ELSEVIER

Polymer 40 (1999) 2605–2617

polymer

Semi-empirical calculations and dielectric spectrometry of molecular units in PEEK

Sabine Verot, Pierre Battesti, Gérard Perrier*

Laboratoire des Matériaux Composites, ESIGEC, Université de Savoie, 73376 Le Bourget du Lac, France

Received 20 March 1998; revised 29 June 1998; accepted 29 June 1998

Abstract

Semi-empirical molecular orbital calculations and dielectric measurements have been conducted on DPE and DPK molecules and on PEEK films containing these molecular units. The calculations were performed using a modified-CNDO/2 method allowing us to take into account the van der Waals impenetrability zone of the electronic corona of the aromatic rings. From the analysis of the relative energy maps, it is shown, amongst other things, that the most probable route for a molecule to move is through gear rotations. The DPE molecule is also found to move more easily than the DPK molecule. Measurements of the dielectric permittivity and of the refractive index were not possible for the DPE molecule in benzene solution due to its low dipole moment, this being confirmed by theoretical calculations. For the DPK molecule, an experimental mean value of 3.15 D is found for μ compared to a calculated value of 3.35 D. The analysis of the dissipation factor isochronal curves shows that the activation energy for the DPK molecule is largely dependent on its concentration in benzene. In the case of PEEK, two relaxations are seen at -106°C and -73°C for a frequency of 1 kHz. A parallel is drawn between isolated molecules of DPK in solution and DPK units that are distant from each other in a polymer chain, and between aggregated molecules of DPK in solution and DPK units that are close together in entangled chains. It is finally shown that the DPK molecular unit in a macromolecular chain is only able to reach the permitted conformations in low energy valleys, corresponding to gear rotation motions.

Keywords: Semi-empirical calculations; Dielectric spectrometry; Molecular motions

1. Introduction

Polymers based on oxy–1,4–phenylene and carbonyl–1,4–phenylene repeating units (poly aryl (ether)′ (ketone)′) are now found to be widely used as thermoplastic matrices for advanced composites [1]. One of the most well known polymer of the series is the semi-crystalline poly (ether–ether–ketone) (PEEK) which is characterized by a good impact behavior and a high solvent resistance conjugated with high values for the glass transition temperature (144°C) and for the melting point (335°C) [2,3]. A lot of work dealing with the subglass relaxations of PEEK and with the conformations of its repeating units has been done in the past few years.

A low-temperature γ-relaxation has been revealed in PEEK by mechanical [4] (-155°C at 7 Hz) and dielectric [5] (-130°C at 400 Hz) spectrometry analyses. Highly-localized wagging of polar bridges has been associated with this relaxation [5], and it was thought that the γ-motions progressively transform into β-motions at higher temperatures.

A β-relaxation is also observed through mechanical and dielectric spectrometry in PEEK; this relaxation is spread over the -100 to $+100$°C range. In particular, it has been shown that the maximum of the dissipation factor tan δ occurred at higher frequencies and lower temperatures for dielectric measurements. In this case, the value of the activation energy was nearly twice as small as in the case of mechanical analysis [6]. The conclusion of the work was that the dielectric relaxation represents a high-frequency, low-temperature component of a broader distribution of motions as observed by mechanical studies. Thus, the dielectric relaxation is thought by the authors to reflect the highly-localized non-cooperative motions of small chain fragments, while the mechanical relaxation encompasses a wider range of segmental motions of a more cooperative nature.

Recent reports [3,7,8] show that the β-relaxation in PEEK could result from the superposition of two processes. The β_1 process could involve local intrachain motions (simple motions of the phenyl rings around the 1,4 axis) whereas the β_2 process seems to be correlated with local chain alignments and arrangements. The β_2 process could be attributed to local motions in ordered regions in the amorphous phase

* Corresponding author. Tel.: +33-479-75-8618; Fax: +33-479-75-8665; E-mail: perrier@univ-savoie.fr

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00517-5

of PEEK, although simple motions having different activation energies are not excluded [8].

Semi-empirical (MNDO) [9,10] and ab initio [11–14] optimizations have been conducted on molecular conformations of diphenyl ether (DPE) and diphenyl ketone (DPK). Semi-empirical molecular-orbital calculations by CNDO (Complete Neglect of Differential Overlap) of molecular units of PEEK [15] (DPE,DPK and the repeating unit EEK) showed that the activation energies associated with isolated crankshaft motions are consistent with the dielectric results of Starkweather and Avakian [6] where the activation energy was ca. 10 kcal.mol^{-1} in PEEK. It was also demonstrated [15] that the ether–ether phenylene ring has a high probability to lie in the PEEK backbone plane, contrary to the ether–ketone phenylene ring which is more likely to be perpendicular to it.

Molecular dynamics simulation (modified TRIPOS 5.2 force field) allowed the analysis of cooperative rotations of phenylene rings and of larger segments of the PEEK chain [16]. In particular, these recent results showed that the ether–ether rings are more mobile than the ether–ketone rings. A conformational flexibility study of the linkages occurring in poly(ether isopropylidene sulfone) (PEIS) and poly(ether isopropylidene ketone) (PEIK) in vacuo was also performed by way of another molecular simulation program [17] (POLYGRAF, Dreiding-II force field). Energy barriers to rotation in these polymers were found to be 4 kcal.mol^{-1} for both ether and ketone linkages.

A conformational analysis of DPE and DPK by means of CNDO/2 has been recently published by some of us [18]. The computations were first run disregarding electronic interactions and steric effects, then introducing them in the calculations using a modified CNDO/2. The absolute minimum energy conformers were shown to have torsional angles (θ_1, θ_2) = (30°, 150°) for DPE and (θ_1, θ_2) = (70°, 110°) for DPK, the mobility of DPE being greater than that of DPK. Considering the polymer chains of some poly (ether)′ (ketone)′, the DPE molecular units were then expected to be more mobile than the DPK ones in regions of local motions and for equivalent steric effects.

We report here our dielectric results on DPE and DPK molecules in benzene solutions and on PEEK polymer films. The experimental activation energies are compared with those given by relative potential energy maps constructed by the use of the modified-CNDO/2 method. The process is validated by a comparative study between calculated and experimental values of the dipole moment of the molecular units.

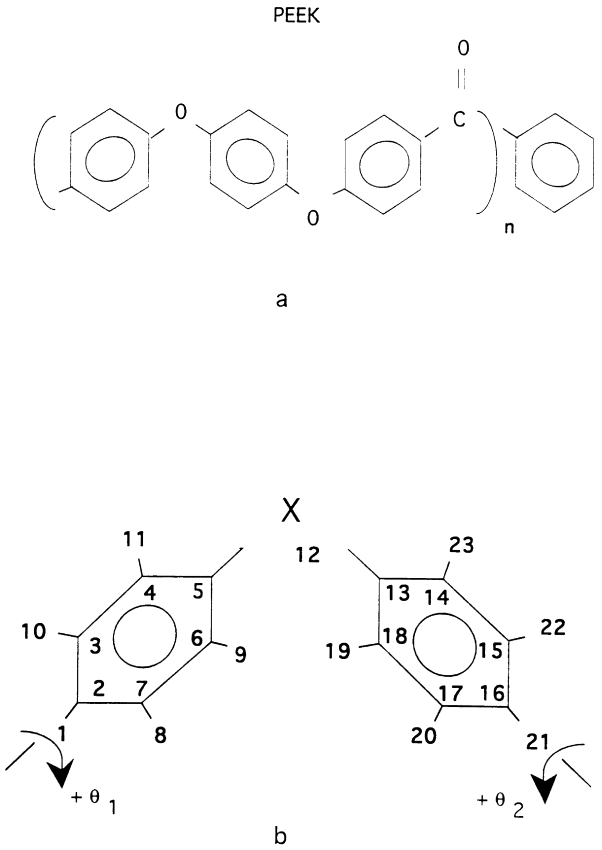

Fig. 1. (a) Molecular formula of PEEK; (b) Agreements for the rotation of the aromatic rings, X being O for DPE and C = O for DPK.

