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Molecular Mobility in Para-Substituted Polyaryls. 3. Low-Temperature Dynamics

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ABSTRACT: The low-temperature mechanical relaxations in poly(oxy-1,4-phenyleneoxy-1,4-phenylene-carbonyl-1,4-phenylene [poly(aryl ether ether ketone, PEEK], poly(thio-1,4-phenylene) [poly(phenylene sulfide), PPS], and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene), [poly(aryl ether sulfone), PES] are investigated. All three polymers exhibit a low-temperature γ relaxation, in the temperature range from 40 to 100 K at 1 Hz. The apparent activation energies for the γ relaxations (15−25 kJ/mol) are close to the values derived from empirical force field molecular mechanics calculations of the "crankshaft motion" in an isolated chain portion. Only polymers with a polar interaromatic bridge (PEEK and PES) exhibit another secondary β relaxation, in the temperature range from 100 to 250 K at 1 Hz. Moreover, the apparent activation energies of the β processes are significantly higher than the activation energies of the γ relaxations. Therefore, it is concluded that polar intermolecular interactions play an important role in the molecular events leading to the β relaxation, whereas the γ relaxation is due to conformational changes mostly controlled by an intramolecular energy.

Introduction

Considerable efforts have been made to identify the local molecular events that should be responsible for the secondary relaxations in *p*-phenylene polymers. The ability to accommodate for a stress with highly activated molecular local motions is probably related to the interesting ultimate mechanical properties of these polymers, such as Bisphenol A polycarbonate (BPA-PC) and poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK). This paper is a contribution for the identification of these local molecular motions. To reach this goal, we compare low-temperature relaxation properties exhibited by different polymers of the same family, but presenting different interaromatic bridges, namely PEEK, poly(thio-1,4-phenylene) (PPS), and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES). Experimental results obtained by mechanical spectroscopy will be compared with theoretical results yielded by molecular mechanics calculations.

PEEK exhibits two sub-*T*g relaxation processes. A low-temperature process (118 K at 7 Hz)[1] will be denoted here as γ. There also exists a higher temperature secondary relaxation (hereafter called β). The β relaxation appears to be complex[2] and results from at least two components.[3] The low-temperature component, β_1, is located at 180 K at 1 Hz and exhibits a low apparent activation entropy. The β_2 component (250 K, 1 Hz) shows a significant positive apparent activation entropy,[3] which reveals a complex or cooperative feature. The strength of the β_1 relaxation is significantly increased by the presence of water,[2,4,5] as is the case for paraphenylene polymers with a sulfone moiety.[6] Dielectric spectroscopy measurements also reveal the γ and β relaxations in PEEK,[5] in agreement with mechanical spectroscopy.

The mechanical relaxations in PPS are less documented. A mechanical relaxation exists near 170 K at 1 Hz and is attributed to "hindered torsion oscillation of the backbone phenylene units".[7]

The mechanical and dielectric secondary β relaxations of various sulfonated paraphenylene polymers, such as PES, have been extensively studied.[8−10] The β relaxation in PES is also complex with different components and presents many common aspects with the β_1 and β_2 relaxations in PEEK (namely, the cooperative feature of the β_2 process, increase of the β process with water content). The chemical structures of PPS, PEEK, and PES are shown in Figure 1.

Experimental Method and Calculations

The dynamic mechanical behavior of PPS, PEEK, and PES was investigated by means of low-frequency mechanical spectroscopy. Two homemade setups were used. A forced oscillation pendulum was used[11] in the temperature range down to 100 K. This apparatus gives the value of the complex shear modulus $G^* = G' + iG''$ as a function of temperature (T) and frequency (f), in the temperature−frequency window [100−500 K]−[10^{-4}−1 Hz]. tan(φ) corresponds to the ratio G''/G'. For lower temperature scans, a free decay oscillation pendulum was used[12,13] in the 1 Hz frequency range. Experiments at low temperature, down to 10 K, are possible with this apparatus (the square of the natural frequency, f^2, is proportional to G', and tan(φ) is defined by the ratio δ/π, where δ is the logarithmic decrement).

