Molecular Mobility in Para-Substituted Polyaryls. 1. Sub-T_g Relaxation Phenomena in Poly(aryl ether ether ketone)

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ABSTRACT: The fine structure of the β mechanical relaxation in poly(aryl ether ether ketone) is shown to result from two components. The low-temperature β_1 process is simple and noncooperative. The β_2 component, occurring at higher temperature, exhibits a cooperative feature. Activation enthalpies distributions, and the evolution of the activation entropy with temperature are determined based on the Eyring–Starkweather analysis, and comparisons are made with the alternative Arrhenius description. The influence of microstructure on the β_1 and β_2 processes is discussed, and possible molecular origins of these relaxations are suggested. The β relaxation features are related to the macroscopic mechanical properties of this polymer.

Introduction

Considerable efforts have been made to understand the molecular dynamics of para-linked phenylene polymers. The simple chemical structure of this family of polymers is described by $[-Ph-X-]_n$, where X can be O, CO, S, SO_2, CH_2, CO_3, etc. and Ph is an aromatic unit. These polymers often exhibit a similar viscoelastic behavior, with a broad, low-temperature, β relaxation and a high-temperature α process associated with the glass transition. A typical mechanical spectrum is shown in Figure 1. A β' relaxation is sometimes described and is attributed to the presence of higher disorder sites within the glassy polymer. Although β' is visible from the data obtained during the first runs, subsequent temperature scans usually do not exhibit this shoulder, because the molecular arrangements of the chains have become more compact. This phenomenon should not be considered as a typical relaxation but rather could be interpreted as an anticipation of the α process. The high concentration of "defects", or "islands of mobility", results in an increase of the molecular mobility. During the temperature scans, the molecular mobility increases, which, in turn, causes the collapse of the defects responsible for the appearance of the β' shoulder.

The influence of the X linkage in para-substituted polyaryls is subtle. Some of the polyaryls are semicrystalline, like poly(phenylene sulfide) (PPS) and poly(aryl ether ether ketone) (PEEK), but the introduction of the SO_2 moiety strongly restricts the crystallization ability of the polymer.[1] The presence of polar linkages (SO_2, CO) or moieties with sterically restricted motions increases the glass transition temperature. The location of the β process is surprisingly less affected.

Our investigations are focused on the dynamic mechanical behavior of PEEK, a high-performance thermoplastic semicrystalline polymer, usually used as a matrix for carbon fiber reinforced composites. It is known for its exceptional mechanical properties at high temperature, associated with excellent fatigue resistance. Table I gives the main physical properties of PEEK. Crystallization phenomena in PEEK have been widely studied probably because the crystalline microstructure determines the properties of the PEEK resin and its related composites. The viscoelastic behavior of this polymer has also been the subject of several investigations.[3-5]

The aim of this work is to provide more information on sub-T_g relaxation phenomena in PEEK and in related polyaryls. The β relaxation is analyzed using the Starkweather method[6-10] and compared with an Arrhenius treatment.

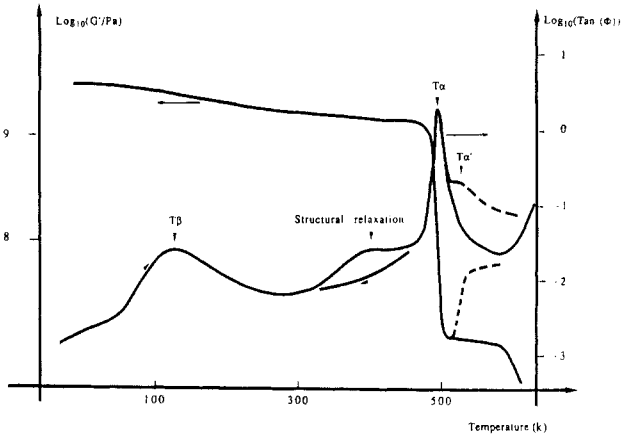

Figure 1. Typical dynamic mechanical behavior of an amorphous para-linked polyaryl. The β relaxation is often broad, and the maximum of tan (Φ) is located, at 1 Hz, near T = 150–200 K. A shoulder can be observed below the α transition. This shoulder is due to the presence of disordered chains in the glassy polymer. The α transition is related to the glass transition. It occurs at relative high temperature: T_α = 360 K for PPS, 420 K for PEEK, and 480 K for PES. If the polymer is semicrystalline and obtained in the amorphous state after quenching, the crystallization phenomenon is observed above T_g (dashed lines). The result is an increase in the modulus and a second tan (Φ) peak attributed to the molecular motions in the amorphous phase hindered by the presence of the crystallites.

Furthermore, the evolution of the β mechanical relaxation spectra with microstructure is investigated. Our analysis of the molecular mobility in polaryls is based on a molecular model of the glass transition developed by Perez et al.[11] Accordingly, the structure of amorphous polymers is described as a regular packing of repeat units in which there are some disorder sites, with an excess of entropy and enthalpy. The molecular displacements are supposed to be initiated in these sites, so that the molecular mobility depends on the concentration of the defects. The motions involved in the α relaxation result from the cooperative and hierarchically constrained combination of the elementary movements giving rise to the β relaxation. Therefore, β is considered as the precursor of the α relaxation. Consequently, it is assumed that the motions responsible for the β relaxation are able to combine to yield to longer range reorganizations. Although the quantitative evidence of this assumption is not provided here, further investigations in this domain are ongoing.