2. Experimental

2.1. Calculations

The calculations were carried out on a VT 420 terminal connected to a VAX 6000-410 computer.

2.2. Materials

Diphenyl ether (DPE) and diphenyl ketone (DPK) were used in solutions of 0.5–12%wt in benzene. The PEEK has

Table 1
Values of the valence angle as determined by physical analysis or used in calculations, for DPE and DPK

Molecule	Valence angle (°)	Method	Reference
DPE	124	X-ray diffraction	[20]
	123	Hückel	[21]
	123	CNDO/2	[22]
	124	Hückel	[23]
	123	C-INDO	[24]
	116	STO-3G	[11]
	124	MNDO	[10]
	117	AM1	[13]
	123	3-21G	[13]
	126	CNDO/2	[15]
	121–122	X-ray diffraction	[25]
DPK	122	X-ray diffraction	[26]
	120	CNDO/2, Hückel	[27]
	120	Rayleigh diffusion	[28]
	119	C-INDO	[24]
	117	MNDO	[10]
	122	MM	[29]
	126	CNDO/2	[15]
	121–122	X-ray diffraction	[25]

been synthesized according to the Kricheldorf method [31], followed by a 80°C–20 min-drying period. The resulting powder was then hot-pressed under vacuum at 400°C and water-quenched to give amorphous films.

2.3. Dielectric measurements

Dielectric determinations of the real part ϵ' and of the imaginary part ϵ'' of the permittivity, and of the dissipation factor tan δ (tan $\delta = \epsilon''/\epsilon'$) were performed on a Dielectric Thermal Analyser (DETA) from Rheometric Scientific, England, allowing measurements over the temperature range -150°C to $+500$°C and over the frequency range 20 Hz to 1 MHz. Isochronal runs with fixed frequencies and ramping temperatures (2°C.min^{-1}) were carried out on the polymer films, and on DPE and DPK solutions using a liquid measurement cell. The solid polymer films (1 mm-thickness) were dried at 140°C for 6 h and heated slightly above their glass transition temperature (150°C) for 10 min prior to measurement in order to cancel the influence of water and to get rid of the thermal history of the material. They were finally gold-evaporated to ensure a good electrical contact with the electrodes. All materials were handled under vacuum and the dielectric measurements were done under a nitrogen flow. The measurement of the refractive indexes of the solutions was conducted on a Sopelem refractometer at room temperature.

3. Calculations

3.1. Method of calculation

Diphenyl ether (DPE) and diphenyl ketone (DPK) were used as model compounds, being the molecular constituents of polymers such as PEEK. The molecular formula of PEEK is given in Fig. 1, together with a schematic view of DPE and DPK showing the rotational angles of the phenyl rings. Each phenyl can rotate to angles θ_1 and θ_2, defined with respect to the C_5XC_{13} plane.

Optimizations using Hartree–Fock theory and the STO-3G basis set on bond angles and bond lengths were first made on the model compounds. The main results obtained are d(C–X) = 1.40 Å for X = O and 1.42 Å for X = CO, and CXC = 117° for both molecules [18]. Concerning the CXC angle, Table 1 lists some values of the angles found in the literature for C(O)C in DPE and for C(CO)C in DPK, together with the analysis or calculation method used [19]. The values are spread over a wide range, being 116°–126° for X = O and 117°–126° for X = CO. It can also be noted that a value of 113° for C(O)C in PPO chains was calculated from TRIPOS 5.2 by Chen et al. [30], and that values of 112.2° for C(O)C and 124.6° for C(CO)C in a PEIK chain were presented from POLYGRAF by Hamerton et al. [17]. Our calculated value, 117° for both DPE and DPK, lies in the lower part of the literature variations. The fact that sub-glass motions are seen to occur at low temperatures induces us to think that the molecule can show a rather low angle between the two phenyls.

Rotational motions of the phenylene rings of the molecular units DPE and DPK in PEEK have been investigated by means of semi-empirical calculations using the CNDO/2 version. CNDO/2 is a semi-empirical method based on quantum mechanics, which can be used to treat molecules that are too large to be handled in ab initio methods. The CNDO/2 program was modified [18] in order to simulate the van der Waals impenetrability zone of the electronic corona of the aromatic ring, which has a thickness of about 3.60 Å. As a matter of fact, steric and electrostatic constraints can exist either between one corona and the aromatic hydrogen atom which is located in front of it, or between two coronas. For this purpose, the H_{19} hydrogen atom position was modified to simulate the half-thickness of the electronic corona, the distance C_{13}–H_{19} being forced to be 1.80 Å in this configuration (Fig. 2). This modification allowed us to take into account the fact that steric and electronic hindrances can exist between the electronic corona and the facing hydrogen atom of the adjacent phenyl (typical position (θ_1, θ_2) = (0°, 90°)), and between the coronas of two adjacent phenyls (typical position (θ_1, θ_2) = (90°, 90°)).

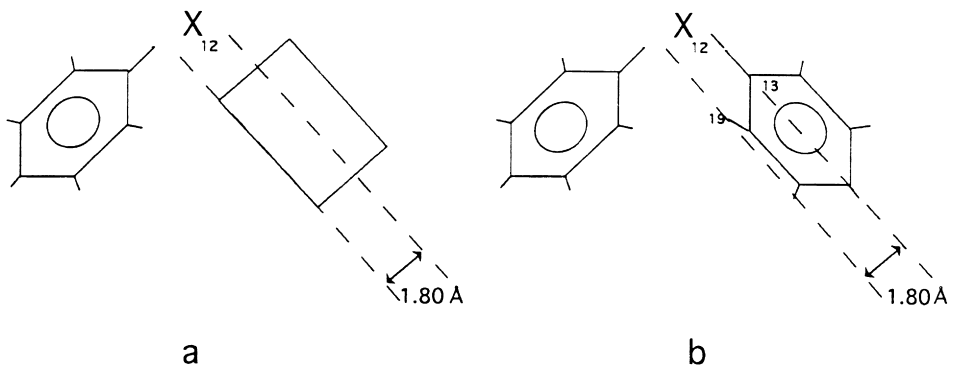

Fig. 2. Schematic representations of the molecular units; (a) The two phenyl rings are orthogonal, showing the half-thickness of the aromatic electronic corona; (b) To take into account this electronic corona, the right phenyl ring is forced to lie in the same plane as the left one, and the position of the H_{19} hydrogen atom is modified.