Elementary molecular mechanics calculations were performed on a simple 80486-based IBM-PC compatible computer. The software used is PC-MODEL.[14] It is based on an empirical force field derived from MM2(P).[15] The program calculates the conformation of minimum energy of a molecule, but also offers

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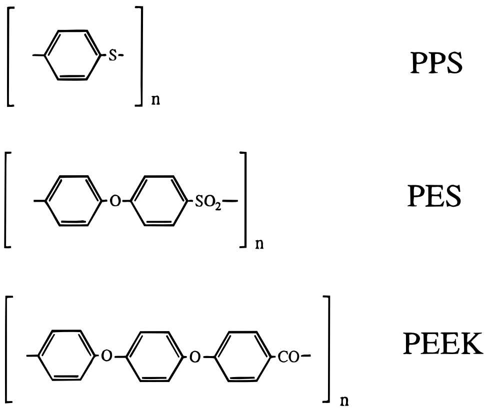


Figure 1. Chemical structures of PPS, PEEK and PES.

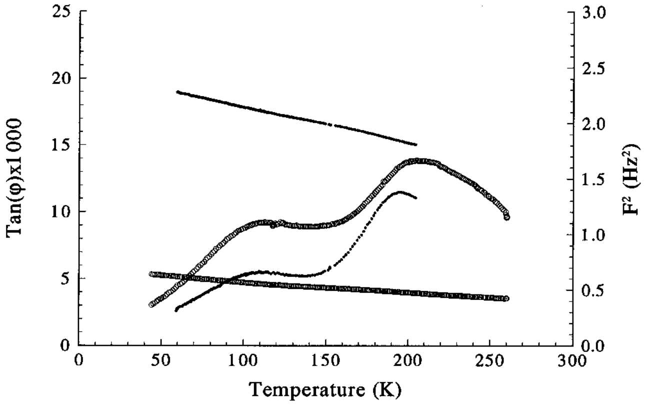


Figure 2. Low-temperature behavior of amorphous PEEK (○) and semicrystalline PEEK (●). The measurements were performed with a free oscillation apparatus. For the amorphous PEEK sample, the ratio f^2/G' is about 2 Hz^2/GPa and depends on the value of the disk inertia I as well as the geometrical characteristics of the sample. For the semicrystalline PEEK sample, f^2/G' is close to 1.22 Hz^2/GPa.

the possibility to define one or two fixed values of torsion angles within the molecule.

The samples used in this study were kindly provided by Solvay France (PPS, grade *T1*, $\bar{M}_w = 37\,000$, crystallinity ratio $X_c = 40\%$) and ICI United Kingdom (PEEK, grade 450G, ca. 10^5, $X_c = 34\%$). PES (amorphous polymer) was purchased from Goodfellow SARL.[16] It was possible to obtain PEEK and PPS in the amorphous state by heating the samples (films with thicknesses not exceeding 0.5 mm) above the melting temperature of the crystalline phase and quenching in water at 15 °C. The drying process consisted of keeping the samples under vacuum for about 15 h.

Results and Discussion

The low-temperature viscoelastic behavior of amorphous and semicrystalline PEEK and PPS in the dry state is shown in Figures 2 and 3, respectively. Figure 4 displays the viscoelastic behavior of dry PES. The apparent activation parameters for the observed relaxations are given in Table 1.

The following observations can be made.

(i) In the dry state, all three polymers exhibit a low-temperature γ relaxation close to 100 K (near 1 Hz).

(ii) PEEK and PES show a β relaxation, in the temperature range from 160 to 260 K (near 1 Hz). PPS exhibits no relaxation in this frequency–temperature domain.

(iii) Semicrystalline (dry) PEEK exhibits γ and β relaxations similar to amorphous PEEK, but the strengths of the γ and β processes are depressed.

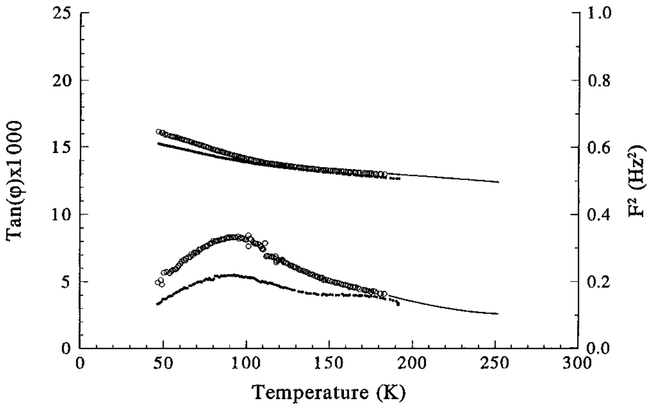


Figure 3. Low-temperature behavior of amorphous PPS (○) and semicrystalline PPS (●) in the dry state. The ratio f^2/G' is about 1.6 and 4.9 Hz^2/GPa, respectively (free oscillation apparatus). The solid line shows complementary data obtained for amorphous PPS in the forced oscillation regime (fixed frequency,1 Hz) at higher temperatures.