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Table I
Main Physical and Engineering Constants of ICI's PEEK 450G[a]

chemical structure	(-Ph-O-Ph-O-Ph-CO-)$_n$
amorphous-phase glass transition temp	T_g = 416 K
crystalline phase structural unit	orthorhombic
lattice parameters	a = 0.788 nm b = 0.594 nm c = 3.050 nm
typical crystallinity ratio	X_c = 35%
enthalpy of fusion	ΔH_f = 130 kJ/mol
surface energies of the crystalline phase	σ_e = 49 erg/cm^2 σ_s = 38 erg/cm^2
melting temp of infinite and perfect crystal	T_f^* = 668 K

Engineering Data for Semicrystalline PEEK 450G

shear modulus at 296 K	1.30 GPa
Young's modulus (1% secant) at 296 K	3.60 GPa
elongation at break (ASTM test method D638) at 296 K, test speed of 5 mm/min	50%
continuous working temp	520 K

[a] Reference 2.

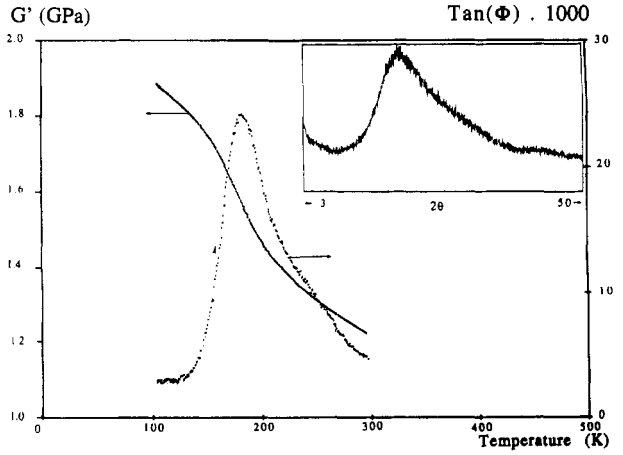

Figure 2. Isochronal at 1 Hz of the β relaxation in amorphous PEEK obtained after quenching. Notice the slight asymmetry of the tan (Φ) curve. The insert displays the X-ray diffraction profile of this amorphous sample.

Experimental Section

PEEK 450G was kindly supplied by ICI Inc., Wilton Research Centre (UK). As-received samples are semicrystalline. The crystallinity ratio evaluated by means of a Perkin-Elmer DSC 7 is ca. 34%. The average molecular weights are M_n = 45 000 and M_w = 90 000. Amorphous samples of PEEK 450G were obtained by quenching the melt at 400 °C in cold water.

Dynamic mechanical spectrometry was performed by means of a homemade high-resolution apparatus.[12] This automated inverted pendulum is specifically designed to study thin samples like films and fibers. It measures the complex shear modulus $G^* = G' + iG''$ as a function of temperature and frequency. The temperature scans are called isochronals. They are performed by increasing the temperature from T = 90 K to T = 600 K at 1 K/min for one or several frequencies. It is also possible to record G^* as a function of frequency at a fixed temperature. The frequency scans are called isotherms. They are performed by decreasing the frequency from 1 Hz down to 0.0001 Hz.

The wide-angle X-ray scattering experiments were performed with a Siemens D500 diffractometer using Cu Kα radiation at room temperature. The measurements of the reflection pattern were made over an angular range from 3 to 50° (2θ), with a 0.04° scan increment.

Methods and Results

Figure 2 displays tan (Φ) = G''/G' and G' (in GPa) on linear scales for an amorphous sample freshly quenched. The maximum of Φ is near 184 K at 1 Hz, where an inflection of G' can be observed. Near 100 K, $1/G\ dG/dT$ = -1.3×10^{-3} K^{-1}, which is the usual order of magnitude for anharmonic effects on the phonon modulus. The tan (Φ) peak is slightly asymmetric, mainly because of the shape of the curve in the temperature interval from 220 to 280 K, where a slight shoulder can be noticed.

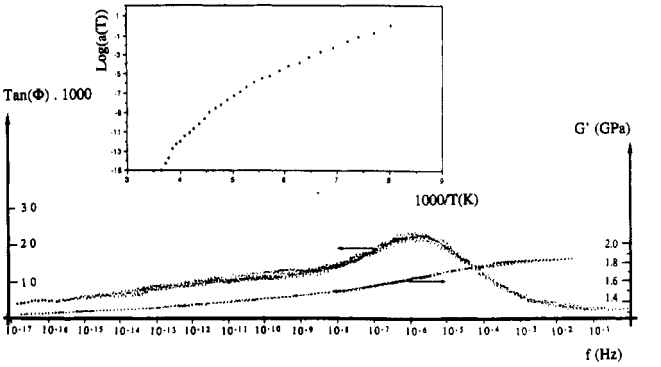

Figure 3. Master curve of the β relaxation in PEEK. This relaxation spreads over at least 16 frequency decades. The insert shows the shift factors used to bring the isotherms on a single curve. The reference temperature is T = 125 K.

Arrhenius Analysis. The β relaxation is frequency dependent, and the master curve could be obtained by shifting the isotherms along the frequency axis. This master curve is displayed in Figure 3 with the corresponding shift factors. If the relaxation is considered as an Arrhenius process, the frequency of the relaxation $f = 1/2\pi\tau$ can be expressed as

$$f = f_0 \exp(-E_a/RT) \quad (1)$$

Therefore, the shift factor is

$$a(T) = a_0 \exp(E_a/RT)$$

where E_a is the apparent activation energy. The high-temperature (i.e., low frequency) side of the β peak in Figure 3 is broad and displays a higher apparent activation energy than the low-temperature (or high frequency) side of the β peak. Below 200 K, the apparent activation energy is of the order of 30–45 kJ/mol. Above 200 K, E_a increases with temperature in the range 30–100 kJ/mol. The threshold T^* at 200 K is in agreement with the location of the slight shoulder of the plot tan (Φ) vs T. The Arrhenius analysis reveals that the β relaxation in PEEK results from a low-temperature process, hereafter called β_1, and a high-temperature one, β_2.