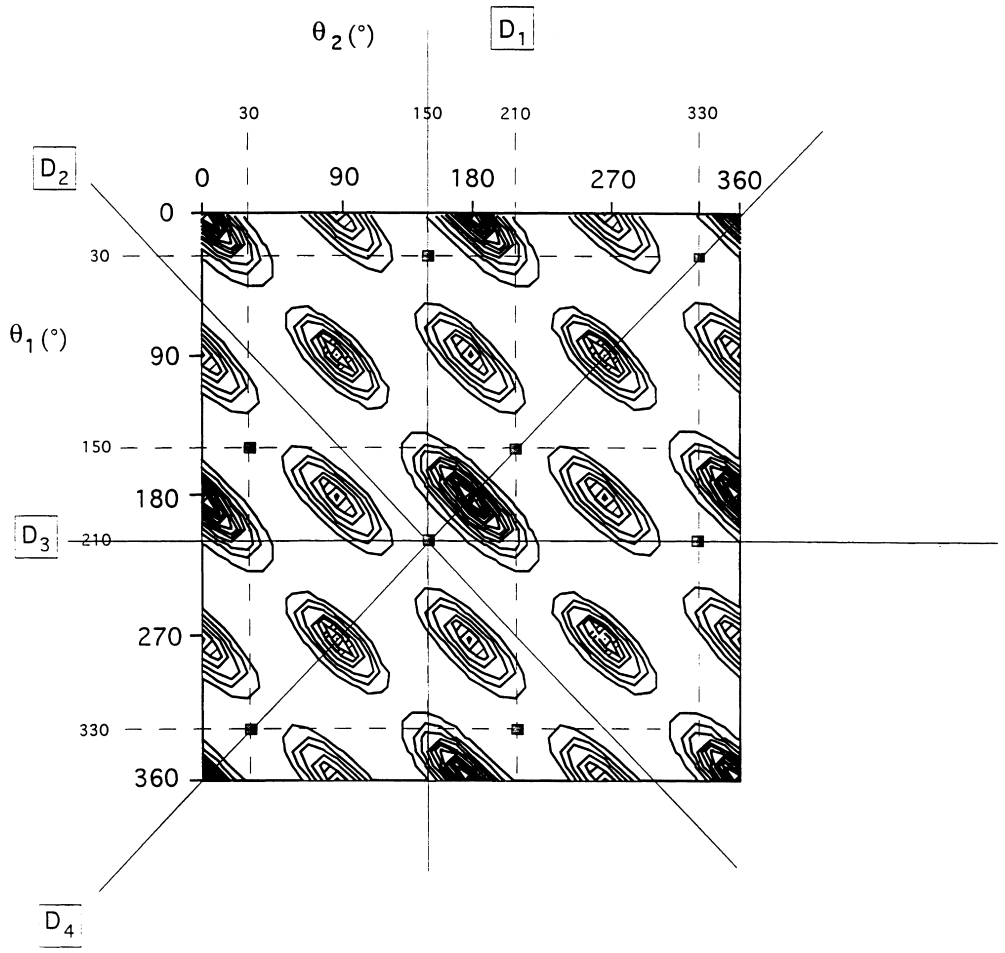

Fig. 3. Energy map and main motion routes for DPE.

3.2. Energy maps

A great number of calculations have been made to assign an absolute energy value for each conformation considering all the possible rotations. The rotational angles θ_1 and θ_2 have been varied in the range 0° to 360° by steps of 10°.

In the case of DPE, the minimum absolute energy is obtained for the conformation defined by the rotational angles $(\theta_1, \theta_2) = (30°, 150°)$ and their symmetrical equivalents. Chen et al. [15] found the minimum energy conformation for DPE to be $(\theta_1, \theta_2) = (30°, 30°)$. This combination is found to be identical to ours, once the agreements for the rotation of the phenyl rings and for the directions of the axes have been considered.

In the case of DPK, the minimum absolute energy is obtained for the conformation defined by the rotational angles $(\theta_1, \theta_2) = (70°, 110°)$ and its symmetrical equivalents. This position can be compared with the (90°, 90°) position found by Chen et al. [15]. The consideration of electronic corona effects by the modified-CNDO/2 is here held responsible for this substantial difference. Moreover, the amplitudes of the motions in DPE and DPK are significantly reduced by the use of the modified-CNDO/2 as compared to the regular CNDO/2 [18].

These results are significantly different from the ones reported by Hamerton et al. [17], which are (90°, 90°) for the ether linkage and (30°, 30°) for the ketone linkage. These linkages were however studied as part of the monomer of the considered polymer (PEIS or PEIK), where the presence of the methyl moieties has a strong constraining effect on the ability of the phenyls to rotate, the motions being limited in very small zones.

For these minimum absolute energies, conformation maps can be drawn showing the values of the relative energy for each conformer. Figs 3 and 4 illustrate the conformations of DPE and DPK, respectively, where each iso-energetic line corresponds to 30 kcal.mol^{-1}. The maximum relative energies are in our case as high as 419 kcal.mol^{-1} for DPE and 368 kcal.mol^{-1} for DPK. Chen et al. [16,30] reported maximum relative energies far above 100 kcal.mol^{-1} for DPE and for DPK, both calculated with TRIPOS 5.2.

3.3. Molecular motions

A great number of motions can be envisaged for the phenyl rings from each possible conformation. Among them, only the simultaneous and the alternated rotations will be considered.

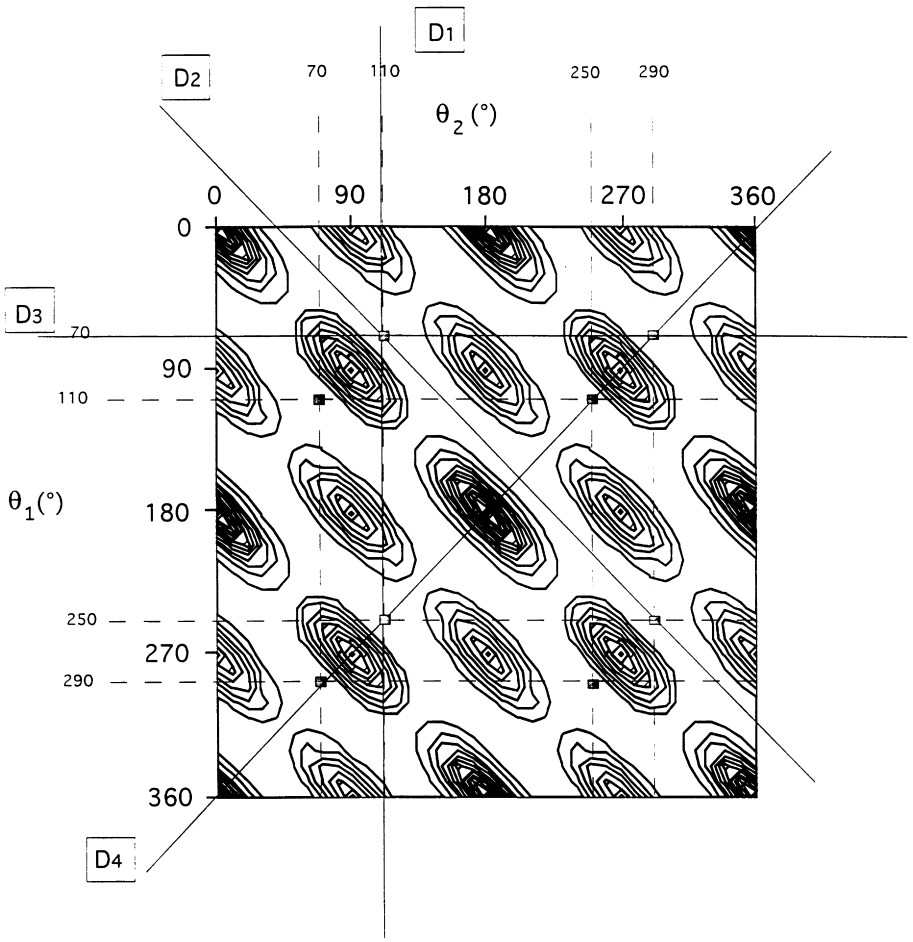

Fig. 4. Energy map and main motion routes for DPK.

