Polymorphic Transitions in Oligo(aryl ether ketone)s Studied by Real Time X-ray Scattering

D. R. Rueda,* F. Ania, F. J. Baltá-Calleja, and I. Šics

Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain

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ABSTRACT: The crystal phase transitions occurring in oligo(aryl ether ketone) samples were studied, in real time, by means of X-ray scattering using synchrotron radiation. One sample is a typical molecular compound with 7 aryl units (m7) while the other two samples, containing 11 aryl units (p11 and m11), exhibit the presence of a polymeric component. In relation to the polymorphic transition previously reported for aromatic polyketones, the phase transition study of the sample p11 clarifies the role of chain length in the thermal behavior of aromatic polyketones. The structural variations, due to crystal phase transitions, as revealed by X-ray diffraction during heating of the samples are not accompanied by the parallel changes in the DSC thermograms. The two endothermic peaks observed for the samples p11 and m11 are associated with the melting of crystals with short and polymeric chains. Although the amount of polymer component reaches about 75% in the case of p11 (30% for m11), it does not exhibit the double melting phenomenon commonly observed for aromatic polyketones. A structural mechanism is suggested to explain the absence of such a phenomenon for the p11 and m11 samples.

Introduction

Poly(aryl ether ketone)s as high-performance thermoplastic materials have received special attention in the past decade.[1,2] Gardner et al. reported on the polymorphism of aromatic polyketones with different keto/ether molar ratios[3,4] crystallized under different conditions and more recently for polyketones containing isophthalic units (1,3 substituted phenylene).[5] Two main crystal polymorphs have been observed in aromatic polyketones: form I and form II following Gardner's notation.[4] The most stable crystal phase, form I, corresponds to the orthorhombic unit cell similar to that of poly(phenylene oxide)[6] and PEEK.[7,8] The chain packing proposed for form II is also orthorhombic with the *a* and *b* axes exchanged with each other[9] or "pseudoorthorhombic" with a single chain per unit cell.[4] The conversion of crystal phase II into phase I, during heating of aromatic polyketones, has been recently studied using synchrotron radiation.[10] It is noteworthy that the polymorphic transition (II into I) is clearly detected by X-ray diffraction but cannot be resolved by DSC calorimetry.[11]

The study of oligomer compounds, as models for aromatic polyketones, is of great validity.[12−17] The influence of the keto/ether molar ratio on the lattice unit cell parameters, melting temperature, and fusion enthalpy observed for two series of oligo(aryl ether ketone)s with 5, 7, 9, and 11 aryl units per molecule has been previously reported.[18] While one series of compounds is made of all 1,4 substituted phenylene rings (series p), the second series has a 1,3 substituted phenylene (isophthalic group) as the central aryl unit (series m). Due to the presence of the isophthalic unit, a remarkable polymorphism was observed for the shortest ($n = 5$) member of the series m.[15,16] However, the longer members of the m series and all members of the p series assume a linear, extended conformation when recrystallized from solution.[18] These oligomer compounds, with a keto/ether molar ratio >0.5, crystallize from solution preferably in the more stable crystal polymorph form I in contrast to what has been observed for aromatic polyketones which exhibit the crystal form II.[11]

Throughout the structural study of these oligo(aryl ether ketone)s, it was found out that the longest members ($n = 11$) of both m and p series showed DSC traces with two melting peaks which were attributed to the melting of crystallites built up with short and polymeric chains.[18] Thus, the concurrent appearance of phases I and II and the two melting peaks (at 327 and 373 °C) in case of the p11 sample has aimed us to follow the crystal phase transition, in real time, as it was done for the aromatic polyketones.[10] Furthermore, we think that these samples (p11 and m11), because of their blend nature, could be also good models to check the *double melting phenomenon* largely discussed in the field of aromatic polyketones.[19−22] This phenomenon entails the appearance, in the thermograms of annealed polyketones, of an additional endothermic peak at about 15 °C above the annealing temperature, T_a, used.[11,23]

The aim of this work is 2-fold: (a) to extend the study of the crystal phase transition of phases II into I, previously reported for aromatic polyketones,[10] to the cases of a pure molecular compound and to a sample with short and polymeric chains; (b) to report on the absence of the double melting phenomenon in the polymer component in the presence of oligomeric chains. We trust that both objectives are covered by the study of the selected samples using synchrotron radiation techniques.