Eyring–Starkweather Analysis. An alternative expression for eq 1 is

$$f = (kT/2\pi h) \exp(-\Delta H^*/RT) \exp(\Delta S^*/R) \quad (2)$$

given by Eyring's theory.

$\Delta G^* = \Delta H^* - T\Delta S^*$ is the activation free enthalpy and can also be written as

$$\Delta G^* = RT \ln (kT/2\pi hf) \quad (3)$$

It can also be shown[6] that E_a is related to ΔH^* by the equation

$$E_a = \Delta H^* + RT$$

thus

$$E_a = RT(1 + \ln (kT/2\pi hf)) + T\Delta S^* \quad (4)$$

Starkweather showed that for many relaxations, the value of E_a obtained by an Arrhenius analysis is in good agreement with

$$E_a = RT'(1 + \ln (kT'/2\pi h)) \quad (5)$$

where T' is the absolute temperature of the loss maximum

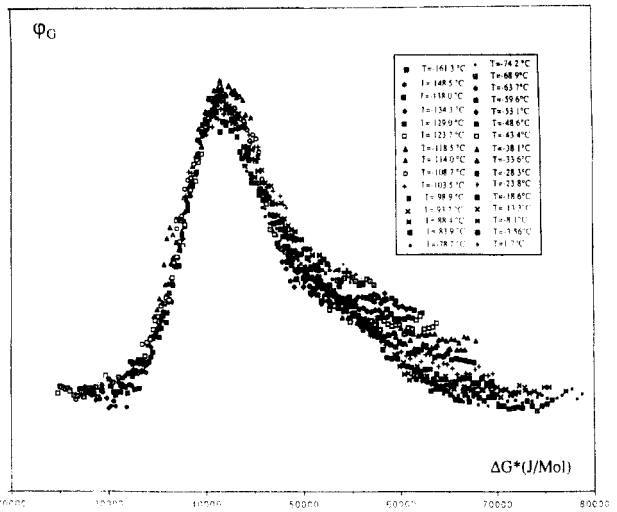

Figure 4. Distribution of the free enthalpy of activation (ΔG^*) for the β transition in amorphous PEEK. The low-temperature-side isochronals form a single pattern. Above 50 kJ/mol, the isochronals do not lead to a single curve, which shows that the relaxation exhibits a positive nonzero activation entropy.

at 1 Hz. This suggests that the entropy of activation is close to zero. Subvitreous relaxation phenomena in polymers are often of that type. They are believed to be simple and noncooperative. In this case, the motions involved are localized and independent from each other. For example, Starkweather studied the relaxation of PMMA and concluded that ΔS^* is zero within experimental uncertainty. Nevertheless, Muzeau et al. recently investigated the features of the sub-T_g relaxation in this polymer[13] by means of a high-resolution mechanical spectrometer. They also applied the Eyring–Starkweather analysis to their data, and they found that the β process exhibits a mean activation entropy near 50 J/(mol·K). Although the apparent activation entropy is found to be significantly different from zero, they do not conclude that the motion is cooperative. The ΔS^* parameter is considered to be a true characteristic of the activation process.

The interpretation of the Starkweather treatment of glass transitions is different. Glass transitions always exhibit a high apparent activation energy.[6] This is interpreted in terms of cooperative and hierarchical constrained dynamics of the glass transition.[11] The corresponding apparent activation entropy is shown to be so high that it cannot be given any physical meaning, and, therefore, the high value of the ΔS^* factor only results from the inability of the Arrhenius and Eyring models to reasonably describe the relaxation associated with the glass transition.

In the case of PEEK, the maximum of tan (Φ) for the β_1 process is located near $T' = 184$ K at 1 Hz, and the value given by eq 5 (i.e., $E_a = 43.0$ kJ/mol) is close to the value obtained by the Arrhenius analysis. For the β_2 component, $T' = 240$ K, and the experimental apparent activation energy is higher than the value given by eq 5 (i.e., $E_a = 56.7$ kJ/mol). Therefore, the β_2 process clearly exhibits a positive activation entropy, whereas $\Delta S^* = 0$ for the β_1 component. The problem now is to decide whether this reflects cooperativity of motions or a feature of the activated state. In both cases, β and α are well separated and the analysis of the sub-T_g relaxation is not affected by the low-temperature tail of the glass transition relaxation, as is the case for other polymers. The distributions of activation enthalpies are shown in Figures 4 and 5. The relaxation spectrum is obtained according to

$$\varphi_G = 2G''/(\pi(G_u - G_r))$$

This description assumes uncorrelated microscopic events,

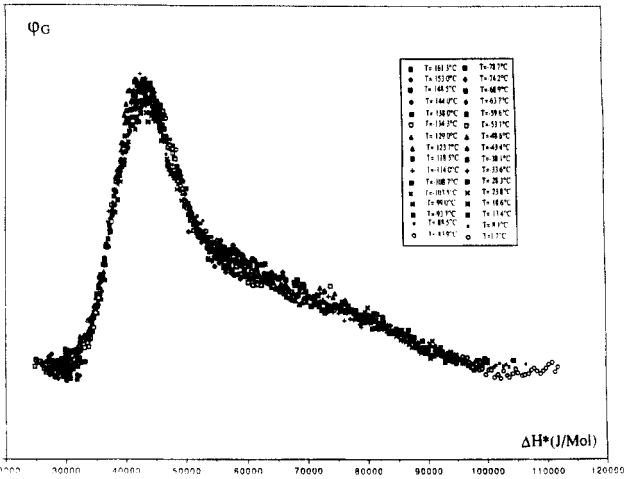

Figure 5. Distribution of the enthalpy of activation (ΔH^*) for the β transition in amorphous PEEK, exhibiting a narrow component, located between 30 and 55 kJ/mol, and a broad component, located between 50 and 105 kJ/mol.

