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On the Observation of a New Morphology in Poly(arylene ether ether ketone). A Further Examination of the Double Endothermic Behavior of Poly(arylene ether ether ketone)

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ABSTRACT: The morphology of solvent-cast or melt-pressed isothermally crystallized poly(ether ether ketone) (PEEK) films was investigated by polarized optical microscropy as a function of crystallization temperature. For crystallization temperatures below 300 °C, only spherulitic morphologies were present whereas, at higher temperatures, a morphological transition from spherulitic to crystal-aggregate-like structures could be observed during isothermal crystallization. As the crystallization temperature is increased, the content in the second type of structures was observed to increase. The temperature dependence of the relative population in these two morphologies can be qualitatively correlated with that of the double endothermic behavior observed when PEEK is heated above its crystallization temperature. The observation of this new morphology for PEEK cannot be explained in terms of a polymorphic behavior, a degradation process, or a fractionation effect during crystallization. At this point we can only speculate that it may be related to the structure of the amorphous liquid phase from which the crystallinity develops.

I. Introduction

The morphology, crystallization, and melting behavior of PEEK have been investigated by several authors.[1–10] A somewhat controversial double endothermic behavior has been reported for samples crystallized from the melt or the glass.[3–9] Various suggestions have been proposed to account for this observation, ranging from a melting-recrystallization phenomenon[1,7–9] to the possible existence of different crystal structures[3,6] or morphologies.[5]

Lovinger et al.[10] reported morphological studies of thin films of PEEK crystallized at temperatures up to 300 °C. Using transmission and scanning electron microscopy, they observed a single type of spherulitic morphology characterized by thin narrow lamellae growing predominantly edge on along the *b*-axis. Lovinger et al.[11] also reported observing a second type of spherulitic morphology for PEEK crystallized from dilute solutions at relatively high temperature (about 220 °C). This second type of morphology consisted of shorter and broader crystal features. A similar behavior was observed by the same authors for single crystals grown from very dilute solution: fibrous crystals at a large undercooling and shorter and broader crystals at a lower undercooling (above 215 °C). Electron diffraction experiments allowed them to demonstrate that these two morphologies correspond to the same crystal structure. In a more recent investigation on films crystallized at or below 330 °C, Bassett et al.[5] suggested that the two melting peaks correspond to different components of the morphology. The broad higher melting peak was assigned to primary lamellae formed at the crystallization temperature, and the lower endothermic peak was suggested to arise from the melting of secondary lamellae grown in between the primary lamellae.

Kumar et al.[2] and Blundell et al.[1] have reported some limited polarized optical microscopy studies on melt-pressed films. If such films are melted at or just above the equilibrium melting temperature, 385 °C,[8,9] very high nucleation densities are observed upon cooling and very little detail of the internal spherulitic structure can be obtained. To circumvent this problem, it is common to use a much higher melting temperature or a longer residence time in the melt.[1,2,8,9] However, such thermal treatment may result in sample degradation[12] as was revealed by our growth rate studies.[13] As a consequence of the intrinsically high nucleation density in melt-pressed films, most of the previous studies did not investigate the crystallization behavior and resulting morphology over a wide range of temperatures and crystallization times.

In this work, we prepared thin films by solution casting following the method of Lovinger.[10] Film thickness control allowed us to considerably decrease the nucleation density and enabled us to carry out morphological studies by polarized optical microscopy over a very wide temperature range (160–320 °C) as a function of time in much finer details without the risk of sample degradation. Much to our surprise, we observed the presence of a new morphological superstructure for samples crystallized isothermally above 300 °C. In this report an attempt has been made to correlate the presence of this new superstructure to the well-known double endothermic behavior of PEEK. It should be pointed out that this comparison must be restricted to crystallization temperatures higher than 300 °C in the differential scanning calorimeter. As for lower temperatures, the kinetics of crystallization is so fast that crystallinity develops before thermal equilibrium can be achieved.

