; secondly, the position of the melting peak of the bulk sample is at 268°C, and for the surface sample is at 265.6°C. Thus, the crystals form and grow in a more irregular way near the mould surface than in the polymer bulk, as we have already observed in PET[18]. Yet, the apparent degree of crystallinity is only about 2% less in the surface (38%) than in the bulk (40%), conversely to PET where a quite clear difference of 15% could be detected[18]. The influence of the chemical structure on the crystallization process must be taken into account in order to explain the strikingly different crystallinity behaviour in surface/bulk between polyamide-6,6 and PET. In this sense, the most important factor is chain flexibility, which is governed by the nature of the chemical groups that constitute the main chain. In polyamide-6,6, the methylene groups make the chain flexible because of rotations about chain bonds; whereas in PET, the benzene rings hinder rotation and stiffen the chain.

Owing to the similarity in bulk/surface crystallinity contents in polyamide-6,6, the correlation between the crystallinity values obtained by d.s.c. and the conformational contents carried out by p.a.-*FT*i.r. can be made with the results obtained with samples from either the surface or bulk.

*Quantitative correlation between p.a.-*FT*i.r. and d.s.c. measurements*

The main purpose of this work is the analysis of the total conformational structure of polyamide-6,6 samples and to monitor its dependence on annealing temperature. This can be done by correlating the results obtained previously by spectroscopic and calorimetric methods.

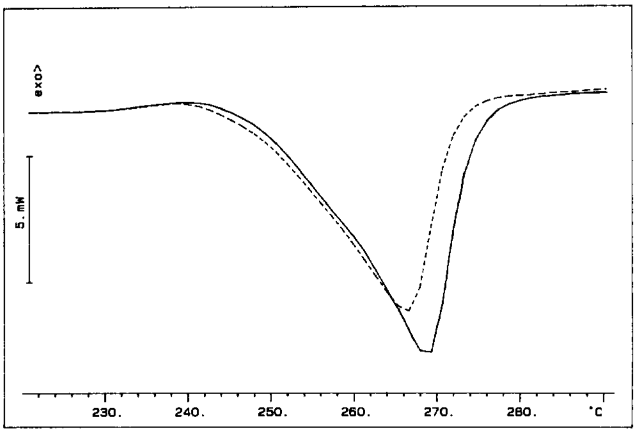

Figure 9 Melting peaks of the unannealed polyamide-6,6: bulk (——) and surface (-----)

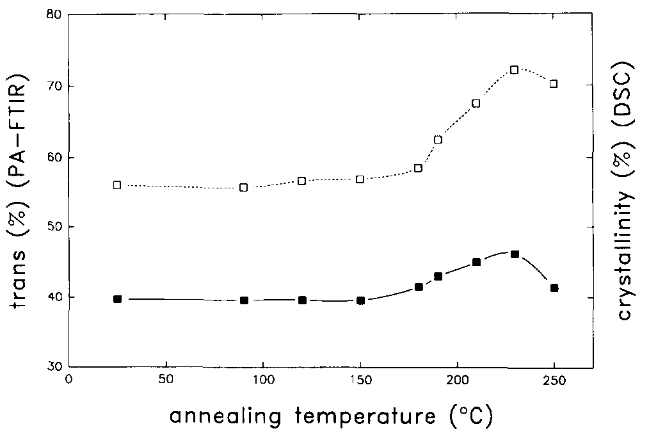

Figure 10 Evolution of total *trans* isomer content obtained by p.a.-*FT*i.r. (□) and degree of crystallinity obtained by d.s.c. (■) with annealing temperature

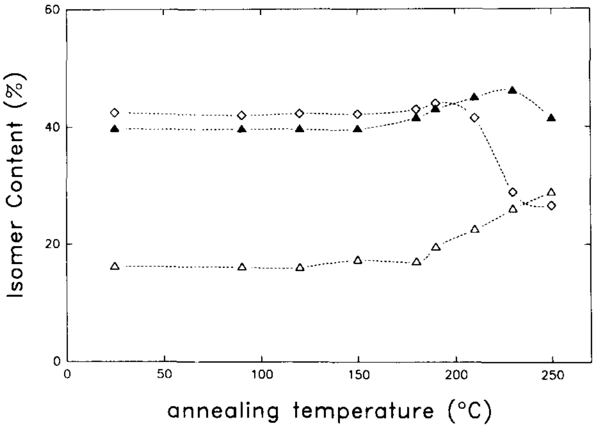

Figure 11 Distribution of rotational isomers in injection-moulded semicrystalline polyamide-6,6 as a function of annealing temperature: (◇) *gauche*, (▲) crystalline *trans*, (△) amorphous *trans*