There are actually two types of simultaneous rotations: the first one consists of rotating the two aromatic rings in opposite directions by increasing or decreasing both rotational angles (gear rotation), whereas the second one makes the two rings rotate in the same direction by increasing one angle and decreasing the other (correlated rotation).

The gear rotation, characterized by a straight line with a negative unity slope on the conformational maps, is considered by several authors as the easiest possible motion. Considering the molecule to lie first at its lowest energy position, such a type of rotation is illustrated by the motions following the D2 lines in Figs 3 and 4 for DPE and DPK respectively. The values of the relative energies taken by the molecules in this way are presented in Fig. 5, where the most probable positions are noted by the arrows.

On the same scheme, the correlated motions can be visualized on the energy maps when the molecule is moving from its low-energy position along a straight line with a positive unity slope corresponding to the D4 lines in Figs 3 and 4. The related picture is shown in Fig. 6 for the two molecules.

If we compare correlated motions with gear motions, it is clear from the figures that gear motions are most likely because of the lower energy barriers encountered. Moreover, the DPE molecule appears to be more mobile than the DPK molecule in the case of gear rotations.

The alternated rotations consist in fixing one of the phenylene rings and allowing the other one to undergo a complete 360° rotation. This motion can be described by considering either a horizontal or a vertical line in the energy maps. Fig. 7 depicts the phenylene ring motion along vertical lines D1 whereas Fig. 8 shows motions along horizontal lines D3. These various rotations do not differ significantly from each other, the energy barriers being very high in all cases, although being lower than in the case of correlated rotations.

From a general point of view, it is thought that an isolated molecule could follow the most favorable energetic path from its most stable conformation by modifying its conformation structure near an energetic barrier, following then a broken line on the energetic map. Such a route will allow the molecule to minimize its energetic jumps.

From these results, it is also possible to suppose that the DPE unit will move more easily than the DPK unit in a polymer chain such as PEEK in the sub-T_g temperature region.

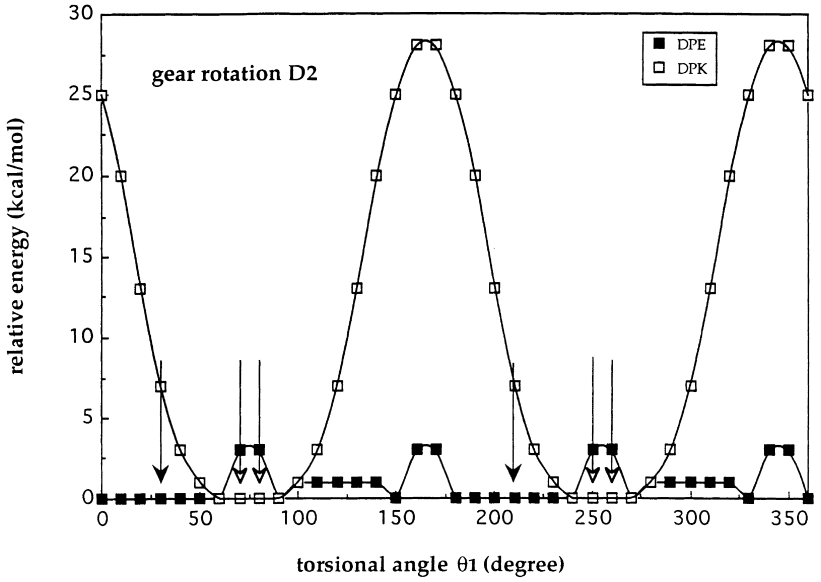

Fig. 5. Variation of the relative energy versus the torsional angle θ_1 for DPE and DPK molecules following a gear rotation route (D2 line). The most probable positions are shown by arrows.

4. Dielectric spectrometry

4.1. Determination of dipole moments

The mean-square dipole moment of a polar molecule in solution can be experimentally determined through the use of the Guggenheim–Smith relation [32a,b,c]:

$$\langle\mu^2\rangle = \frac{27k_bTM}{4\pi\rho N_a(\epsilon_1+2)^2}\left\{\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right\} \quad (1)$$

where N_a is the Avogadro number, k_b the Boltzmann constant, T the absolute temperature, M the molecular mass of the solute, ρ the density of the solvent and w the weight fraction of the solution. ϵ is the permittivity and n is the refractive index of the solution, the 1 subscript referring to the pure solvent. This method has been applied to the determination of dipole moments in the case of model compounds [33,34] and polymers in solution [35–37].

A series of solutions with increasing concentration of DPE and DPK in benzene has been prepared. Dielectric and refractivity measurements allow us to assign a value to the permittivity and refractive indices of the solutions and of the solvent. Figs 9 and 10 represent respectively the variation of the permittivity ϵ and of the refractive index n as functions of the weight fraction of DPK in benzene. The slopes of the straight lines give the values of dϵ/

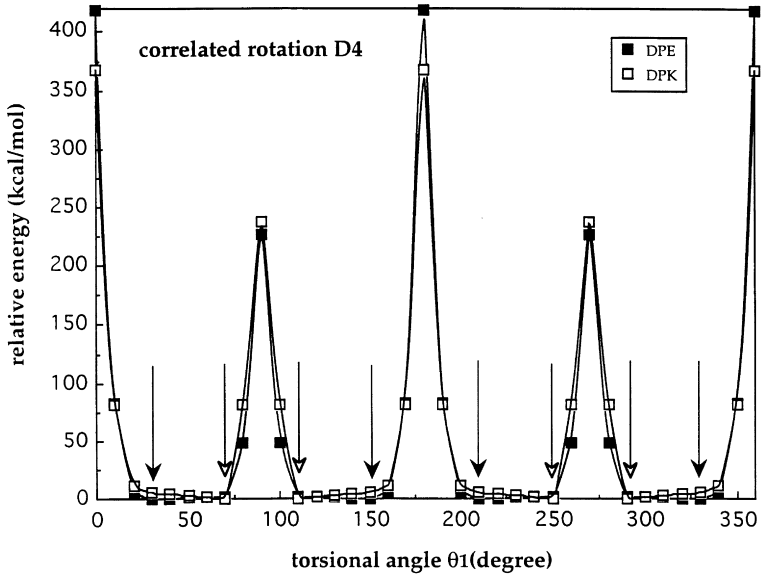

Fig. 6. Variation of the relative energy versus the torsional angle θ_1 for DPE and DPK molecules following a correlated motion route (D4 line). The most probable positions are shown by arrows.