II. Experimental Section

In this study, we used a commercial-grade PEEK (380G), obtained from ICI. Its molecular weight averages, M_n and M_w, were calculated to be 1.35×10^4 and 3.6×10^4, respectively.[14] PEEK samples were crystallized isothermally by quenching from the melt at 390 °C in a Perkin-Elmer differential scanning calorimeter Model II used under a nitrogen purge. The heating scans were performed from the crystallization temperature only, at a typical heating rate of 5 °C/min. For optical microscopy, thin films (less than 5–10 μm thick) were cast from a 0.22% w/w solution in benzophenone following the procedure described by Lovinger.[10] The films were first dried in a vacuum oven at 160 °C for 24 h and subsequently heated in a hot stage to 385 °C for 5 min under a nitrogen atmosphere. A Zeiss Axioplan polarizing optical photomicroscope equipped with a Linkam hot stage was

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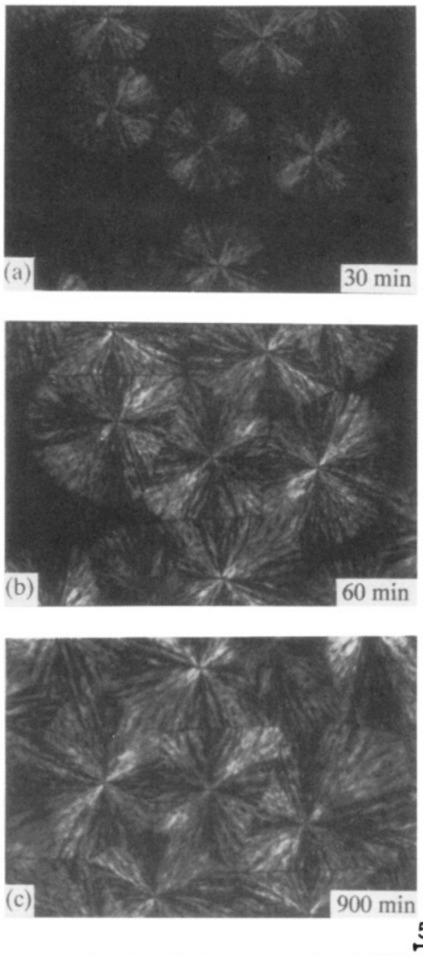

Figure 1. Polarized optical micrographs of PEEK films crystallized isothermally from the melt at 295.7 °C for the indicated crystallization time, t_x.

used to measure growth rates[13] and observe any morphological changes with crystallization temperature and time.

III. Results

Microscopy Results. Figure 1 shows polarized optical micrographs of PEEK crystallized at 295.7 °C, for indicated crystallization times t_x, for solution-cast samples. All samples exhibit a typical spherulitic morphology, as was reported by others. The spherulites are 20–40 μm in size and are volume filling in less than 60 min, indicating that primary crystallization is complete in short times at this temperature. We shall refer to this type of spherulite as belonging to type I morphology.

Figure 2 gives micrographs for solution-cast PEEK films crystallized at 300.7 °C for the indicated times, t_x. The nucleation and growth processes at this temperature are, as expected, slightly slower than at lower crystallization temperature and result in the formation of spherulitic structures of type I, very similar to these observed in Figure 1. However, for longer crystallization times ($t_x = 260$ min), a second type of structure nucleates and grows with time. We shall refer to this type of structure as type II morphology. For even longer crystallization times, an increase in both number and size of type II crystal aggregates is observed. Note that the growth of type II structures after being initiated on the type I spherulites proceeds first more or less along the spherulite radius and then out in the free melt. At 300.7 °C the nucleation of type II structures is fairly intense and often predominant at the edge of type I spherulites. Under these crystallization conditions the nucleation of type II structures was not observed in the absence of type I spherulites. The "birefringence"[15] of these new crystalline entities is always much larger than that observed for the common PEEK spherulites of type I.