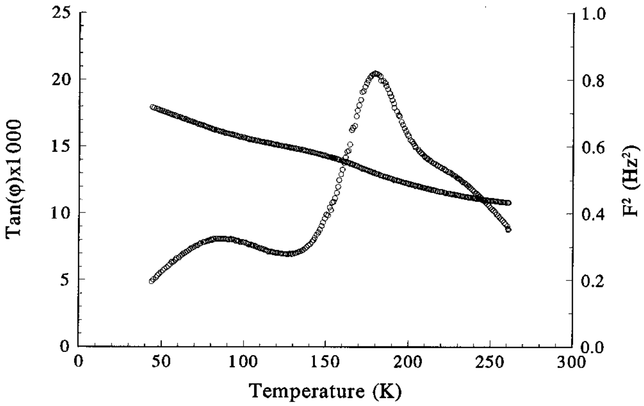


Figure 4. Low-temperature behavior of amorphous PES, obtained with a free oscillation apparatus. The ratio f^2/G' is close to 1.6 Hz^2/GPa.

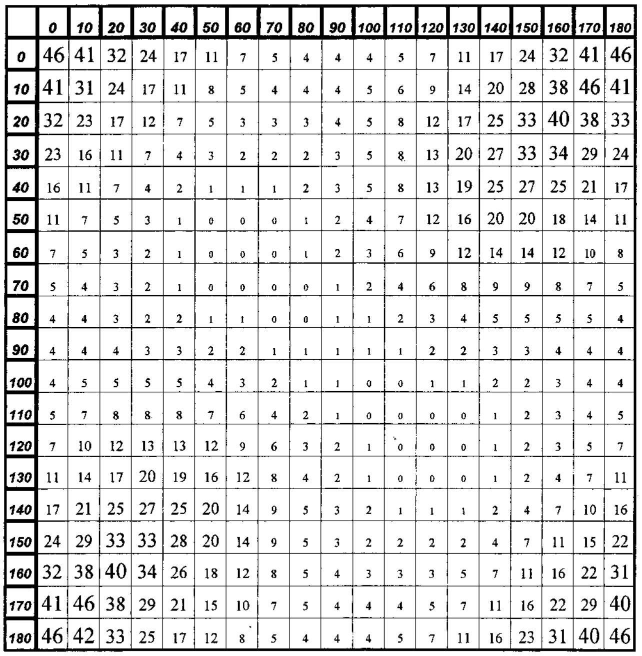
Table 1. Apparent Activation Parameters of the Arrhenius Law[a] $\tau = \tau_0 \exp(E_a/RT)$ for the γ, β_1, and β_2 Mechanical Relaxation Processes in PEEK, PPS, and PES

	γ process		β_1 process		β_2 process	
polymer	$\tau_0(\gamma)$ (s)	$E_a(\gamma)$ (kJ/mol)	$\tau_0(\beta_1)$ (s)	$E_a(\beta_1)$ (kJ/mol)	$\tau_0(\beta_2)$ (s)	$E_a(\beta_2)$ (kJ/mol)
PPS	$5{\cdot}10^{-12}$	20				
PES	$5{\cdot}10^{-12}$	18	$5{\cdot}10^{-15}$	50	$5{\cdot}10^{-22}$	100
PEEK	$5{\cdot}10^{-12}$	25	$5{\cdot}10^{-14}$	45	$5{\cdot}10^{-22}$	100

[a] For the γ processes, the frequency scanning is not available (free decay oscillation measurements) and the Starkweather approximation is used (neglect of the entropic term) *i.e.* $E_a(\gamma) = RT'(1 + \ln(kT'/2\pi hf))$. T' is the temperature where G'' is a maximum. For the β processes, the more usual approach (based on the shifts of frequency scans) is possible with the use of a forced oscillations spectrometer.[3,11]

(iv) Semicrystalline (dry) PPS exhibits a γ relaxation similar to amorphous PPS, but the strength of the γ is smaller.