Experimental Section

Materials. The oligo(aryl ether ketone)s samples were synthesized by Prof. de Abajo and co-workers. A description of the preparation, thermal properties, and crystalline structure for the samples can be found in ref 18. Molecular compounds were denoted by m*n* and p*n*, where *n* is the number of aryl units and m and p refer to the 1,3 and 1,4 substituted phenylene ring in the center of the molecule, respectively. The schematic chemical formulas of the samples investigated are

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1,3-bis($\phi-K-\phi-E-\phi-K-$)phenylene m7

1,3-bis($\phi-E-\phi-K-\phi-K-\phi-E-\phi-K-$)phenylene m11

1,4-bis($\phi-E-\phi-K-\phi-K-\phi-E-\phi-K-$)phenylene p11

where ϕ is the 1,4 substituted phenylene ring and E and K refer to the ether (O) and ketone (CO) groups, respectively.

While m7 is a pure molecular compound, m11 and p11 also contain a fraction of *polymeric* chains. Consequently, the latter two samples showed two endothermic peaks at 240 and 265 °C (sample m11) and at 327 and 373 °C (sample p11) (see below in Figure 11). DSC traces revealed that the high-temperature peak, associated to the polymeric component, represents about 50% in the case of p11 and only about 18% for m11 of the total melting enthalpy.

Experimental Techniques. For the thermal study a Perkin-Elmer DSC-4 calorimeter was used. Thermograms were recorded at usual conditions: a heating rate of 10 K/min, under nitrogen flow, and about 5−10 mg of sample. The calorimeter was calibrated with indium standard. Thermal treatments of the samples were carried out inside the calorimeter. For the X-ray investigation of the crystal phase transition, the facilities of the synchrotron radiation beamline A2 at HASYLAB (DESY, Hamburg, Germany) were used. Wide- and small-angle X-ray scattering (WAXS and SAXS) patterns were simultaneously recorded, in real time, during heating of the sample. A wavelength $\lambda = 0.15$ nm was used. Frames were collected during 10 s (for m7) and 20 s (for p11 and m11) using a waiting time of 1 ms. Sintered samples were wrapped with aluminum foil to improve thermal contact and to prevent or at least reduce the loss of material when molten. A heating rate of 10 K/min was used in a vacuum oven throughout the experiments. The analysis of consecutive WAXS and SAXS frames concerning peak intensity and angular position was done by means of a fit program in order to give a detailed description of the structural variations during heating of the sample. The WAXS crystallinity index was measured as the ratio between the area of Bragg's reflections and the total area for each consecutive X-ray pattern.

Results

Time-Resolved Structural Variations during Heating. (a) Crystal Phase Transition of the Molecular Compound m7. Figure 1 shows the changes of the WAXS intensity profiles for the sample m7 during heating, at 10 K/min, up to above the melting temperature. The WAXS pattern for the starting material mainly corresponds to the polymorph of phase II as revealed by the lower angle reflection at about 15.5° (010^{II}). The WAXS patterns of Figure 1 reveal an abrupt change in intensity at about 164 °C. Figure 2 shows the intensity peak variation observed for three of the reflections at about 15.5°, 17.5°, and 22.5° (2θ) which were indexed as 020, 023−024, and 110, respectively of an orthorhombic unit cell (form II).[18] For simplicity these reflections were denoted considering their angular position by the increasing numbers 1, 2, and 3. A slight increase of intensity during heating to 150 °C is observed for the three reflections. At about 164 °C a crystal−crystal phase transition occurs. Thus, while the first reflection nearly disappears, the second one becomes the most intense reflection 110 of the new orthorhombic unit cell (form I) and the third reflection loses intensity and changes into the 200 reflection. From Figure 2 and considering the heating rate used and data collection time, one can say that the phase transition takes place within a narrow interval (≤10 K) of temperature. The new crystal phase is stable up to about 220 °C. Then a drastic loss of intensity of all crystalline peaks, associated with the melting of the sample, is observed. The sharpness of both processes, crystal phase transition and melting, for this oligomer compound is noteworthy. Figure 3 shows the variation of the lattice spacings calculated for the three reflections mentioned above. A small discontinuity in the spacing variation around 164 °C is observed for the three reflections.