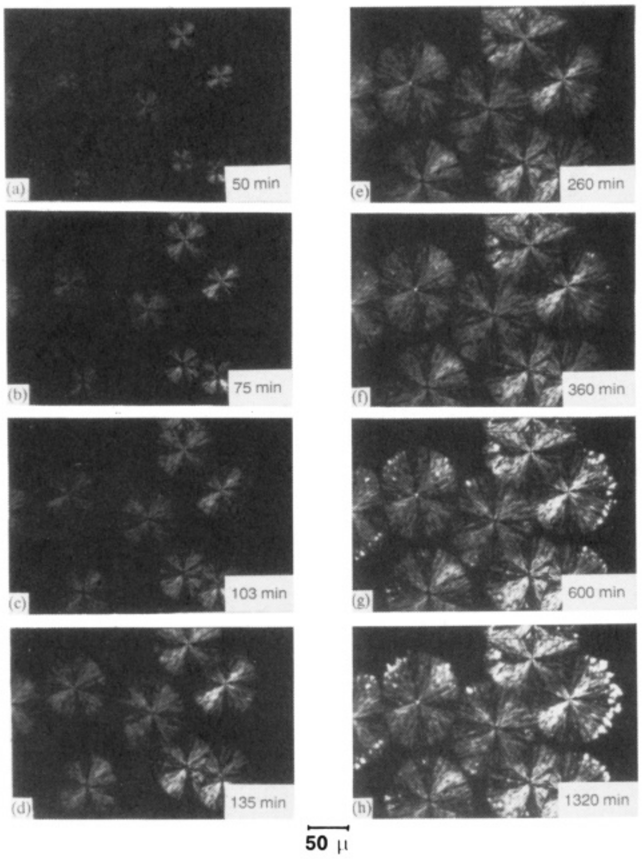

Figure 2. Polarized optical micrographs of PEEK films crystallized isothermally from the melt at 300.5 °C as a function of crystallization time, t_x.

This unique morphology observed here was not only limited to PEEK crystallized from the melt. Similar behavior was also observed for glassy films annealed at 300 °C or above, in PEEK/ULTEM blends[16] and in lower molecular weight end-capped PEEK synthesized by the ketimine route.[17] It should be pointed out here that what we call the type II morphology has also been recently oberved by others in PEEK[18] and in poly(arylene ether ketone ketone) copolymers.[19]

As the crystallization temperature is increased (cf. Figure 3, for $T_x = 305.7$ °C), the nucleation density of both type I spherulites and type II structures decreases and the regularity of type II structures increases. It is also worth noting in Figures 2 and 3 that the growth of type I spherulites stops approximately at the time when type II structures nucleate (cf. Figures 2 and 3 for crystallization times larger than about 260 min). If, however, the sample that was crystallized at 305.7 °C is rapidly cooled to a lower temperature (i.e., 270 °C), the growth of type II structures is interrupted and that of type I spherulites is reinitiated. Figure 3h shows this behavior for a crystallization time of 1320 min at 305.7 °C after further cooling to 270 °C. A similar behavior was observed for all samples initially crystallized in the temperature range where type II structure could form. To further investigate this morphological transition during the growth process, we carried out isothermal studies of the time dependence of the spherulite radius. Figure 4 displays plots of spherulite radius versus crystallization time for the growth of type I spherulites at the indicated crystallization tem-

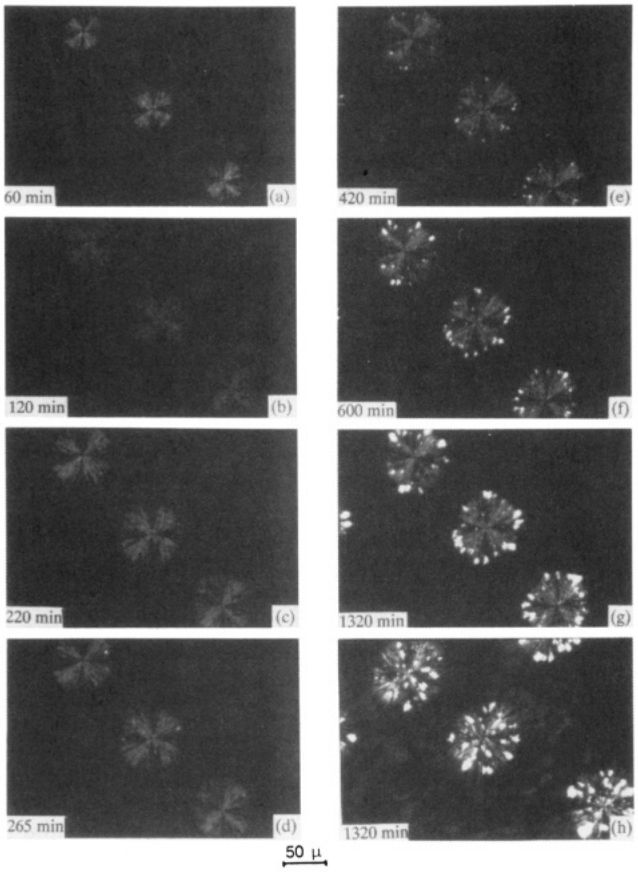

Figure 3. Polarized optical micrograph of PEEK crystallized isothermally from the melt at 305.5 °C for indicated t_x (a–g) and cooled to 270.8 °C and crystallized isothermally at 270.8 °C to observe the growth of type I morphology (h).