The fact that the β relaxation process could not be found in PPS clearly indicates that it is to be associated with molecular events that are possible in PEEK and PES, but impossible in PPS, in spite of the strong similarities between the chemical structures of these three polymers. If this difference is due to intramolecular reasons, then the conformational energy map of diphenyl sulfide is expected to be significantly different from that of diphenyl ketone, diphenyl sulfone, and



	0	10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160	170	180
0	46	41	32	24	17	11	7	5	4	4	4	5	7	11	17	24	32	41	46
10	41	31	24	17	11	8	5	4	4	4	5	6	9	14	20	28	38	46	41
20	32	23	17	12	7	5	3	3	3	4	5	8	12	17	25	33	40	38	33
30	23	16	11	7	4	3	2	2	2	3	5	8	13	20	27	33	34	29	24
40	16	11	7	4	2	1	1	1	2	3	5	8	13	19	25	27	25	21	17
50	11	7	5	3	1	0	0	0	1	2	4	7	12	16	20	20	18	14	11
60	7	5	3	2	1	0	0	0	1	2	3	6	9	12	14	14	12	10	8
70	5	4	3	2	1	0	0	0	0	1	2	4	6	8	9	9	8	7	5
80	4	4	3	2	2	1	1	0	0	1	1	2	3	4	5	5	5	5	4
90	4	4	4	3	3	2	2	1	1	1	1	1	2	2	3	3	4	4	4
100	4	5	5	5	5	4	3	2	1	1	0	0	1	1	2	2	3	4	4
110	5	7	8	8	8	7	6	4	2	1	0	0	0	0	1	2	3	4	5
120	7	10	12	13	13	12	9	6	3	2	1	0	0	0	1	2	3	5	7
130	11	14	17	20	19	16	12	8	4	2	1	0	0	0	1	2	4	7	11
140	17	21	25	27	25	20	14	9	5	3	2	1	1	1	2	4	7	10	16
150	24	29	33	33	28	20	14	9	5	3	2	2	2	2	4	7	11	15	22
160	32	38	40	34	26	18	12	8	5	4	3	3	3	5	7	11	16	22	31
170	41	46	38	29	21	15	10	7	5	4	4	4	5	7	11	16	22	29	40
180	46	42	33	25	17	12	8	5	4	4	4	5	7	11	16	23	31	40	46

Figure 5. Molecular mechanics energy map (in kJ/mol) of diphenyl sulfide, as a function of the torsion angles (ω_1 and ω_2) of phenylene units. $\omega_1 = \omega_2 = 0°$ for a planar molecule.

diphenyl ether, in order to induce a difference in the local degrees of freedom of macromolecular chains.

It is also possible to consider that the differences in the dynamic behavior of PEEK, PES, and PPS are due to intermolecular reasons. Actually, another feature of PPS is the absence of strongly polar moieties in the polymeric chain, while PEEK and PES contain a polar ketone and sulfone moiety, respectively. PEEK and PES are not isolated examples, and polar para-substituted polyaryls often exhibit a β process, like in poly(sulfonyl-1,4-phenylenethio-1,4-phenylene)[17] with the presence of the sulfone group and in BPA-PC with the carbonate moiety. Accordingly, the β process could be due to motions, implying (polar) intermolecular interactions.

These two hypotheses will be tested in the remainder of the paper, in order to explain the absence of a β process in PPS (particularity of PPS related to intramolecular rearrangements energies *or* particularity in the intermolecular interactions).

Moreover, observations iii and iv lead to the following conclusions.

(i′) The γ and β relaxations both occur in the amorphous phase.

(ii′) No relaxation specifically occurs in the crystalline phase.