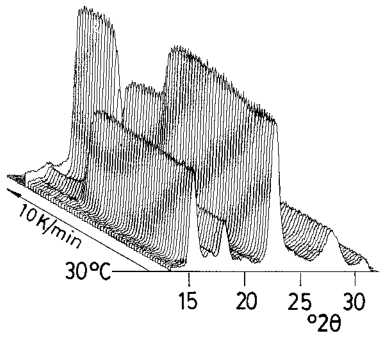

Figure 1. Change of WAXS intensity profiles during heating of sample m7.

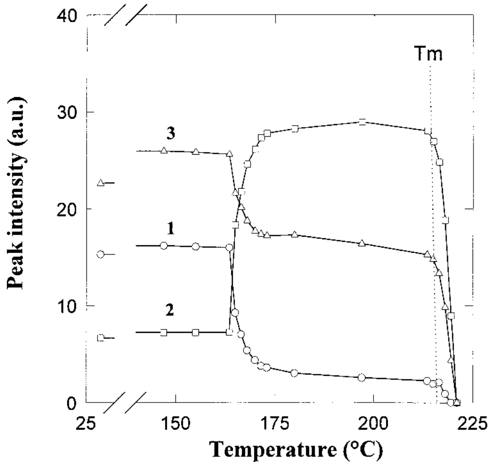

Figure 2. Variation of peak intensity for three main reflections of Figure 1 during heating of m7. (1, 2, and 3 denote the main reflections of increasing diffraction angle, respectively). The melting point of the sample is indicated.

(b) Crystal Phase Transition of Sample p11. Figure 4 shows the variation of WAXS (top) and SAXS (bottom) intensity profiles recorded simultaneously during heating of the sample p11 at 10 K/min from 300 °C till the complete melting of the sample. This sample clearly shows important variations of the SAXS intensity profiles with temperature, revealing the partial polymeric nature of the sample. The WAXS pattern also confirms the coexistence of both crystal polymorphs II and I (reflections at about 15.5° (010^{II}) and about 20.5° (111^{I})). Figures 5 and 6 show the variation with temperature of the peak intensity and lattice spacings observed for the main Bragg's reflections. Concerning the peak intensity (Figure 5), a slight increase is observed for all reflections up to about 280 °C. For higher temperatures, while 010^{II} decreases until a complete disappearance at about 340 °C, the other reflections increase and go through a maximum. This maximum is followed by a rapid intensity decrease till the total disappearance of the reflections at about 380 °C. An inflection point in intensity at temperatures around 340 °C is observed. WAXS patterns of p11 above the latter temperature (340 °C) exclusively show reflections from the crystal phase I. Concerning the lattice spacings (Figure 6), a distinct change around 280 °C is

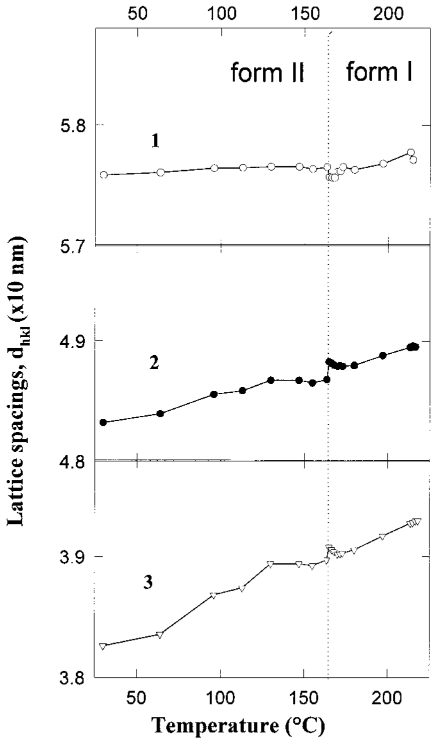

Figure 3. Variation of lattice spacings for the three reflections of Figure 2 during heating of sample m7.