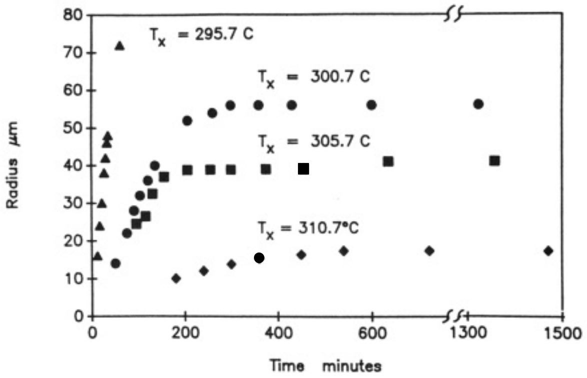

Figure 4. Plot of radius vs time during the growth of type I PEEK spherulites at the crystallization temperature T_x.

peratures. This plot clearly indicates that, at $T_x = 295.7$ °C, there is a linear increase in the radius with time until the spherulites impinge on each other. It should be recalled (cf. Figure 1) that, for this crystallization temperature, no type II structure could be observed, even after 900 min of crystallization time. However, for higher crystallization temperatures, the radius initially increases linearly with time but then displays a nonlinear behavior before becoming invariant. The time where this nonlinear behavior sets in corresponds approximately to the time for the appearance of type II structures. Even though we have not quantified the growth rates of type II structures, it is clear that they grow much slower than type I spherulites.

The morphological appearance of type II structures is very much dependent on crystallization time, temperature, and film thickness. If the film thickness was decreased by casting from a more dilute solution (0.05% w/w), the type II structure was not observed at crystallization temperatures around 300 °C. If, on the other hand, the film thickness was much larger (30 µm and above, as obtained by compression molding), the spherulitic nucleation density was quite large and it was difficult to distinguish clearly the two structures. Figure 5 displays micrographs for a melt-pressed PEEK film crystallized at 325.5 °C for the indicated crystallization times. Since the nucleation density in such films is much higher than that in solution-cast films, it is more difficult to distinguish clearly the two morphologies. One can, however, observe major differences between optical micrographs taken after 3.5- and 19-h crystallization times. At early times, the structures formed are predominantly spherulitic (type I morphology), whereas for longer crystallization times, the type II morphology has nucleated and grown to the extent that, now, one barely resolve the type I spherulitic structures.[20] These observations demonstrate that the appearance of a type II structure is not an artifact arising from the low thickness characteristic of solvent-cast films. Furthermore, since previous crystallization studies[1,6,9,10] were limited to a lower temperature range and shorter crystallization times, it is understandable why the type II morphology had not been clearly identified until now.