It can be observed in *Figure 10* that the total *trans* isomer content obtained by p.a.-*FT*i.r. is higher than the degree of crystallinity obtained by d.s.c. over the range of T_{ann}, even at the highest temperatures, conversely to PET behaviour[18], where both measurements tend to coincide in this temperature range. Therefore, the conformational behaviour of polyamide-6,6 with annealing temperature seems to be very different from that of PET.

Since in the crystalline phase only *trans* conformation can appear, the apparent degree of crystallinity was used as a measure of the ordered *trans* isomer content. From the difference between total *trans* and crystalline *trans* contents, an estimation of amorphous *trans* isomer content and its evolution as a function of annealing treatment can be obtained. The evolution of rotational isomers in polyamide-6,6 is drawn in *Figure 11*. No conformational change can be observed up to $T_{ann} = 180°C$; beyond this temperature, the *gauche* conformation decreases, whereas the amorphous *trans* isomer content (*ta*) shows a linear increase, with the equation:

$$ta = 0.17T_{ann} - 14$$

and the crystalline *trans* tends to show a slight linear increase followed by a decrease at 250°C, which was related to premelting or degradation.

From these results, it seems that the crystalline regions in polyamide-6,6 are quite rigid owing to the limited mobility of the amide group. This conclusion agrees with those of other authors[13,30], who reported that the hydrogen bonds and the H-bonded sheet structure is maintained even near the melting temperature. The crystallinity increase can be related to crystal perfection and fold-surface smoothing of the crystalline layers. Most of the conformational changes occur in the amorphous phase where the hydrogen bonds have less organization than those of the crystalline regions and, therefore, the molecular mobility is higher.

CONCLUSIONS

The main purpose of this paper was to study the evolution of the conformations in polyamide-6,6 as a function of thermal treatment by the correlation between spectroscopic (p.a.-*FT*i.r.) and thermal (d.s.c.) techniques.

Using the band centred on $1650\,cm^{-1}$ as an internal reference band, the spectroscopic behaviour on annealing of the bands situated at 936 and $1146\,cm^{-1}$ was monitored. The former increases in intensity when the annealing temperature rises beyond 180°C, whereas the latter decreases. Moreover, a bandwidth decrease in the band at $936\,cm^{-1}$ from 23 to $20\,cm^{-1}$ in samples annealed above 180°C was detected. Two shoulders situated at 1335 and $1224\,cm^{-1}$ in the spectra of samples annealed at the highest temperatures indicate the existence of regularity in chain-folding conformation.

Comparison with the study of PET suggests that the spectral changes in the bands of polyamide-6,6 situated at 1146 and $936\,cm^{-1}$ can be attributed to *gauche/trans* isomerism induced by annealing because this thermal treatment provides enough energy to promote molecular conformational changes. Further, we have demonstrated that polyamide-6,6 verifies a two-phase conformational model, similarly to PET. From this model, the evolution of total *trans* and *gauche* isomer contents with annealing temperature was obtained. The constraint due to H bonds only seems to be overcome beyond 180°C, where the conformational changes appear.

As far as the thermal behaviour is concerned, a great similarity with PET was again found. Beyond 150°C two endotherms (LM and HM peaks) appear in the thermograms: the LM peak continually shifts towards higher temperatures and grows in size with increasing T_{ann}, while the HM peak temperature remains almost constant over a large range of T_{ann} and, eventually, only one endothermic peak can be detected in the thermogram. On the other hand, the sum of the integrated areas of the two peaks remains almost the same over the annealing range, but the LM peak area rises when the annealing temperature increases whereas the HM peak area decreases. We suggest that the low endothermic peak can be attributed to melting or reorganization of crystals with increasing perfection and fold-surface smoothing of the crystalline layers due to annealing treatment, and the high endothermic peak to melting of reorganized crystalline structure during d.s.c. heating. The influence of fabrication process in polyamide-6,6 seems not to be as important as in PET; we suggest that this behaviour can be related to the chemical structure of the molecules, which would facilitate easier crystallization.