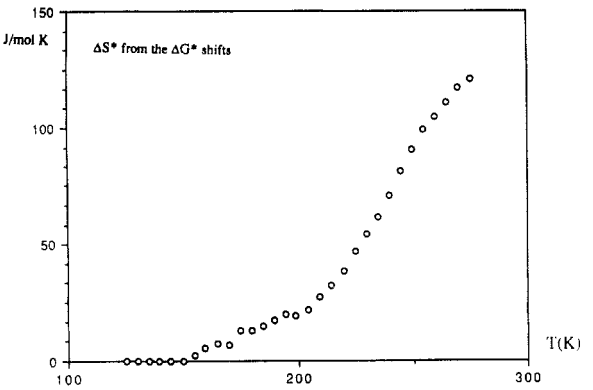

Figure 6. Entropy of activation (ΔS^*) for the β transition in amorphous PEEK plotted against the temperature of the shifted isotherm. Below $T^* = 200$ K, the activation entropy is close to zero. Above T^*, ΔS^* increases from 50 to 130 J/mol.

represented by a generalized Maxwell model. ΔG^* is given by eq 3. For each value of T and f, it is possible to calculate φ_G and ΔG^*. The distribution is obtained thanks to a series of isotherms in the temperature range from 105 K to 275 K. As expected, on the low-temperature side of the β relaxation all the isotherms fall on a single curve, while the data on the high-temperature side of the peak are scattered. To rebuild a single pattern of the β_2 component, it is necessary to shift the isotherms along the ΔG^* axis. The result is a distribution of ΔH^*, which is the superimposition of two components. The energy shift factors are used to evaluate the activation entropy according to cumulated shift factor = $T\Delta S^*$. Figure 6 shows the activation entropy thus calculated versus temperature. It can be seen that at low temperatures the activation entropy is close to zero, and in the temperature range of the β_2 component, ΔS^* increases. The consistency of the method is illustrated in Figure 7, where the activation energy evaluated from the Arrhenius analysis is compared with the apparent activation energy obtained from eq 4, using the values of $T\Delta S^*$ deduced from the shifts of the free enthalpy distribution. As expected, these two similar treatments lead to similar results, although they proceed, in one case, from a shift in the log (frequency) scale and, in the other, from a shift in the free activation enthapy scale.

Influence of Microstructural State on the β Relaxation of PEEK. The precise effect of thermomechanical treatments and induced microstructure on the subvitreous relaxations is still a matter of debate. For example, physical aging (or structural relaxation) is

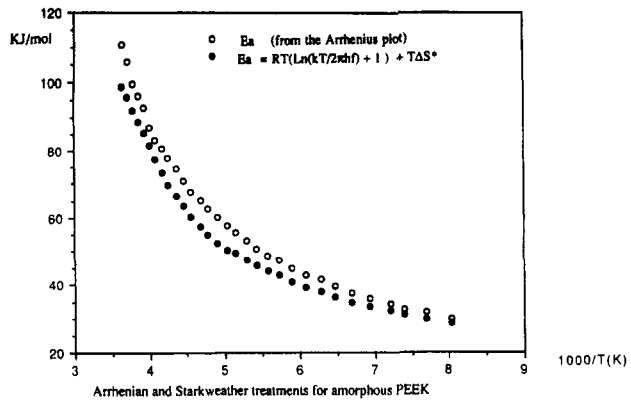

Figure 7. Apparent activation energy (E_a) deduced by a pure Arrhenius analysis of the β relaxation in amorphous PEEK (○) and E_a obtained by the Eyring–Starkweather analysis (●).

Table II
Samples of Various Microstructures Studied in This Work with Their Corresponding Thermomechanical History

sample no.	state	mechanical and thermal treatments
1	amorphous quenched (light brown, transparent)	quenched in cold water from the melt (at 400 °C)
2	amorphous annealed	sample 1 annealed at 125 °C for 20 h
3	semicrystalline (gray, opaque)	sample 1 heated from 23 to 240 °C at 1 °C/min and cooled from 240 °C at −6 °C/min; crystallinity level: 34%
4	rolled (birefringent)	sample 1 (amorphous) rolled at 23 °C; (initial dimensions, 0.44 × 2.30 × 14.00 mm³; final dimensions, 0.23 × 2.98 × 20.66 mm³)
5	drawn (transparent, slightly milk-like) (birefringent)	amorphous sample heated at 140 °C drawn in 2 s with a drawing ratio of 2.7 (the drawn sample is semicrystalline)