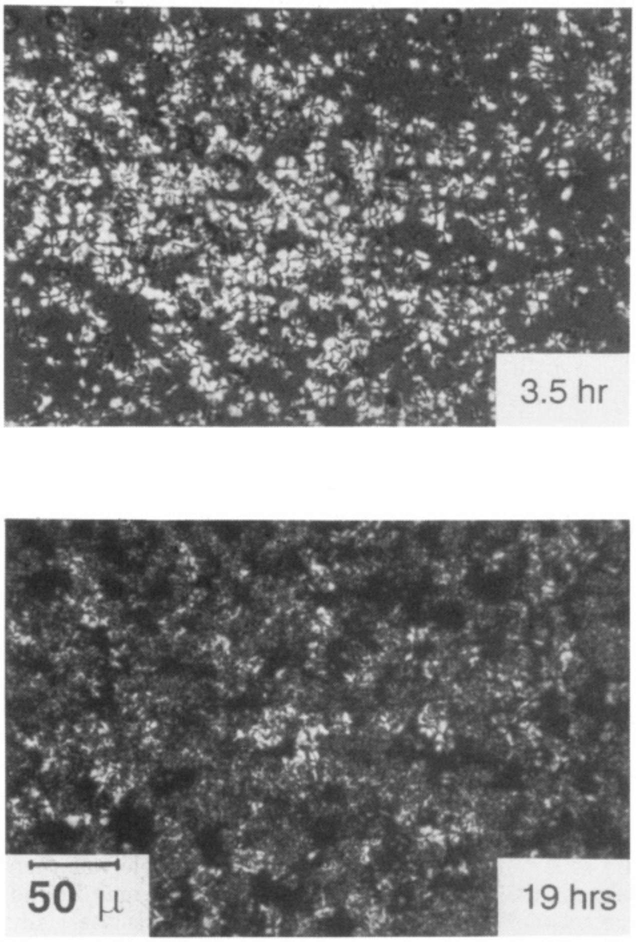

Figure 5. Polarized optical micrographs obtained with melt-pressed PEEK films of thickness about 35 µm crystallized isothermally from the melt at 325.5 °C for the indicated crystallization time, t_x.

Since the type II structure is only observed at high crystallization temperature for long crystallization times, one must ensure that it is not an artifact resulting from degradation processes. A growth rate study was performed to investigate this possibility. Figure 6 displays a plot of radius versus time at a crystallization temperature of 295.7

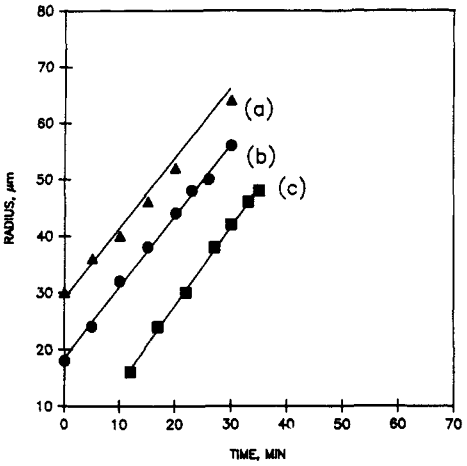

Figure 6. Plot of radius vs time for the growth of PEEK spherulites subjected to different conditions of crystallization (see text for details).

°C for samples subjected to various treatments. All samples were first cast on cover slips from a 0.22% w/w solution and dried as described previously. The first sample was initially crystallized at 300.7 °C for 8 h, a time sufficient to allow for both the formation of the type II structures and the halt of type I spherulitic growth. This sample was then cooled to 295.7 °C where the type I spherulitic growth was reinitiated until the spherulites were volume filling (see Figure 3h). Growth measurements were carried out during the isothermal stage at 295.7 °C and are reported in Figure 6a. The same sample was then heated to 390 °C for 3 min to ensure complete melting and cooled quickly to 295.7 °C where it crystallized isothermally in the type I morphology. Growth rate measurements were performed during the isothermal stage and are represented by the plot in Figure 6b. Finally, a fresh sample was crystallized at 295.7 °C after being melted at 390 °C for 3 min (Figure 6c). It is clear that all growth rates at 295.7 °C are identical within experimental error and that no type II structure was formed at that temperature in any of the samples. The invariance of the crystal growth through these various thermal cycles clearly suggests that degradation has not taken place at this temperature and does not give rise to type II structures.

In order to investigate any potential correlation between the existence of a new morphology and the well-known double endothermic behavior, we carried out heating studies on samples exhibiting both morphological types. The birefringence of type II structures exhibited a marked decrease about 10 °C above the crystallization temperature. Upon further heating, the birefringence was observed to increase slightly until it completely vanished at the melting temperature. On the other hand, the birefringence of type I spherulites exhibited a continuous decay from the crystallization temperature until the melting temperature. Type II structures completely melted just a degree or so above type I spherulites. This difference in melting behavior will be discussed qualitatively in the next section.

Although these observations are only qualitative, they do suggest that these two morphologies are thermodynamically quite different. These observations also suggest that some transformation does take place in the type II structures upon heating some 10 °C or so above the crystallization temperature.