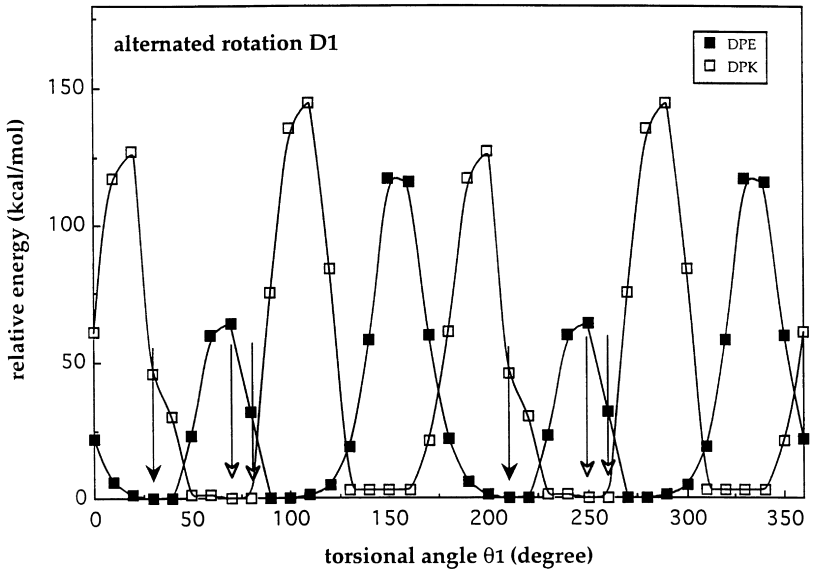

Fig. 7. Variation of the relative energy versus the torsional angle θ_1 for DPE and DPK molecules following an alternated motion route (D1 line). The most probable positions are shown by arrows.

dw and dn/dw to be replaced in Eq. (1). The values of ϵ_1 and n_1 for pure benzene are graphically determined, being the intercepts of the graphs. A value of 2.09 is found for ϵ_1, the discrepancy being 7% with the mean value of the literature which is 2.25. Concerning the refractive index, a value of 1.5007 is found for n_1, showing a discrepancy of 0.03% with the mean value of the literature which is 1.5011. A dipolar moment of 3.35 D is then calculated for the DPK molecule. No variation of either the permittivity or the refractive index with increasing concentration was found for DPE in benzene. This is probably due to a weaker dipole moment for this molecule, leading to poor dielectric and optical signals in the experimental methods used.

In order to verify this hypothesis for DPE and to confirm the value of $\mu = 3.35$ D for DPK, calculations of the dipole moments were done using CNDO/2. The torsional angles θ_1 and θ_2 have been varied by increments of 10°, so a great number of conformations (361) were considered for each molecular unit. The regular CNDO/2 method was used because the artefact which was introduced in the modified-CNDO/2 induced large perturbations in the determination of the dipole moment.

In the whole range (0°–180°) for θ_1 and θ_2, the dipole moment varies from 1.50 to 1.63 D for DPE, while it varies from 3.04 to 3.24 D for DPK. The mean values are respectively 1.56 D for DPE and 3.15 D for DPK.

These values of the dipole moment for DPE and DPK are somewhat larger than the ones reported in the literature,

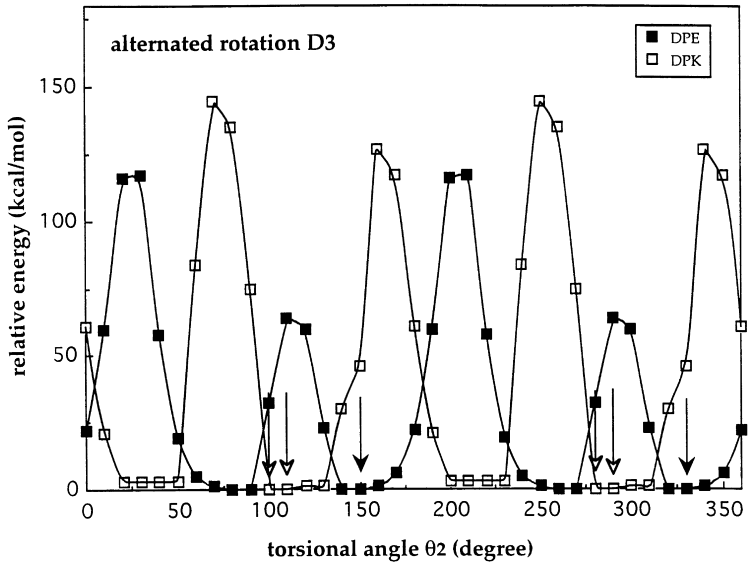

Fig. 8. Variation of the relative energy versus the torsional angle θ_2 for DPE and DPK molecules following an alternated motion route (D3 line). The most probable positions are shown by arrows.

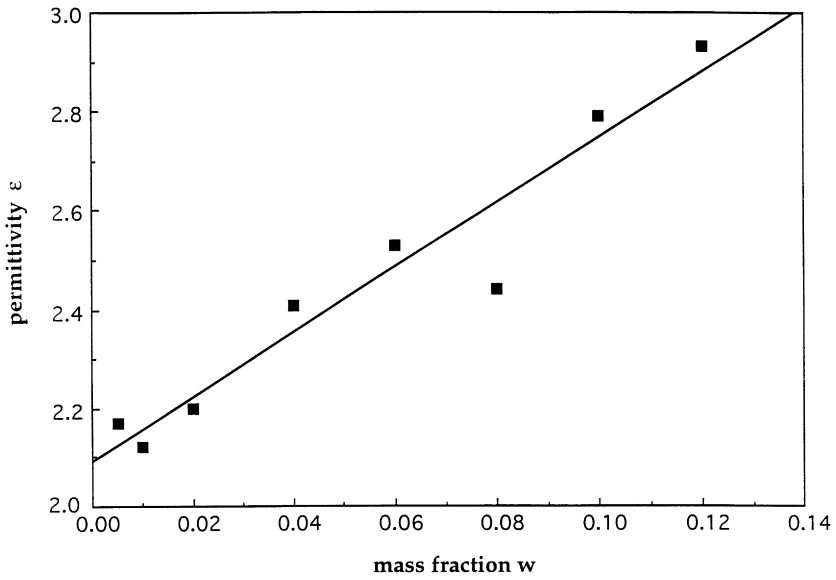

Fig. 9. Variation of the permittivity versus the mass fraction for DPK solutions in benzene.

especially for DPE. For example, one study, using C-INDO [38] for the calculations, claims respective values of 1.23 D for DPE and 3.10 D for DPK [24]. These values were for the equilibrium conformations of $(\theta_1, \theta_2) = (35°, 35°)$ for DPE and (30°, 30°) for DPK. $\mu = 3.10$ D is also our calculated value for $(\theta_1, \theta_2) = (30°, 30°)$ in the case of DPK.

4.2. Dielectric relaxations

Dielectric spectrometry experiments have been conducted on solutions of DPE and DPK in benzene and on films of a polymer containing DPE and DPK as molecular units, namely poly (ether–ether–ketone) (PEEK).

4.2.1. Solutions

Two different concentrations were tested for the solutions, a low weight fraction of 1% and a higher one of 10%. As usual, we consider the DPK molecules to be isolated in the 1% dilute solutions, while some intermolecular interactions are thought to be present in the 10% solution with a main part of the molecules forming aggregates.