believed by Johari to significantly affect the β process,[14] whereas Struik thinks[15] that it mainly leaves β unchanged. To our knowledge, the effect of orientation on the sub-T_g processes of polyaryls has not been studied so far. To better understand the nature of β_1 and β_2 in PEEK, different microstructural states have been obtained using various thermomechanical treatments described as in Table II. An isochronal at 1 Hz measured for each sample is displayed in Figures 2 and 8–11. The inserts in Figures 2, 8, and 11 display the WAXS profiles of the corresponding samples. The tan (Φ) vs T pattern for the β relaxation for a semicrystalline sample (Figure 8) exhibits a main process below 210 K and a well-defined shoulder above 220 K. These components are located in the same temperature ranges as the β_1 and β_2 processes in amorphous PEEK. Therefore, we assume that the bimodal aspect of the β relaxation in semicrystalline PEEK is of the same nature and reflects the same components as in amorphous PEEK. Consequently, it can be said that the semicrystalline sample exhibits an enhanced β_2 process and a smaller β_1 component, compared with the β relaxation of the amorphous sample obtained just after quenching (Figure 2).

The sample heat treated near T = 400 K (Figure 9) exhibits the same β_1 component as in the quenched amorphous state, but the β_2 process is more apparent.

The amorphous rolled sample (plastic strain near 100%) also exhibits a well-defined high-temperature component (Figure 10), while the low-temperature component is very similar to the β_1 process of the pure amorphous sample.

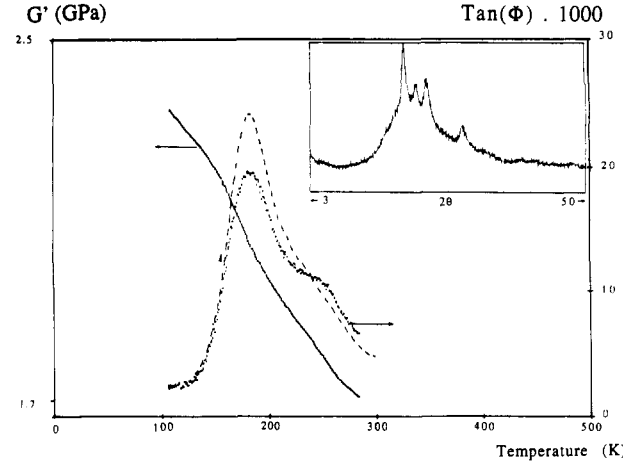

Figure 8. Isochronal at 1 Hz of the β relaxation is semicrystalline PEEK obtained after the crystallization of an amorphous sample. Notice the smaller β_1 component and the prominent β_2 process. The insert shows the (well-known) reflection peak of this semicrystalline sample. The dashed lines display the β relaxation pattern of the amorphous quenched sample for a comparison.

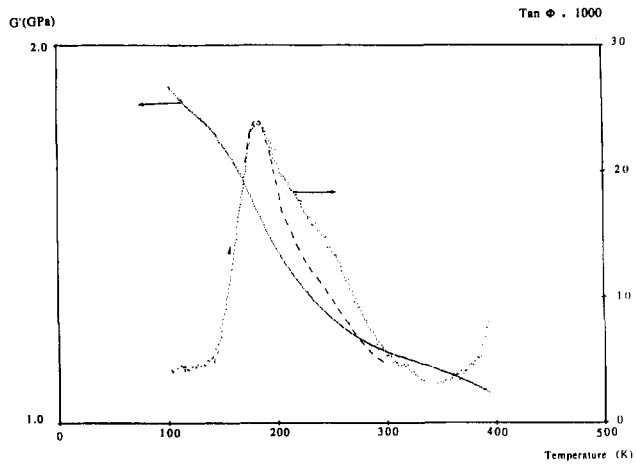

Figure 9. Isochronal at 1 Hz of the β relaxation in amorphous annealed PEEK. The β_2 process is more apparent than in the quenched state. The dashed lines display the β relaxation pattern of the amorphous quenched sample for a comparison.

Again, the location of the high- and low-temperature components suggests that they coincide with the β_1 and β_2 components of the amorphous state. The structural relaxation can be observed above 300 K. On cooling at 6 K/min, this shoulder disappears. At the same time, an apparent increase of G' can be observed. This is due to the change of the geometry of the sample (i.e., the width of the sample increases). We have evidence that this sample is not semicrystalline, (i) because the α relaxation is similar to the relaxation peak of the amorphous sample and (ii) because if the rolled sample is annealed at 400 K, the β relaxation peak becomes similar to the relaxation peak of the amorphous annealed sample whereas annealing has no significant effect on the semicrystalline sample.

The β relaxation pattern of the drawn sample (drawn in 2 s at 140 °C, with a drawing ratio of 270%) is displayed in Figure 11. The diagram shows a small β_1 component and a well-defined β_2 relaxation (Figure 11). It can be seen on the diffractogram that these samples became semicrystalline on drawing. The diffraction pattern is modified by anisotropy, as only two main peaks are present near 2θ = 18.2° and 2θ = 22.6°.