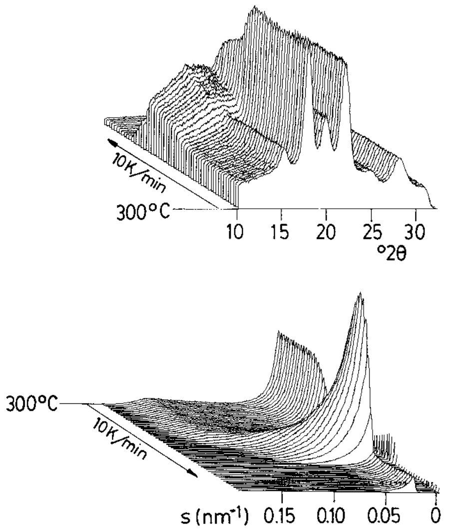

Figure 4. Change of WAXS (top) and SAXS (bottom) intensity profiles, recorded simultaneously, during heating of sample p11.

also detected suggesting the starting of crystal reorganization. For temperatures below 280 °C the spacing of 010^{II} remains nearly constant or it decreases while the spacing of the other reflections increases. This increase, which could be related to a thermal lattice expansion, seems to be larger for reflections related to phase II than for reflections of phase I (111^{I}). Above 280 °C the increasing rate for the lattice spacing is smaller. Particularly, the plot corresponding to the 100^{II}−200^{I} reflection (see Figure 6) shows a minimum near 340−350 °C and then slightly increases up to the melting temperature of the sample.

Figure 7 shows the variation of the crystallinity index during heating of the p11 sample. The starting crystallinity value is about 50%, which remains constant up to temperatures near to 300 °C. Above this temperature a slight increase is observed up to 330 °C followed by a rapid decrease down to 25% at about 340 °C. Finally the crystallinity further decreases and becomes zero after melting of the sample. The results indicate that half of the crystalline signal is related to the polymeric component. From the crystallinity index (50%) the relative amount of polymer component is estimated to be about 75%.

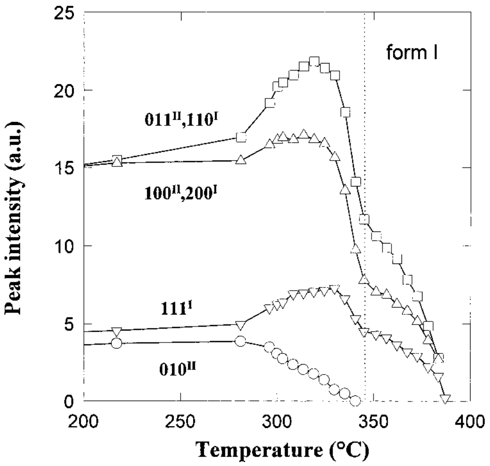

Figure 5. Variation of peak intensity of the four lowest angle reflections of Figure 4 (top) during heating of sample p11.

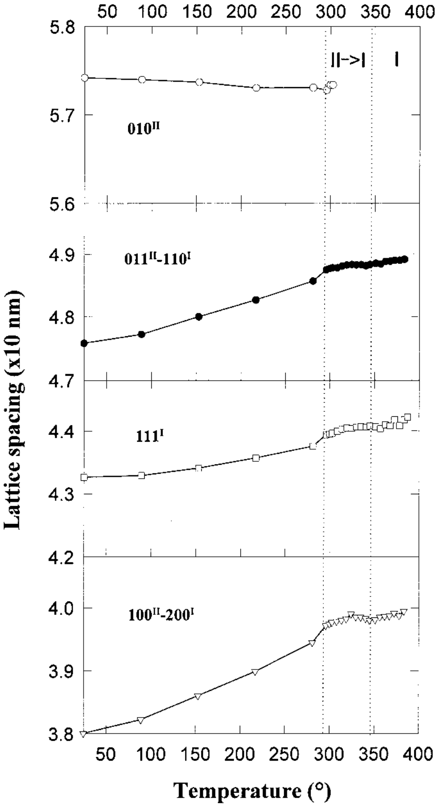

Figure 6. Temperature dependence of lattice spacings calculated for the four reflections of Figure 5.