A relaxation peak can be seen on isochronal curves for DPE and DPK in the temperature range (− 150°C, − 50°C). However, the intensity of the peak in the case of DPE is extremely low and very difficult to extract from the noise. For this reason, the dielectric studies of the relaxations will only be reported for DPK. These experimental difficulties

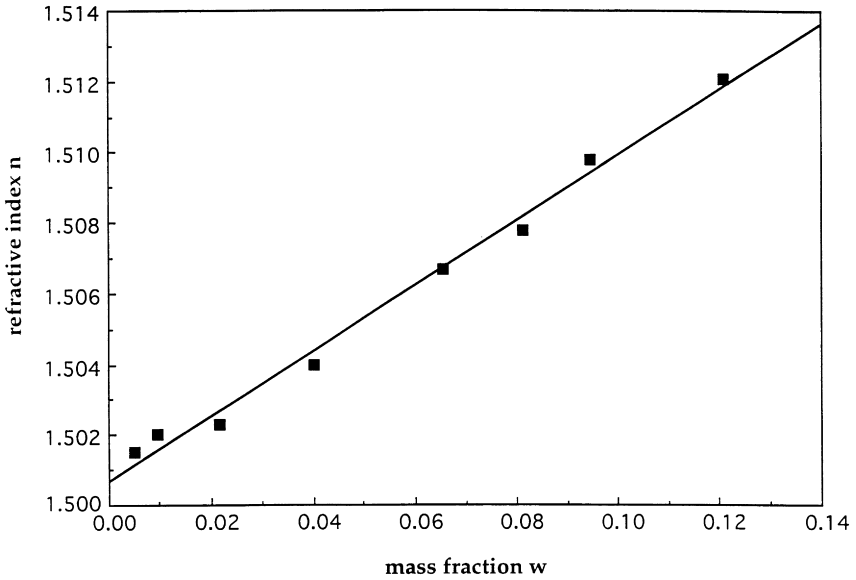

Fig. 10. Variation of the refractive index versus the mass fraction for DPK solutions in benzene.

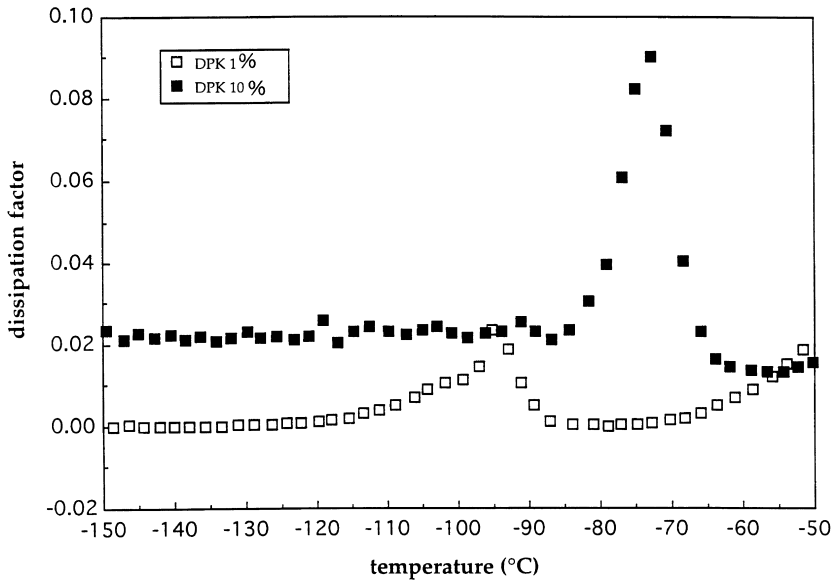

Fig. 11. Variation of the 1 kHz-isochronal dissipation factor versus temperature for 1%wt and 10%wt solutions of DPK in benzene.

may be attributed to the weak intensity of the dipole moment of DPE.

The 1 kHz-isochronal tan δ curves for solutions of DPK 1%wt and 10%wt are presented in Fig. 11. There is evidence of a relaxation peak in the dielectric dissipation factor curves of the solutions. It lies at -96°C for DPK 1% and -73°C for DPK 10%. The variation of the temperature of the maximum of tan δ with frequency allows the dielectric spectrometry apparatus to determine the activation energies of the relaxations through an Arrhenian analysis. These activation energies are listed in Table 2, together with the 1 kHz-frequency temperature location of the dissipation factor maximum.

It can be seen that the activation energy seems to be largely dependent on the concentration of DPK in benzene, being 62.5 kcal.mol^{-1} for 1%wt and 43.9 kcal.mol^{-1} for 10%wt. Concerning the relaxation of the dilute solution of DPK, one may consider that the molecules are isolated, being dispersed in the solvent at this low concentration (Fig. 12a). Under these conditions, the oscillatory movements of the two phenylene rings can proceed with broad amplitudes from the most stable position. The possible types of phenylene motions have been described above. These large oscillations are then shown to require somewhat large energies (62.5 kcal.mol^{-1}) to be sustained.

On the other hand, in the more concentrated solution, the molecules can be considered to be aggregated, at least for a great part of them (Fig. 12b). For this solution, two DPK molecules can be considered as stacked one on top of the other in a head-to-tail position, due to the presence of partial charges on the ketone functionality. In this case, the amplitudes of the oscillations of the phenyls are limited by the neighboring molecules. These constrained phenyls need a more elevated thermal agitation to be put in motion; the maximum of the relaxation is then shown to appear at -73°C for the 10% solution instead of -96°C for the 1% solution. From this state, the motions being more limited, the energy needed to maintain these oscillations is in turn lower (43.9 kcal.mol^{-1}).

The conformations for which the relative energy is greater than 62.5 kcal.mol^{-1} thus cannot be reached by the diphenyl ketone molecule in any case. The dipole moment values for these forbidden conformations have been subsequently removed in order to calculate a μ value that would be the actual one. The same average value is nevertheless found, that is $\mu = 3.15$ D. A 3-D representation of the dipole moment is given in Fig. 13 as a function of the θ_1 and θ_2 torsional angles. On this graph, the values of μ greater than 3.15 have been leveled for continuity reasons.

4.2.2. Polymer film

In the case of the polymer film, the 1 kHz-isochronal tan δ curves for dried annealed PEEK are shown in Fig. 14. A low temperature peak is seen, which is located at -106°C. Moreover, a wide zone of dissipation appears in the region -90°C to -50°C, a slight maximum being seen

Table 2
Temperature locations of the tan δ maxima and corresponding activation energies for DPK solutions and for PEEK film

Sample	Temperature of the tan δ maximum (°C)		E_a (kcal/mol)	
DPK 1% solution	−96		62.5	
DPK 10% solution		−73		43.9
PEEK film	−106	−76	12.5	–

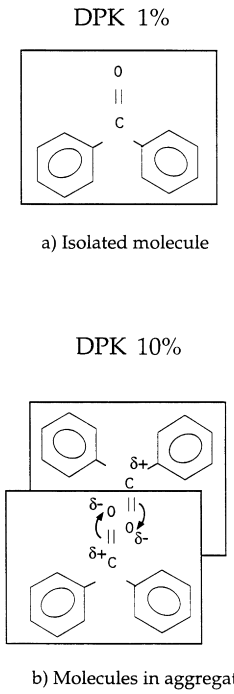

Fig. 12. Schematic representation of isolated (a) and aggregated (b) DPK molecules.

at − 76°C. An activation energy of 12.5 kcal.mol^{-1} is calculated relative to the first phenomenon. The activation energy was not able to be determined for the (− 90°C, − 50°C) region of the dissipation factor.