From these experiments, it can be concluded that the microstructure does not influence the temperature location of the components but does change the magnitude of each process. The high-temperature component is well defined

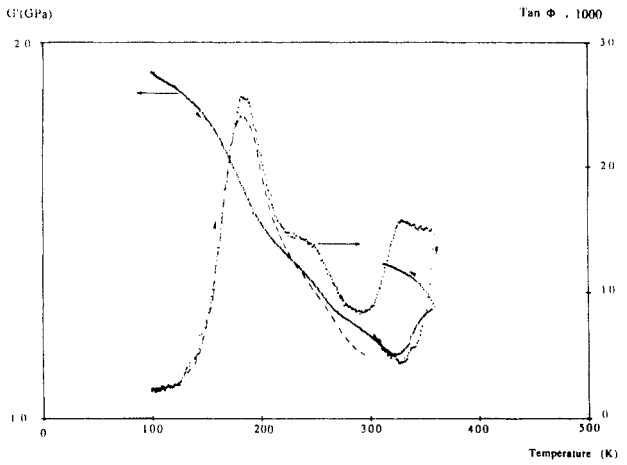

Figure 10. Isochronal at 1 Hz of the β relaxation in rolled amorphous PEEK. The β_2 process is well defined. The shoulder above 300 K shows the presence of defects within the glassy polymer. The dashed lines display the β relaxation pattern of the amorphous quenched sample for a comparison. The plot also displays the dynamic mechanical behavior when the sample is cooled at 6 K/min and shows the effects of the reorganization of loosely packed chains. The increase of the G' is due to a change in the sample dimensions during the high-temperature part of the scan.

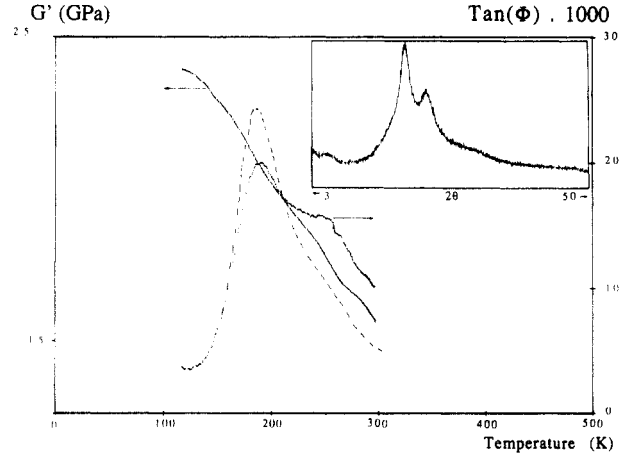

Figure 11. Isochronal at 1 Hz of the β relaxation in drawn PEEK. The β_2 process is prominent. The insert shows the diffraction profile different from Figure 8, probably because of anisotropy. The larger width at half-height of the diffraction peaks could result from a smaller size of the crystallites. The dashed lines display the β relaxation pattern of the amorphous quenched sample for a comparison.

for oriented and semicrystalline microstructures, whereas it is only exhibited after an analysis of the isotherms (Starkweather and Arrhenius treatments) for the quenched amorphous sample.

Discussion

Bimodal Aspect of the β Relaxation in PEEK. The Starkweather treatment of the β process clearly shows that this mechanical relaxation is broad and is due to two components: (i) The β_1 component is noncooperative and is well described by an Arrhenius or an Eyring equation with ΔS^* close to zero. The apparent activation energy of β_1 is near 43.0 kJ/mol. Furthermore, the preexponential factor (f_0) of the Arrhenius analysis is close to 10^{13}. (ii) The β_2 component is located at higher temperature and exhibits a positive activation entropy. Since on the high-temperature side of the β_2 component $\Delta S^*/R$ is near 15, we believe that this value is too high to be a true activation parameter, but rather results from a cooperative feature of the motions involved in the β_2 process. Therefore, the enthalpy distributions should only be considered as apparent near the β_2 component.

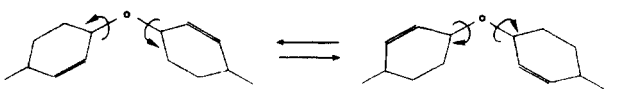

Figure 12. Counterrotational motion of two adjacent phenyl rings.

Effect of Water. According to Sasuga and Hagiwara,[4,5] the β mechanical relaxation in PEEK also results from the superimposition of a relaxation phenomenon, near 170 K, due to the activated motions of water adsorbed on the polar region of the macromolecular chains. We have noticed no significant effect of water on the β relaxation of PEEK: a sample of amorphous PEEK treated at 350 K in water for 24 h exhibits the same β relaxation shape as a sample heated at 350 K in air for 24 h. Furthermore, no significant variations of the weights of the samples could be measured in these experimental conditions. Even if PEEK and poly(aryl ether sulfone) (PES) have similar viscoelastic behaviors below T_g, the presence of the sulfone moiety in PES seems to have more effect on the moisture absorption than the ketone group in PEEK. Moreover, it is known that PEEK is highly resistant to a large variety of solvents and that only very little water can be found in this polymer (<0.5%). We concluded that it was not possible to vary the water content enough to significantly affect the dynamic mechanical behavior, and the occasional presence of water could thus be neglected.