Simultaneous WAXS and SAXS experiments were also carried out on sample m11 (Figure 8). In contrast to sample p11, sample m11 did not show any crystal phase transition during heating. This would be consistent with the presence of phase I in the starting material. Let us recall the absence of the reflection 111^{I} (at about 20.5°) characteristic of the orthorhombic phase I in the case of aromatic polyketones based on the

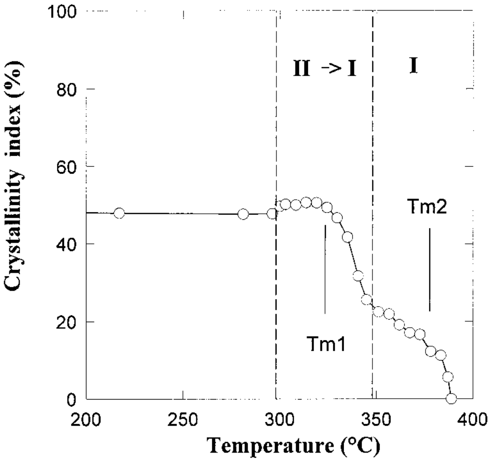

Figure 7. Change of WAXS crystallinity index observed during heating of p11. The two melting points are indicated.

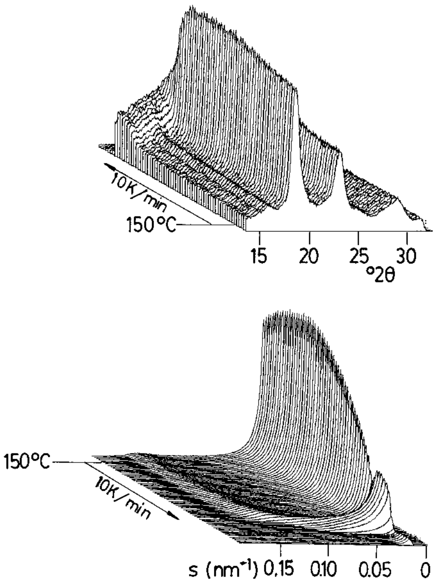

Figure 8. Change of WAXS (top) and SAXS (bottom) intensity profiles, recorded simultaneously, during heating of the sample m11.

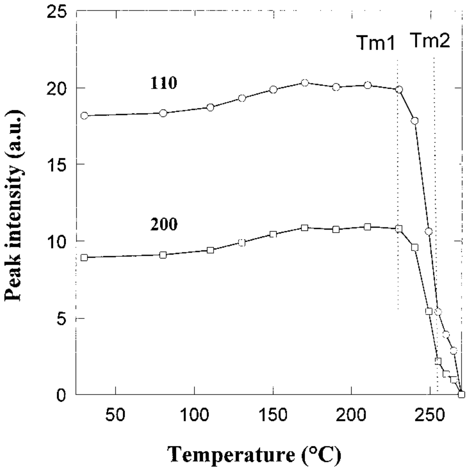

Figure 9. Variation of peak intensity of the two main reflections of Figure 8 (top) during heating of m11. The two melting points are indicated.

isophthalic unit.[5] Figure 9 shows the intensity variation observed for the most representative reflections: 110^I (18°) and 200^I (23.5°). The intensity increases above 100 °C (T_g = 95 °C) and remains constant up to the first melting temperature (240 °C). Then the intensity abruptly decreases about $^4/_5$ of its value at 255 °C and finally decreases down to zero at 270 °C. The intensity variation of WAXS reflections during heating is consistent with the DSC trace reported[18] for sample m11 and shown below in Figure 11. The crystallinity index, measured at room temperature in the 5−40° 2θ interval, appears to be 68%. Hence, the relative amount of polymer component for m11 turns out to be about 30%.