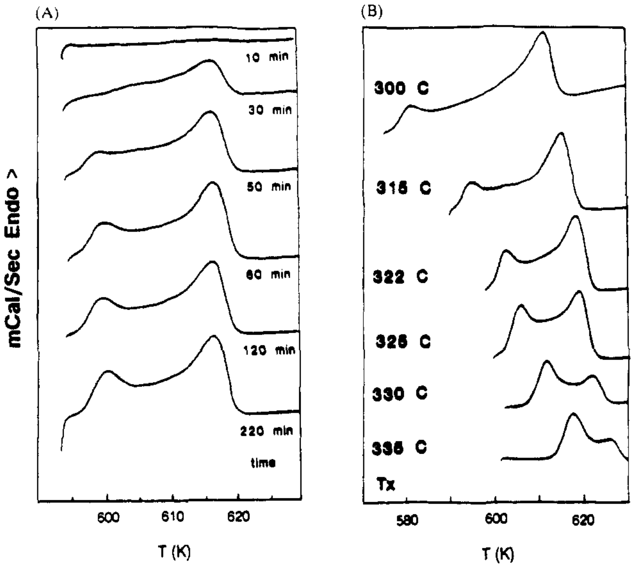

Figure 7. DSC melting endotherms of PEEK crystallized isothermally from the melt at (A) T_x = 320 °C for indicated crystallization times and (B) at the indicated crystallization temperatures.

DSC Results. The observation of two distinct types of morphology for melt-crystallized PEEK led us to reexamine the nature of PEEK's multiple endothermic behavior. On Figure 7A we show the DSC traces for the heating of samples crystallized at 320 °C for various lengths of time. We can distinctly see that the high-temperature endotherm appears first and alone for short crystallization times and that the low temperature endotherm only develops in samples crystallized for longer times. Similar observations were made by Cheng et al.[3] and Bassett et al.[5] Figure 7B shows the variation of the double endothermic behavior of PEEK with crystallization temperature, T_x, for very long crystallization times. As T_x is increased from 300 to 335 °C, there is a relatively larger temperature shift for the low-temperature endotherm than for the high-temperature endotherm. Furthermore, the ratio of the heat of transition of these two endothermic processes changes considerably with crystallization temperature. Above T_x = 330 °C, the relative area of the lower endotherm becomes larger than that of the higher endotherm.

IV. Discussion

It is now clear that, if films of PEEK are crystallized at temperatures higher than about 300 °C for long periods of time, a second type of morphology can be observed. These type II structures only nucleate on the type I spherulites, densely at low temperatures and much less at higher temperatures. The type II morphology can be described as crystal aggregate like. At all temperatures the growth occurs more predominantly parallel to the radius of type I spherulites. The birefringence[15] of the type II structure is higher than that of the type I spherulites. The relative content of type II structures in isothermally crystallized thin films increases with crystallization temperature. The observation of two different morphological structures for bulk-crystallized PEEK samples by polarized optical microscopy is consistent with the results of the study by Lovinger et al.[11] on crystals grown from dilute solution. To investigate the crystallographic nature of this new morphological structure, we also obtained wide-angle X-ray diffractograms for films crystallized at 250 and 335 °C for extended periods of time. The diffraction profiles for these two films (not shown here) do not exhibit any marked difference, except for variations in the diffraction peak half-width, which can be interpreted in terms of changes in crystal size and perfection with the temperature of crystallization. A similar conclusion based on electron diffraction results was drawn by Lovinger et al.[11] for the two morphologies of crystals grown from dilute solution. Thus, the two morphologies seem to correspond to the same crystal structure.

Comparison of the melting behavior observed by DSC and optical microscopy suggests that the low-temperature DSC endotherm must involve some transformation within the type II structure, whereas the high-temperature broader endotherm corresponds to the melting of crystals from both type I and type II morphologies. We do not believe at this point that the type II structures undergo exclusively a simple melting recrystallization process since melting studies at heating rates from 2.5 to 40 °C/min on samples crystallized at 320 °C failed to show any noticeable variation of the heat of fusion for the second endotherm with heating rate. This observation should be taken with some caution, since the melting range of this polymer is very broad and the deconvolution of the two endotherms is not a straightforward task. A change in the retardation of type II structures upon heating was apparent under the microscope in the vicinity of the lower endothermic transition observed in the DSC. However, the ultimate melting temperature of type II structures was slightly higher than that of type I spherulites. This could be explained by a partial melting recrystallizaton of type II structures.