From the correlation between p.a.-*FT*i.r. and d.s.c. measurements, the conformational evolution as a function of annealing temperature was obtained. The crystalline regions in polyamide-6,6 seem to be quite rigid owing to the limited mobility of the amide group. Below 180°C, no conformational change can be detected; beyond this temperature, the increase of the crystalline *trans* content can be related to crystal perfection and fold-surface smoothing of the crystalline layers. However, most of the conformational changes occur in the amorphous phase where the hydrogen bonds have less organization than that of crystalline regions and, therefore, the molecular mobility is higher.

As a conclusion, the hydrogen bonding, in both crystalline and disordered phases, works as a pin, preventing conformational mobility up to the point where enough energy is supplied to the molecules.

ACKNOWLEDGEMENTS

This research was funded by the Comisión Interministerial de Ciencia y Tecnología/CICYT (Program MAT90-914).

REFERENCES

1 Bunn, C. W. and Garner, E. V. *Proc. R. Soc.* 1947, **39**, 39

2 Atkins, E. D. T., Hill, M., Hong, S. K., Keller, A. and Organ, S. *Macromolecules* 1992, **25**, 917

3 Brill, R. *J. Prakt. Chem.* 1942, **161**, 49

4 Starkweather, H. W., Jr and Jones, G. A. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 467

5 Xenopoulos, A. and Wunderlich, B. *Colloid. Polym. Sci.* 1991, **269**, 375

6 Gurato, G., Arneros, A. and Canal, P. *Makromol. Chem.* 1979, **180**, 537

7 Köenig, J. L. and Itoga, M. *J. Macromol. Sci.-Phys.* (*B*) 1972, **6**(2), 309

8 Anton, A. *J. Appl. Polym. Sci.* 1968, **12**, 2117

9 Köenig, J. L. and Agboatwalla, M. C. *J. Macromol. Sci.-Phys.* (*B*) 1968, **2**, 391

10 Starkweather, H. W. and Moyniham, R. E. *J. Polym. Sci.* 1956, **19**, 363

11 Jakes, J. and Krimm, S. *Spectrochim. Acta* (*A*) 1971, **27**, 19

12 Coleman, M. M. and Painter, P. C. 'Encyclopedia of Polymer Science and Engineering', Wiley, New York, 1987, Vol. 8, p. 92

13 Garcia, D. and Starkweather, H. W. *J. Polym. Sci., Polym. Phys. Edn.* 1985, **23**, 537

14 Vidrine, D. W. *Appl. Spectrosc.* 1980, **34**(3), 314

15 Mackenzie, M. W. 'Advances in Applied Fourier Transform Infrared Spectroscopy', Wiley, New York, 1985, p. 161

16 Bell, J. P., Slade, P. E. and Dumbleton, J. H. *J. Polym. Sci.* 1968, **6**, 1773

17 Lin, S. B. and Köenig, J. L. *J. Polym. Sci., Polym. Symp.* 1984, **71**, 121

18 Quintanilla, L., Rodríguez-Cabello, J. C., Jawhari, T. and Pastor, J. M. *Polymer* 1993, **34**, 3787

19 Starkweather, H. W., Jr, Zoller, P. and Jones, G. A. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1615

20 Bell, J. P. and Dumbleton, J. H. *J. Polym. Sci.* 1969, **7**, 1033

21 Gordon, G. A. *J. Polym. Sci.* 1971, **9**, 1693

22 Starkweather, H. W., Jr *Macromolecules* 1989, **22**, 2000

23 Murty, E. M. and Yehl, T. W. *Polym. Eng. Sci.* 1990, **30**(4), 1595

24 Cannon, C. G. and Harris, P. H. *J. Macromol. Sci.-Phys.* (*B*) 1969, **3**(2), 357

25 Boerio, F. J. and Bahl, S. K. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 1029

26 Lin, S. B. and Köenig, J. L. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 2277

27 Fakirov, S., Fisher, E. W., Hoffmann, R. and Schmidt, G. F. *Polymer* 1977, **18**, 1121

28 Rubin, I. I. 'Encyclopedia of Polymer Science and Engineering', Wiley, New York, 1987, Vol. 8, p. 102

29 White, J. L. 'Encyclopedia of Polymer Science and Engineering', Wiley, New York, 1987, Vol. 10, p. 634

30 Murthy, N. S., Curran, S. A., Aharoni, S. M. and Minor, H. *Macromolecules* 1991, **24**, 3215