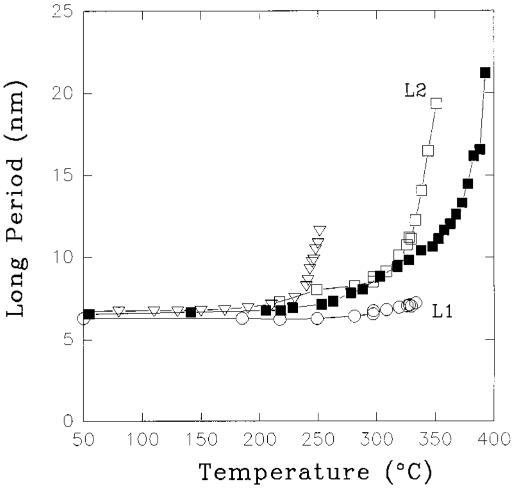

Figure 10. Variation of SAXS long periods as a function of temperature observed for samples p11 (circles and squares) and m11 (triangles) compared with polymer L data (filled symbols).

(c) SAXS Development during Heating for the p11 and m11 Samples. The SAXS intensity profiles of Figures 4 and 8 (bottom), were analyzed after Lorentz correction[24] by s^2 (where $s = 2\sin(\theta)/\lambda$) by using a fit program. A single SAXS maximum (Gaussian peak) with a long period L1 of about 6 nm, is resolved for the lower temperatures. L1 remains nearly constant up to 200 °C. Above this temperature and particularly for p11, the shape of the SAXS maximum changes by increasing its intensity mainly from the inner side (lower angular region). Therefore, a second maximum L2 is used to analyze the SAXS intensity profiles. From the angular position of peaks, the long periods L1 and L2 were calculated. The temperature dependence of L1 and L2 is shown in Figure 10. In the case of sample m11 there is no such a clear resolution of the SAXS maximum L2 before the disappearance of L1. Consequently, only a L curve (triangles) is drawn for m11. For comparison, we have also drawn the L variation observed for an aromatic polyketone sample.[10] The similar behavior shown by the polymeric component of p11 (curve L2) and the polyketone sample (filled symbols) is evident.

Influence of Molecular Weight on the Thermal Behavior. From DSC traces[18] (see Figure 11), the WAXS (Figure 7), and the SAXS information, it appears that p11 and m11 can be considered as blends of oligomeric and polymeric materials. The amount of polymeric material is about 75% in the case of p11 and only about 30% for m11. Therefore, we thought it interesting to study the influence of short-chain molecules on the thermal behavior of the polymeric component. Particularly, we have focused our interest on the "double melting phenomenon", commonly observed for aromatic polyketones. Thus, to check the double melting phenomenon, samples p11 and m11 were thermally treated at different temperatures for some