A dynamic mechanical spectrometry study of the sub-glass relaxations for dried amorphous commercial PEEK [8] reported that for a frequency of 1 Hz, the spectrum of the mechanical dissipation factor showed a maximum at − 80°C with a shoulder at − 30°C. The activation energy of the maximum was determined to be 12 kcal.mol^{-1}. Another mechanical study gave a value of 10.3 kcal.mol^{-1} for a relaxation peak located at − 89°C for 1 Hz [7].

Mechanical and dielectric spectrometry experiments have been concurrently performed on a series of polymers containing phenyl rings in their main chain [6]. The activation energies of the β relaxation was evaluated to be 10–11 kcal.mol^{-1} by dielectric measurements, being slightly lower and appearing at a lower temperature compared to the same polymer under mechanical measurements. The conclusion was that the β dielectric relaxation is a high-frequency–low-temperature component of a large distribution of internal motions that are able to be seen in mechanical spectrometry. Another study of the dielectric behavior of amorphous PEEK revealed a broad dissipation peak in the (− 100°C, − 30°C) region, having an activation energy of 13.9 kcal.mol^{-1} [39].

No low-temperature dielectric relaxation has been pointed out for the DPE molecular unit under our experimental conditions. There are likely motions in this molecule, but the set-up sensitivity does not allow their measurement because of its low dipole moment. This apparent lack of dielectric activity of the DPE molecule can also be due to the fact that the DPE oscillations have been shown to be very easy around the C–O bond [18,40].

Consequently, it is thought that the DPK molecule is probably the governing unit of the sub-glass relaxations for this kind of polymer. Figs 15 and 16 illustrate correspondences between the origin of the various relaxations for DPK solutions and in PEEK polymer that can be worked out from the dielectric results.

The low-temperature relaxation in the polymer could be of the same type as the relaxation revealed for DPK molecules considered as isolated (1% solution). Thus, this relaxation can be considered as reflecting the mobility of the DPK units that are distant from each other, i.e. concerning the short linear segments being less congested by the neighboring molecules (Fig. 15). The only restraint for these segments is due to the presence of neighboring DPE units in the same macromolecular chain, inducing two effects: the motions

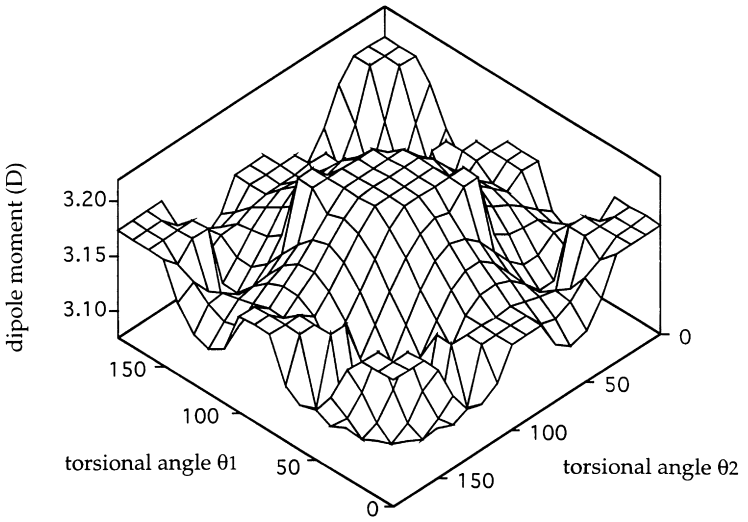

Fig. 13. 3D-representation of the calculated dipole moment of an isolated DPK molecule.

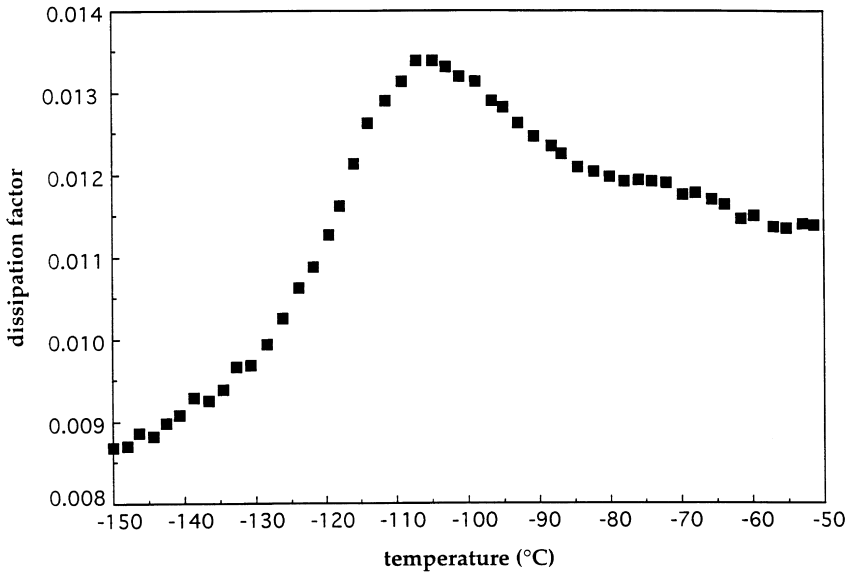

Fig. 14. Variation of the 1 kHz-isochronal dissipation factor versus temperature for PEEK.

must be of smaller amplitude than those observed for the isolated DPK molecule, and the rotations of the DPK must be gear rotations [19]. As a matter of fact, gear rotations are the easiest motions with the lowest activation energies, the energetic barrier being 28 kcal.mol^{-1} on the D2 route in Fig. 5.

It is experimentally observed that the sub-glass relaxation appears at a lower temperature for PEEK (− 106°C) than for DPK (− 96°C) with a lower energetic contribution of 12.5 kcal.mol^{-1} instead of 62.5 kcal.mol^{-1}. The hypotheses expressed by Laskowski et al. [11] and by Chen et al. [16,30] are then corroborated: at a given temperature, the rotation of one or two rings needs a higher activation energy (large amplitudes) than for the same rings located in a longer chain (weak amplitudes).

Concerning the other sub-glass relaxation in PEEK, a similarity can be noted with the relaxation of the aggregated DPK molecules in the 10% solution (Fig. 16). It can then be said that this relaxation can reflect the mobility of the constrained DPK units, having its origin in chains that are entangled or forming balls. In such chains, the DPK units can lie closer together to a certain extent and can be subjected to greater constraints than in the case of distant molecules. This second sub-glass relaxation is located at a slightly lower temperature (− 76°C) than for the aggregated molecules (− 73°C).

The DPE and DPK molecular units are then shown to have an unequal participation in dielectric relaxations. The DPK molecule, being more rigid and having a greater dipole

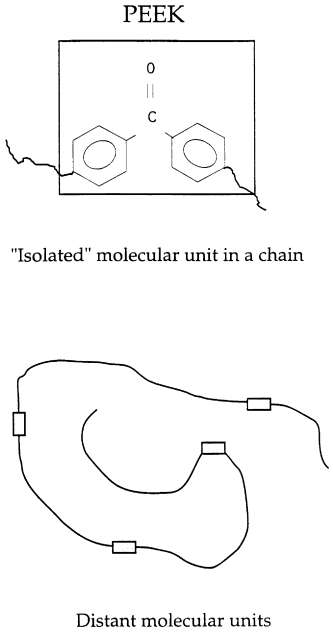

Fig. 15. Molecular assignment of the lower β-relaxation in PEEK.