A similar type of morphological transformation during the isothermal growth of poly(1,3-dioxolane) was reported by Prud'homme et al.[21] and Alamo et al.[22] However, no mechanism for such a growth transition was proposed.

Concerning the origin of the type II morphology, we can rule out solvent effects since these structures are also observed in melt-pressed PEEK films. Furthermore, judging by the variation in content and melting temperature of type II structures with crystallization temperature, we do not believe that chemical or molecular weight fractionation could explain our observations. One can also rule out the possibility of degradation as a cause for the existence of type II structures on the basis of our growth rate study on samples of differing thermal history. From the wide-angle X-ray diffraction and polarized microscopy studies, we must rule out the formation of type II structures by a solid-state phase-transition process.

A possible explanation for the origin of these two structures may be given by correlating our observations with those reported by Cheng et al.[3] For samples crystallized isothermally from the melt state, they observed a continuous decrease in both the glass transition temperature and the "rigid amorphous phase" content with crystallization temperatures ranging from 210 to about 300 °C. For higher crystallization temperatures, the glass transition temperature was constant and no rigid amorphous phase could be detected. A logical but maybe unwarranted conclusion could be that type I spherulitic structures are associated with the presence of a non-fully relaxed amorphous phase (amorphous phase containing a rigid fraction), whereas the type II structures are only observed when the amorphous phase is completely relaxed. According to this proposed explanation, our concept of the rigid amorphous phase is not compatible with the belief that this phase corresponds to the unrelaxed crystal–liquid interfacial region. If such was the case, it would be difficult to explain how the crystal–liquid interfacial region could vanish for temperatures of crystallization higher than 300 °C. We tend to associate this phase with a nonequilibrium liquid state of inherently long relaxation time. Experiments to examine more rigorously this proposed correlation are currently being carried out and will be reported shortly.

It should be noted here that we have only investigated the morphology and the melting behavior of samples crystallized from the melt state (for $T_x > 300$ °C by DSC). We did not observe the type II structure by polarized optical microscopy for crystallization temperatures below 295 °C. The low-temperature endotherm which we assigned to some transformation of the type II structure has, however, also been observed for samples crystallized below 295 °C from the glass. Two possible explanations for these seemingly contradictory statements can be offered. First, because of the rapid kinetics of crystallization of type I spherulitic structures at temperatures below 295 °C, the growth of type II structures may be limited spatially by the faster nucleation and growth of type I spherulites. The resulting type II structures would therefore be of small size and not readily resolved from type I structure by microscopy. Second, a more simple explanation could be that the nature of the low-temperature endotherm is not exactly the same for samples crystallized from the glass (at low temperature) and from the melt (at higher temperature). Two observations could substantiate this view. First, the double endothermic behavior of PEEK is much more heating rate dependent for samples crystallized from the glass than for those crystallized from the melt. Second, the peak temperature of the upper endotherm is fairly independent of crystallization temperature for samples crystallized from the glass, whereas it increases linearly with crystallization temperature for melt-crystallized samples. This points toward a larger extent of melting recrystallization during heating for samples crystallized from the glass.

Finally, we point out that the type II morphology has been observed by Phillips et al.[18] at temperatures lower than 300 °C. As mentioned earlier, we did not make such observations. This disparity might be accounted for by differences in the molecular weight or in sample thickness or by the effect of melting temperature and residence time in the melt state.

V. Conclusions

In this paper we have reported the observation of a new morphology in poly(ether ether ketone), which develops predominantly at high crystallization temperatures and long crystallization times. The relative ratio of the population of the classical spherulitic morphology to that of the type II structures is observed to vary with crystallization temperature qualitatively in the same manner as the ratio of the enthalpies of the high- and low-temperature endotherms. Further, we proposed that the low-temperature endothermic peak observed during heating of PEEK samples isothermally crystallized from the melt is associated with some reorganization and melting of the type II structures. We believe that type I and type II morphologies are characterized by the same crystal structure and that type II morphology does not result from fractionation, segregation, or degradation processes. Finally, we tentatively correlated the relative population in these two structures to the rigid amorphous phase content in samples crystallized under different conditions.

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