Number of Structural Units Involved in the β Transition. The molecular mechanisms related to the β relaxation in PEEK are not definitely understood, as is the case for almost all polymers. Nevertheless, an excellent review on the molecular processes giving rise to the β relaxation in Bisphenol A polycarbonate (BPA-PC) is given by Jho and Yee.[16] It is shown that the secondary relaxation cannot be due to the activated motions of a single moiety in a monomer unit. Neither the individual mobility of the phenyl ring nor the motion of the isopropyl and carbonate units can be responsible for the β process. On the contrary, the β relaxation in BPA-PC is shown to involve "cooperatively" several repeating units (say 5 to 9) along the chains. The argument is based on the dynamic mechanical behavior of copolymers of BPA-PC and tetramethyl-Bisphenol A polycarbonate (TMBPA-PC) which have well-resolved separated β processes. The alternating copolymer exhibits only one "averaged" secondary relaxation. If the block length is increased to 9 units, then the two β relaxation peaks are restored at their corresponding temperature. We see no reason why the phenyl ring motions themselves (the 180° flips, augmented by small-angle fluctuations about the same axis[17-19]) could result in a relaxation process in PEEK if it is not the case in BPA-PC. Moreover, the ketone and ether linkages in PEEK have no individual mobility. Therefore, the β process in PEEK should concern several pairs of phenyl rings (say 5 to 9). The collective feature of the β process in BPA-PC-like polymers is also supported by the energy maps of the aromatic dimers which can be found in polycarbonate, PEEK, PES, and PPS. In all cases, the potential distribution is a function of the twist angles (ϕ_1 and ϕ_2) of the rings with respect to the plane of the linkages.[20-24] The twist angles can follow counterrotational motions (see Figure 12)which define favorable energetic valleys in the ϕ_1-ϕ_2 plane. Consequently, the rotations of two adjacent phenyl rings are believed not to be independent. To sum up, the motions resulting in the β transition, considered as a main global process, are described as collective motions of several structural units.

The β_1 Process Reflects Local Intrachain Motions in the Amorphous Phase. The intensity of the β_1 process

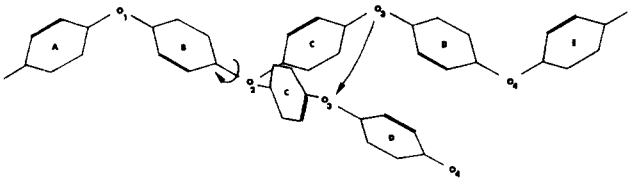

Figure 13. Elementary step of a type 2 transition. A first rotation of the tail $O_2O_3O_4O_5$ occurs around the (O_1O_2) axis. To keep the chain parallelism, a rotation of the same type is expected, for example, in O_4.

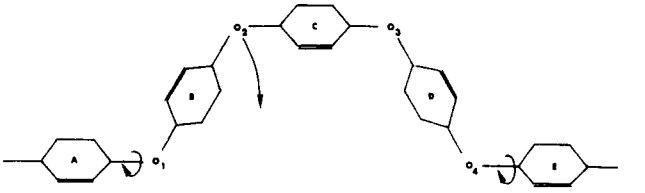

Figure 14. A crankshaft motion supposes the existence of a common axis of two phenyl rings separated by a least three other rings. These motions leave the adjacent tails unchanged but consist in the rotation of the central phenyl units.

in PEEK is descreased with increasing crystallinity levels. As the amount of amorphous material is lower, it is not surprising that the relaxation due to motions in this phase is less apparent. Nevertheless, the presence of the crystallites has no influence on the position of the β_1 peak at 1 Hz and does not change the activation energy, enthalpy, and entropy. Within the experimental uncertainty, there is no significant difference on the Arrhenius plots for a semicrystalline sample and for an amorphous sample. Moreover, the other thermomechanical treatments have no significant effect on the β_1 process. If the β_1 relaxation is insensitive to the microstructure, i.e., the way the macromolecular chains are packed together, it can be argued that they mainly reflect intrachain local interactions.

Molecular Motions Resulting in the β Transition. In the reference attached to one of the rings, the counterrotational motion of two phenylene units may consist of a rotation possibly of 80° around the fixed axis because the stable conformation is defined by a tilt angle of the aromatic rings with respect to the plane of the ether and ketone linkages near ±40°.[20-24] Figure 13 shows such a rotation in a chain segment of five rings linked by oxygen atoms. The fixed axis is supposed to be (O_1O_2). The counterrotational motion supposes the rotation of the chain $O_2O_3O_4O_5$... around (O_1O_2). At the same time, ring c between (O_2O_3) can rotate (around (O_2O_3)) to find an easier energetic path. Such a motion is described in the Helfand classification as a type 3 motion. It is now well admitted that these motions are unlikely, because they suppose the rotation of the attached tails in the highly viscous medium. Nevertheless, if a second counterrotational motion occurs around (O_3O_4) (or (O_5O_6)) in the opposite direction, the parallelism between the chain $O_2O_3O_4O_5O_6$... before and after the transition is maintained. This defines a type 2 transition. The simulation of local transitions in polyethylene-like polymers[25] leads to the conclusion that type 2 transitions are more probable than others. After such motions, the translated chain is left in a constrained state, and the probability of transition of the neighboring bonds is strongly increased. This is why type 2 motions often occur in pairs. The fact that the two transitions occur in this ordered but sequential process is thought to explain why the activation energy observed is only about one barrier height, associated with one trans–gauche± conformational jump.[26] This double-stage process could concern 10 rings or more, if 5 rings are involved in a type 2 transition as in Figure 13. This is in agreement with the supposed number of phenylene units acting in the β process in BPA-PC. Moreover, the zero activation entropy of the β_1 relaxation could be related to the sequential feature of these elementary intrachain molecular motions. Nevertheless, the apparent activation energies for the β_1 process in BPA-PC, PES, PPS, and PEEK are significantly higher (say 40–45 kJ/mol) than the energy corresponding to the counterrotational motion of phenyl rings in the corresponding dimers.[20-24] This could be due to intermolecular noncooperative interactions and/or the requirement to pass over a larger barrier if adjacent rings are not in a favorable conformation. Other types of motions can also be considered such as the crankshaft[27] or, more generally, type 1 motions.[28] Figure 14 displays an elementary crankshaft with 5 rings. This motion can also be understood by combination of simultaneous counterrotational motions in O_4 and O_1. The tails located between O_1 and after O_4 stay unchanged, but the $O_1O_2O_3O_4$ segment rotates around an axis made by (O_0O_1) and (O_4O_5). The existence of such a common axis could be a restriction to these motions. Moreover, they are assumed to require the jumping over two barrier heights instead of one barrier for the type 2 motions.