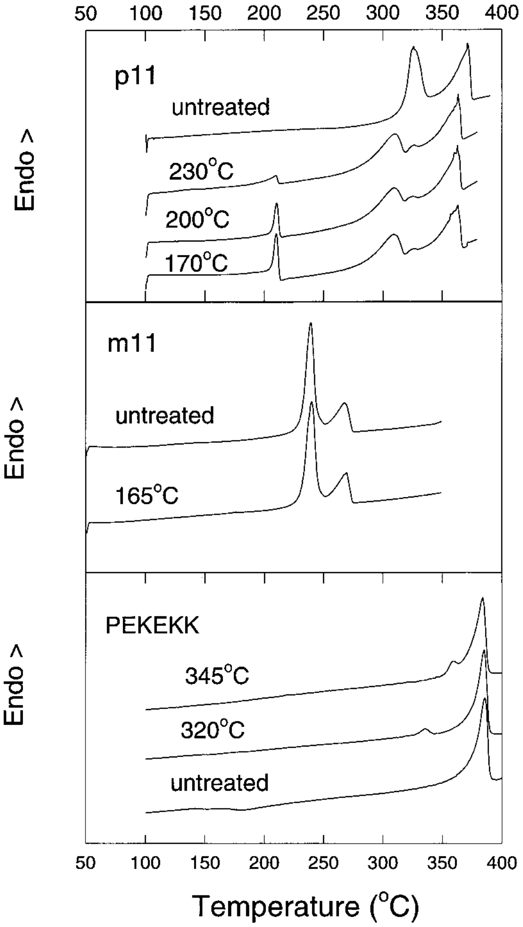

Figure 11. First DSC traces recorded for p11 (top), m11 (middle), and PEKEKK (bottom) samples before and after annealing at different temperatures.

period of time (1−2 h). Figure 11 illustrates the first DSC traces for p11 and m11, respectively, before and after annealing at different temperatures. For comparative purposes, a plot showing the double melting phenomenon exhibited by a polyketone sample,[11] treated at 320 and 345 °C for 40 min, has been also presented. While the DSC traces from annealed m11 remain "unchanged", those from annealed p11 show a new endothermic peak, which appears at the same temperature (about 210 °C) for the different T_a values used. Therefore, it can be said that the "double melting phenomenon of polyketones" is not observed for the above samples even if they contain a polymeric fraction. The structural meaning of the new endothermic peak observed for p11 is under investigation. In advance, we can say that there are no significant differences between the X-ray diffractograms recorded at room temperature and those for the samples annealed at different T_a.

Discussion

Polymorphic Phase Transitions. Previously, we have pointed out that the crystal phase transition of aromatic polyketones (conversion of form II into I) observed by X-ray diffraction[10] is not resolved by DSC; i.e., no distinct enthalpic peak or slope changes in the DSC traces were observed at the temperature phase transition. Throughout the study of oligo(aryl ether ketone)s, the shortest molecular compound m5 exhibits a rich polymorphism (two different polymorphs when recrystallized from solution and two other polymorphs after crystallization from the glassy state).[15,16] All these polymorphs show a distinct melting temperature. Furthermore, a different molecular conformation was found for the two crystal polymorphs obtained from solution. The polymorphism detected here for the next member of the series, m7[18] (Figure 1), turns out to be undetectable by DSC. In this case the molecule assumes the linear-extended conformation and the *c* lattice parameter (chain length) remained constant during the crystal phase transition.[18] It seems that the absence of endothermic signal during the crystal phase transition II to I of polyketones is due to the absence of changes in the molecular conformation and only affects the lateral packing and chain arrangement in the crystal unit cell. Thus, the enthalpy changes, if any, involved in this phase transition are totally balanced during the DSC recording. Nevertheless, the possibility that the II to I phase transition could be considered as a second-order transition should not be ruled out.

The crystal phase transition of m7 (Figure 2) is better defined than that observed for p11 (Figure 5). The temperature interval of the phase transition is very much dependent on the perfection and size distribution of crystallites, which ought to be poorer for a polymer material in relation to a molecular compound.

Influence of the Blend Nature on the Thermal and Structural Variations during Heating. The results presented in Figures 5 and 7 for p11 point to a separate, independent melting of both the oligomer and polymer fractions. The structural data of Figure 7 suggest that the melting of the oligomer crystals(<340 °C) occurs before the melting of the polymer crystalline fraction. This is in agreement with the two endothermic peaks observed for p11 (327 and 373 °C); the lower temperature is associated with the melting of crystals from the oligomer component. Thus, the two endothermic peaks cannot be related to the crystal phase transition (II to I). Indeed, the crystal phase transition occurs during melting of the oligomer fraction. This becomes evident by comparison of the results shown here for p11 (Figures 5 and 7) with those reported for the aromatic polyketones (Figures 3 and 5 in ref 10). In the case of a polymer material a crystal−crystal phase transition occurs and the intensity of reflections of phase I is maximum when reflections of phase II disappear. On the contrary, for p11 the maximum intensity of the reflections of phase I occurs some degrees before the total disappearance of phase II.