Molecular Mechanics Calculations and Origin of the γ Process. The conformational energies of diphenyl ether, diphenyl ketone, diphenyl sulfone, and diphenyl sulfide were calculated by means of molecular mechanics. As an example, the conformational energy map of diphenyl sulfide is given in Figure 5. This Figure displays the minimum static conformational energy (in kJ/mol) as a function of the torsion angles of the phenylene units, using the conformational notation of Klyne and Prelog.[18,19] Thus, $\omega_1 = \omega_2 = 0°$ for a planar molecule. The results obtained are in good qualitative agreement with other calculations,[8,20−29] and experimental results available in the literature.[30−38] All molecular mechanics energy maps exhibit a maximum energy at $\omega_1 = \omega_2 = 0°$, and the location of the minimum slightly depends on the interaromatic linkage. The minimum energy of diphenyl ketone is close to $\omega_1 = \omega_2 = 40°$, and that of diphenyl ether is near 55°, and the minimum conformation of diphenyl sulfide is located at about 60°. The torsion angles for the minimum energy conformation of diphenyl sulfone are located between 60° and 85°. In each case, there are large valleys of low energy. East/south to north/west motions, of two adjacent phenyl rings correspond to "gearwheels" (i.e. "disrotatory"[20] or "in phase"[39]). Starting from the minimum energy conformation, no high intramolecular energetic barrier has to be overcome in this direction. East/north to west/south motions require a degree of gearwheel motions, otherwise a significant energy is necessary. At the top of the (0,0) hill, the bond angle of the interaromatic linkage, Θ_{max}, is different from the bond angles of the minimum energy conformation Θ_{min}. Thus the ratio $(\Theta_{max} - \Theta_{min})/\Theta_{min}$ is close to 7% for diphenyl ketone, 10% for diphenyl ether, and 15% for diphenyl sulfone and diphenyl sulfide.

An important point is that the direct comparison of these similar intramolecular energy maps does not explain the difference of the local degrees of freedom in PPS with respect to PEEK and PES as revealed by mechanical spectroscopy. There seems to be consistency between the conformational energy of the planar molecules and the activation energy of the β process in PEEK and PES, but the fact that there is no β process in PPS shows that there are no direct relations. To go a step further, it was also possible to evaluate the minimum energy required for a crankshaft type of motion, involving five aromatic rings. We concluded that the local minimum energy of the crankshaft is met when all diphenyl units are in the minimum conformation energy (Figure 6) and that the intramolecular energy associated with the rotation of a symmetrical and minimized crankshaft oligomer is between 5 and 10 kJ/mol. The experimental values of the corresponding relaxations are expected to be higher than these calculated estimates for at least two reasons: (i) the motion itself of the crankshaft can be different from the minimum energy path, and (ii) the steric hindrance of the surrounding medium (intermolecular interactions) is not taken into account in the present calculation.

During these calculations, the extreme torsion angles ω and ω' were maintained at opposite values ($\omega = -\omega'$) and increased by step increments. Moreover, the distance between the extreme interaromatic linkages could be fixed to the value of the minimum energy geometry, but this induced little effect on the calculated energies. The internal rotations of aromatic rings in a PPO crankshaft are displayed in Figure 7. The crankshaft rotation is made easy thanks to out-of-phase (90°, 90°) or in-phase transitions (0°, 90°) performed by adjacent rings, in order to maintain the internal aromatic rings close to the minimum energy conformation. These transitions thus introduce small oscillations of aromatic rings which are superimposed with the global rotation of the chain portion, in agreement with NMR studies.[40,41] We noticed similar transitions in PPS, PEEK, and to a lesser extent PES.

The activation energy involved in the β_1 mechanical process in PEEK and PES is close to 45 and 50 kJ/mol, respectively, as deduced from mechanical spectroscopy (Table 1). These values are significantly higher than the calculated estimates obtained by molecular mechanics. Moreover, the PPS crankshaft is able to rotate like the PPO, PEEK, and PES oligomers. This again implies