β_2 Process in PEEK. Another description of the β molecular processes in phenylene polymers is based on the hypothesis that the amorphous medium is locally organized in microdomains of typical dimension 2–7 nm. Evidence for these organized regions has been established for a wide range of polymers (for a review, see ref 29). The concept of closely packed macromolecular chains has been invoked by Scheafer et al.[30] to explain ^{13}C NMR results in BPA-PC. In the "bundles", translation and rotations of the rings are believed to occur in a cooperative way due to interchain interactions. These motions should exhibit significant positive activation entropy, because they involve correlated motions of the chains within a bundle. Moreover, the angular geometry of the ether and ketone groups is even more favorable to chain alignment in PEEK than in BPA-PC, because of the banana-like structural unit shape of BPA-PC in the stable conformation.[16] As the β_2 process in PEEK exhibits a large positive activation entropy, it can be suggested that it may involve motions in these organized regions within the amorphous material. A similar conclusion has been reached by Sasuga et al., who attributed this component of the β relaxation in PEEK to motions of organized and/or oriented moieties. Such regions are believed to exist in the interphase between amorphous and crystalline phases, which can explain why the β relaxation of semicrystalline and drawn PEEK exhibits a pronounced β_2 component (Figures 9 and 11). It is also interesting to notice that the bundles seem to be sensitive to electron beam irradiation, which clearly causes disorder in the amorphous media.[4,5] After irradiation, the magnitude of the β_2 component decreases, while the shoulder related to the presence of a high defect concentration increases. Nevertheless, the bundles can coexist with a high defect concentration, as in the case of the rolled sample (Figure 10), because of the orientation induced by this mechanical treatment. The structural relaxation pattern is very well defined, but the sample is optically birefringent, and therefore local alignment of the chains results in a well-defined β_2 component. The microstructure of the drawn sample is obviously the most favorable to chain orientation, and the β_2 component is the most developed. Moreover, the bundle hypothesis is also in agreement with the results obtained for the annealed sample. The size of these organized microdomains is believed to increase with annealing time below the glass temperature,[31] and a slightly more prominent β_2 component is observed here.

Correlations with the Macroscopic Behavior of PEEK. Numerous studies have been undertaken to elucidate the interrelations between the molecular dynamics involving the β process and the macroscopic mechanical behavior well below the glass transition temperature. For example, in BPA-PC[32] or in poly(aryl ether sulfones),[33] after the addition of an "antiplasticizer" (polychlorinated bi- or terphenyls), the α relaxation is shifted toward lower temperatures, but at the same time, the β relaxation disappears. Even if the plasticizer restricts the long-range intermolecular interactions and therefore decreases the glass transition temperature, the local intramolecular local motions are apparently blocked, particularly the phenyl ring flips. The polymer then becomes brittle. Therefore, the existence of a pronounced β transition is related to a ductile behavior, and the molecular mechanisms responsible for the plastic deformation must involve the motions concerned in the β process. It is also natural to think that if these motions are highly activated a ductile behavior is expected. In PEEK at room temperature the frequency of the β_1 relaxation may be of the order of 10^5–10^7 Hz, because the energy of such motions is low (see the Eyring equation). This is in good agreement with the ductile behavior of this polymer at room temperature (i.e., $T = T_g - 120$ K) although the area of the β peak is not particularly high. It is also the case for BPA-PC, amorphous PPS, and PES. Other correlations have been established between the fracture toughness, G_{IC}, and (i) the magnitude of the β process and (ii) the frequency of the β transition.[34,35] G_{IC} is shown to be an increasing function of the area under the β peak and the frequency of the β transition. As a consequence, polymers with a β relaxation located at low temperature (i.e., T'_β near 170 K at 1 Hz) are more likely to exhibit a high toughness and a ductile behavior, as is the case for PEEK, BPA-PC, and PPS. This makes this type of material particularly suited for engineering applications, as it is the case for high-performance fiber-reinforced composites. It is also known that the features of the β process are of a first importance for the plastic behavior of polymers. Simulations have been recently carried out to reconstruct stress–strain curves well below the glass transition temperature when the β characteristics are involved[36] on the basis of the quasi-punctual defect model of Perez et al.

Conclusion

The structure of the β process in PEEK has been investigated thanks to an extensive study of isotherms according to Arrhenius and Starkweather treatments. Both approaches lead to the conclusion that the β peak results from the superimposition of two processes, called β_1 and β_2. The β_1 process is well described by the Eyring equation using a zero activation entropy and an activation energy near 43 kJ/mol. This component is surprisingly insensitive to microstructure. This shows that it should involve local intrachain motions. In relation to previous works in this field, the possible molecular motions that could lead to a sub-T_g relaxation are suggested, and a study of their correspondence with molecular mechanics calculations is in progress. The β_2 component exhibits a high positive apparent activation entropy, reflecting a cooperative feature. Since the amplitude of the β_2 process is correlated with local chain alignment and arrangement, this component is attributed to local motions in ordered regions in the amorphous phase of PEEK. The relation between the ultimate mechanical properties of PEEK and the β relaxation features is believed to lie in the location of the sub-T_g β_1 process in the temperature scale, leading to especially high frequencies of the corresponding degrees of freedom at ambient temperature.

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