A question arises about which crystal polymorph (I or II) is present in the two components of sample p11 (according to Figure 4 (top), both crystal polymorphs I and II are present): does the oligomer component assume crystal phase II as well? We know that aromatic polyketones with a keto/ether molar ratio similar to that of p11 (0.6) assume crystal phase II.[11] Thus, we believe this is the most probable situation for the polymer component of p11. Furthermore, oligomers of series p directly crystallize in the crystal form I.[18] Therefore, the presence of phase I in the original sample should be attributed to the oligomer component. This oligomer component would be responsible for the lower temperature peak (327 °C) observed for p11. Just at this temperature the maximum intensity of WAXS reflections is observed (Figure 5). The higher melting peak (373 °C) should be exclusively related to the polymer component whose contribution is about 50% of the crystalline material according to Figure 7. The data shown in Figure 5 are shifted to lower temperatures by about 10 °C in relation to those reported for PEKEKK.[10] This may be due to a lowering temperature effect caused by the molten oligomeric material.

The variation of SAXS patterns during heating of samples p11 (Figure 4 (bottom)) and m11 (Figure 8 (bottom)) and the calculated long periods (Figure 10) can be also explained in the light of the nature of blend materials. Thus, the presence of a SAXS maximum of about 6 nm (equal to the molecular length for 11 aryl units) which remains nearly constant during heating can be related to the oligomeric component that does not undergo chain reorganization upon annealing, in contrast to the chain reorganization of the polymer component yielding as result the important SAXS variation of Figure 4 (bottom). The variation of L2, as well as that observed for m11 above 225 °C, is typical of a polymeric material which undergoes lamellar thickening upon annealing.[25,26]

Absence of a Double Melting Phenomenon in the Polymer Component. In contrast to the common observation for annealed aromatic polyketones (presence of a new endothermic peak correlated to the annealing temperature)[19,23] (Figure 11 (bottom)), the DSC results shown in Figure 11 indicate a dissimilar behavior of the polymeric component for p11 and m11 samples in relation to that exhibited by aromatic polyketones. In addition to the observed structural changes (crystal thickening and crystal perfection) in the microstructure of annealed polyketones,[22] some rearrangement of disordered chain segments appears to occur upon annealing of the polymer.[21] Thus, we think that the endothermic peak related to T_a could be visualized as an “enthalpy excess” localized in chain segments of disordered material. According to the morphology of a polymer sample, many of the amorphous segments should lie between adjacent lamellar crystallites which prevent propagation of the stored segmental relaxation, via free chain ends. In the case of samples m11 and p11, probably due to the presence of a considerable amount of short molecules, the fraction of polymeric chains should be more detached and/or disentangled from each other. Consequently, improved propagation of localized segmental states along the chain could occur. This might be a main reason for the absence of a new endothermic peak related to the annealing temperature in the DSC traces shown in Figure 11 (top and middle).

Conclusions

From the above results we can draw the following conclusions:

The polymorphic transition (from II to I) of the molecular compound m7 is very sharp, as revealed by WAXS, in comparison to the phase transition of the polymer component of sample p11 or that reported for PEKEKK.[10]

The phase transition for the sample p11 occurs about 10−25 °C below the temperature reported for PEKEKK samples.[10] This can be attributed to the influence of the oligomer crystals which melt during the chain rearrangement occurring in the polymer crystals of form II.

The variation of the two long periods during heating of p11 confirms the blend nature of the sample. L1 (6 nm) is associated with the lamellar thickness of crystals with linear, extended molecules. The L1 value remains nearly constant with increasing temperatures, and it disappears during melting of the molecular crystals. On the other hand, L2, which is associated with the polymer component, continuously increases till the SAXS maximum disappears because of the structural reorganization during heating.

No “double melting phenomenon” was observed for samples p11 and m11 even if they contained a polymer chain component. It is proposed that, due to the presence of short molecules, there is an enhanced propagation of relaxed segmental states created on sample annealing. This propagation takes place along the polymer chains which, in our case, are more detached from each other than for typical polyketone samples.

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