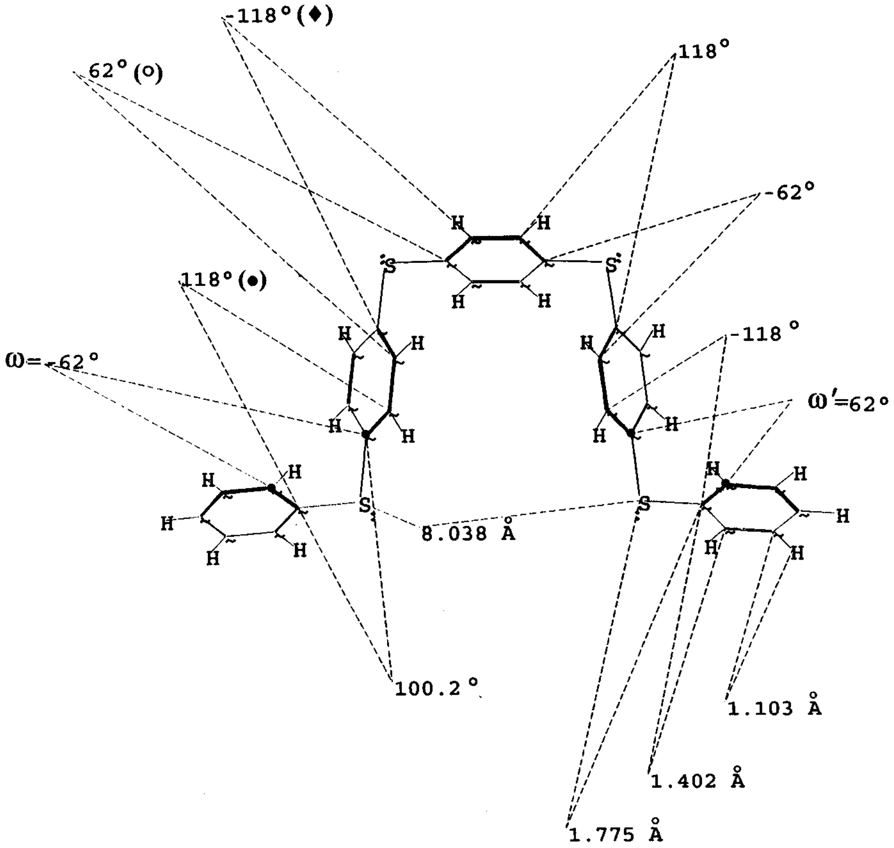


Figure 6. Minimum conformation energy geometry of a oligomer with five aromatic rings, PPS, revealing the minimum energy conformation of diphenyl sulfide at (Φ_1, Φ_2) = (62°, 62°) and equivalent geometries (Figure 5). The right and left side of this chain portion are symmetrical (enantiomeric). For the calculated rotation energies of these crankshafts, the extreme torsion angles ω and ω' are fixed, so that $\omega = -\omega'$, and increased simultaneously by 10° increments.

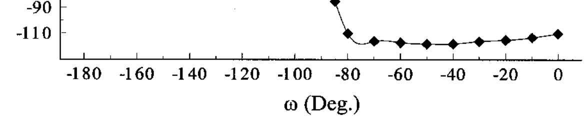


Figure 7. Evolutions of internal torsion angles in the left side of a PPO chain portion analogue of Figure 6, during a crankshaft rotation. ω is the extreme torsion angle and displays the rotation of the crankshaft from −180° to 0°. The rotation of the second ring is indicated by two complementary torsion angles (●) and (○). The central ring also rotates, according to the curve shown (◆). These limited rotations (●; ○; ◆) are associated to changes between the stable conformations of corresponding molecules with two phenylene rings. The right side of the crankshaft is symmetrical, and opposite values are found for internal torsion angles.

that the β relaxation in PES and PEEK cannot be attributed to an isolated crankshaft rotation.

As there is no definitively assessed relation between the β process and calculated rotations, it is natural to pay attention whether the agreement is better for the γ process, which is found for each investigated polymer. In order to access the apparent activation energy from our free decay viscoelastic measurements, the Starkweather treatment[42] is used to calculate the activation energy distributions, φ_G, according to

$$E_a = RT\left[ln\left(\frac{kT}{2\pi hf}\right) + 1\right] + T\Delta S^*$$

$$\varphi_G = \frac{2G''}{\pi(G'_u - G'_r)}$$

where ΔS^* is the (positive) activation entropy, T the absolute temperature, f the torsion frequency, h Planck's constant, and k Boltzmann's constant. Neglecting of the entropic term leads to good estimations for the E_a distributions displayed in Figure 8. The γ processes are widely distributed, which reveals that a variety of motions/events are involved. Nevertheless, the most probable energies of these distributions ($E_a(\gamma)$) which are listed in Table 1 are consistent with (i.e. lower than) the low-temperature tail of the activation energy distributions found for the β_1 processes in PEEK[3] and in PES. These energies are also in better agreement with calculated estimations for the rotation of crankshafts than the β processes. Moreover, we also notice a better agreement with the experimental values revealed by NMR in dilute solutions of PPS[43,44] ($E_a(\gamma$,PPS) is close to 14 kJ/mol) and in BPA-PC[45,46] (13 kJ/mol). This leads us to assign the γ relaxation modes to very local rearrangements of a few rings, such as crankshaft-like motions, with possibly a small influence of neighboring chain portions.

Effect of Water. The presence of small amounts of water in PPS, PEEK, and PES induces changes in the relaxational features, as displayed in Figure 9. The

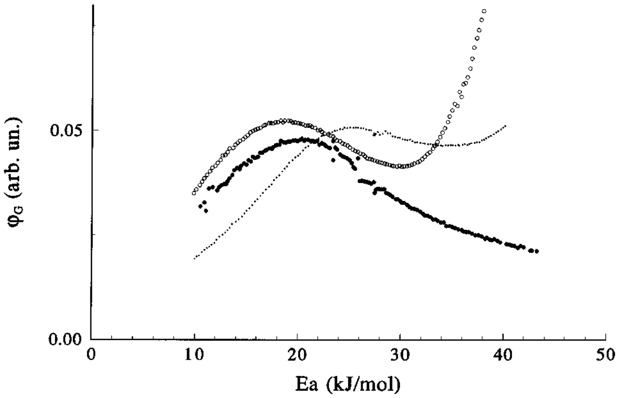


Figure 8. Calculated distributions of activation energies in the γ relaxation domain, for PPS (●), PEEK(·) and PES (○) from free oscillation decay measurements. The activation energy values are approximated by $E_a = RT(1 + \ln(kT/2\pi hf))$ and the spectrum of the distribution φ_G is assumed to be proportional to G''.

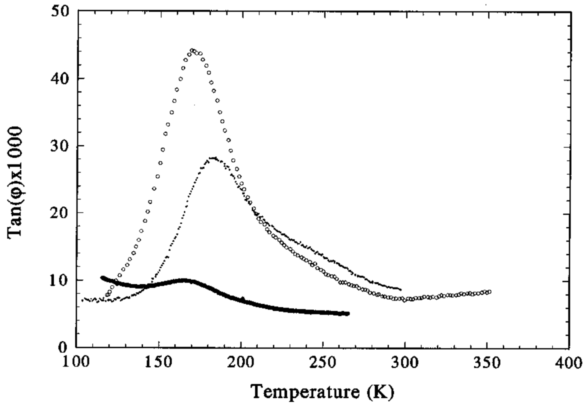


Figure 9. Relaxation spectra of amorphous PPS (●), PEEK (·) and PES (○) (fixed torsion frequency, 1 Hz) with water content in equilibrium with ambient atmosphere. The low-temperature component β_1 of the relaxation process is increased in PES and PEEK. A relaxation process appears in PPS, presenting similarities with the β_1 component of PEEK and PES.

effect of water depends on chain polarity. In the case of chains with polar interaryl bridges, the low-temperature component of the β process is much increased. This feature is well-known for PES.[6] It is smaller for PEEK[2] but also apparent. For PPS, the presence of water induces a specific and reversible relaxation phenomenon located at 1 Hz near 175K. Moreover, the apparent activation energy of this process is close to 40 kJ/mol, with a pre-exponential time close to the Debye time. Thus, the introduction of polar water molecules leads to a relaxation phenomenon presenting common aspects with the low-temperature component of the β relaxation found in polar para-substituted polyaryls. The origin of this relaxation or component associated with the presence of water is usually ascribed to the motions of water molecules themselves, but water molecules can also be considered as polar sites which increase the interactions of a chain with the surrounding medium. Consequently, the similarities between this water-induced mechanical relaxation process and the low-temperature component of the β relaxation can be another indication that polar interactions of chains with their surrounding medium are necessary in the β process. Finally, it is to be noted that there is a similarity between the viscoelastic behavior of PPS and PM_2PO (i.e., poly(oxy-2,6-dimethyl-1,4-phenylene)) in good agreement with the low value of the dipolar moments of both diphenyl ether (1.15 D) and diphenyl sulfide (1.5 D). No secondary mechanical relaxation can be observed in dry PM_2PO above −200 °C (at 11.0 Hz)[47], whereas water can induce a relaxation process with the features of the β_1 relaxations.[48]

Origin of the β Processes. The motions resulting in the β_1 process cannot be directly attributed to individual motions of chain portions like crankshaft rotations. Nevertheless, there are different ways to interpret the higher activation energies for this relaxation by introducing the interactions of surrounding chain segments.

First, the surrounding medium can induce polar interaction sites, with a consequence being that the chain portion is likely to change conformation in a deeper potential well. Thus, the value of the activation energy can be separated into an intramolecular and an intermolecular term:

$$E_a(\beta_1) = E_a(\text{intra},\beta_1) + E_a(\text{inter},\beta_1)$$

A reasonable value for $E_a(\text{inter},\beta_1)$ should fit with dipolar interaction energies and lie between 10 and 20 kJ/mol.[49] The resulting intramolecular component $E_a(\text{intra};\beta_1)$ is not far from the values obtained for the γ processes. Thus, it can be argued that from an intramolecular view, the β_1 motions are similar to the γ rearrangements, but they could involve relaxing species in a stronger interaction state, induced by the attractive or repulsive forces between polar interaromatic moieties.

Another analysis for the interpretation of the relatively high apparent activation energies for the β process consists of the modeling of cooperative effects between structural units, as in the coupling model, introduced by Ngai. Accordingly, the effective relaxation time is given by

$$\tau_\beta = [(1 - n)\,\omega_c^{\,n}\tau_o]^{1/(1-n)}$$

where τ_o is the relaxation time when the mutual interactions between the relaxing units have no effect yet, i.e. at short times when $t < 1/\omega_c$. The exponent $n \in [0,1]$ is a correlation or coupling parameter. Thus, relaxation β begins with an elementary rearrangement, but the whole process is slowed down as coupling effects develop. From the above relation, a scaling relation follows:

$$E_a(\beta_1) = \frac{E_o}{1 - n}$$

This model has been applied to the β relaxation in BPA-PC.[50] The value found for the correlation parameter is $n = 0.66$, and the primitive relaxation rate is also given with an activation energy close to 13 kJ/mol, which is close to the values obtained by molecular mechanics calculations and NMR spectroscopy. If this analysis is applied to the β_1 relaxations in PEEK and PES, the expected values for n associated with the β_1 relaxation times are expected to be close to the correlation parameter determined in BPA-PC. The value of E_o that can be deduced from the scaling energy law is again in agreement with the experimental values found for $E(\gamma)$ and calculated for the crankshaft motions. Moreover, the values given in ref 5 for the β process in PEEK are $E_a(\beta_1) = 50$ kJ/mol and $n = 0.73$ [this value of n can be derived from the Havriliak−Negami shape parameters (~0.5/0.5) used to fit the the β_1 relaxation process,[5] and the conversion to n is performed with published Tables[51]]. The resulting value of E_o is 13.5 kJ/mol, in good agreement with molecular mechanics calculations and the corresponding value for BPA-PC.

Thus, the primary process for the β_1 relaxation could be similar to the γ process (which can also be found in BPA-PC[1]). This shows that the γ process can be related to the first β event but is followed or accompanied by slower and cooperative rearrangements due to the repulsions and attractions of polar moieties of the relaxing species and in the surrounding medium. The effect of interaromatic polarity is thus to develop cooperative rearrangements following the primary motion.

The effect of intrachain polarity is also to induce a β_2 component, bearing relations to the principal glass transition relaxation, as the activation parameters found after an Arrhenius analysis have no physical value, because of cooperative effects. For example, the activation energy exceeds 100 kJ/mol and the preexponential time is lower than 10^{-20} s in PEEK.[3] Thus, it is not possible to separate $E_a(\beta_2)$ into an intramolecular [close to $E_a(\gamma)$] and an intermolecular term, as can be done for the β_1 component. Nevertheless, in the frame of the coupling scheme, it is still possible to suggest that γ could be a primitive process for the cooperative β_2 relaxation, if high values for n (close to 0.8) are chosen, reflecting high coupling effects. This is in agreement with the assignment of the β_2 component to motions in more ordered regions in PES[6] and PEEK.[2,3]

Conclusion

There are several types of sub-T_g molecular motions in all-para-substituted polyaryls, such as PEEK, PPS, PES, BPA-PC. Conventional apparatus provide an easy characterization of the β mechanical relaxations. There also exists a low-temperature process (γ) which compares better with molecular mechanics calculations of ideal crankshaft rotations together with high-frequency spectroscopies, such as NMR. The comparison of the molecular mobilities of different paraphenylene polymers with small interaromatic linkages leads to the conclusion that polar intermolecular interactions are necessary for the β relaxations. Consequently, no direct relation between calculated reorganizations of isolated chain portions and the β processes should be expected.

It is worthwhile to notice that the introduction of non-para-substituents in the chain can induce changes in the low-temperature dynamics of *p*-phenylene polymers. Steric interactions probably contribute to shift the low-temperature processes toward higher temperatures.[41,52,53] Moreover, it is also known that the interaromatic bridge itself is likely to yield steric hindrances if it is large enough. In this last case, the calculated energy values (*via* MM or other force field calculations) from single chain portions and activation energies extracted from experiments are expected to stay in reasonable agreement.

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References and Notes

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