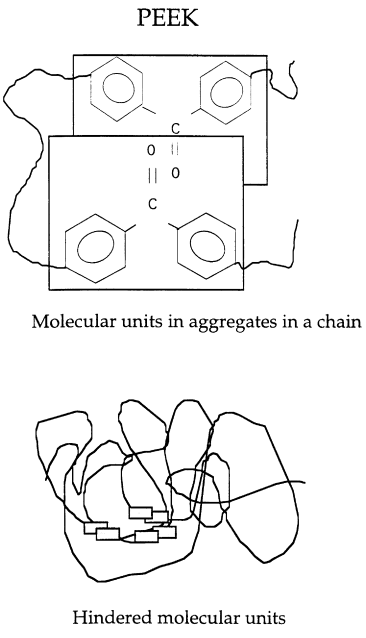

Fig. 16. Molecular assignment of the higher β-relaxation in PEEK.

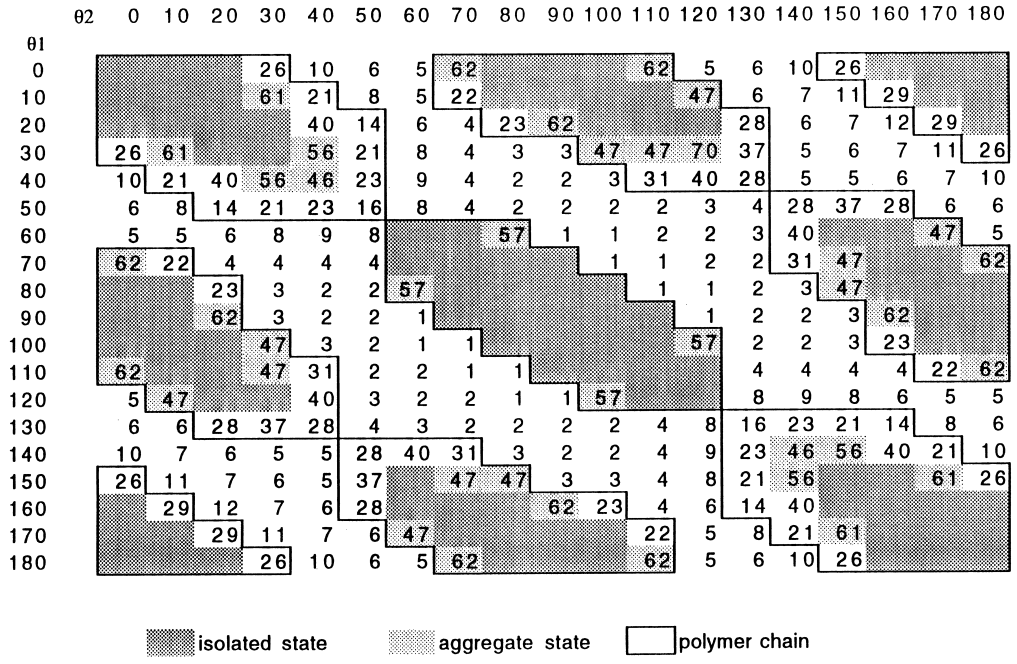

Fig. 17. Energy map for the DPK molecule in an isolated state, an aggregated state and a hindered state in a polymer chain. The energy is expressed in kcal.mol^{-1}. The forbidden conformation zones are indicated.

moment, must be the main one responsible for the dielectric signal in low-temperature relaxations. Being the determining factor in dielectric spectrometry, the DPK molecular unit could then be used as a probe for the sub-glass relaxations in linear aromatic polymers having ketonic bridges.

5. Correlation with calculations

It is now possible to correlate the values of the energetic contributions given by the CNDO/2 calculations with those of the activation energies obtained from the dielectric investigations. In the case of a DPK molecule considered as being isolated, an activation energy of 62.5 kcal.mol^{-1} has been experimentally determined. One may consider that the conformations for which the energetic contribution is higher than this value would not be reached by the molecule. With the same reasoning, a DPK molecule lying in an aggregate would not reach conformational energy values higher than 43.9 kcal.mol^{-1}. For molecules of DPK in a polymer chain, the probability of reaching energy values higher than 12.5 kcal.mol^{-1} could be considered as very low.

This can be seen in Fig. 17 where the forbidden conformations have been illustrated by a heavy darkening when DPK is considered in an isolated state and by a light darkening in the case of an aggregate. These forbidden conformations have been framed in the case of DPK in a PEEK polymer chain. A DPK molecule in a polymer chain has fewer degrees of freedom, in that it presents a lower number of conformations, compared to the same molecule considered as isolated or in aggregate. The DPK molecular unit in a macromolecular chain is only able to reach the permitted conformations located in low energy valleys. From Fig. 17, it is also shown that these valleys follow negative slope diagonals, corresponding to gear rotations, which have been shown to be the most favorable.

6. Conclusions

Semi-empirical calculations on DPE and DPK molecules, and experimental dielectric measurements on PEEK plastic films and on its DPE and DPK molecular units in benzene solution have been done in this study. The calculations on these repeating units using a modified-CNDO/2 method confirmed previous reports revealing that the DPE molecule has a higher mobility than the DPK one. This suggests that the motions of the DPK units can be the determining element in a polymer chain containing DPE and DPK, such as PEEK. The easiest routes for the motions of the phenylene rings are those followed by gear rotations. The dipole moment of DPE is calculated to be rather weak compared to the one of DPK. This is confirmed by permittivity and refractive index measurements.

The temperature location and activation energy of the relaxation for the DPK molecule is seen to depend on its concentration in benzene. The double β relaxation in PEEK is interpreted in considering two classes of DPK units, the former being distant from each other in a single molecular chain on the one hand, and the latter being closer together in entangled or ball-forming chains on the other hand. A DPK molecular unit in a macromolecule such as PEEK can only reach the permitted conformations in low energy valleys corresponding to gear rotation motions.

Acknowledgements

Dr. B. Sillion and Dr. R. Mercier (Laboratoire des Matériaux Organiques, Solaize, France) are gratefully acknowledged for their participation in the synthesis of the polymer material.

References

[1] Cattanach JB, Cogswell FN. In: Pritchard G, editor. Developments in reinforced plastics—5, Chapter 1. New York: Applied Science (Elsevier), 1986.
[2] Dawson PC, Blundell DJ. Polymer 1980;21:577.
[3] Sasuga T, Hagiwara M. Polymer 1985;26:501.
[4] Ahlborn K. Cryogenics 1988;28:234.
[5] Jonas A, Legras R. Macromolecules 1993;26:813.
[6] Starkweather HW Jr, Avakian P. Macromolecules 1989;22:4060.
[7] David L, Etienne S. Macromolecules 1992;25:4302.
[8] Bas C, Verot S, Battesti P, Alberola ND. Polymer Engineering and Science 1996;36:244.
[9] Abraham RJ, Haworth IS. J Chem Soc, Perkin Trans 1988;2:1429.
[10] Hay JN, Kemmish PJ. Polymer Commun 1989;30:77.
[11] Laskowski BC, Jaffe RL, Komornicki A. Int J Quant Chem 1986;29:563.
[12] Schaefer T, Penner GH, Takeuchi C, Tseki P. Can J Chem 1988;66:1647.
[13] Kendrick J. J Chem Soc, Faraday Trans 1990;86:3995.
[14] Abraham RJ, Haworth IS. Polymer 1991;32:121.
[15] Chen CL, Chang JL, Su AC. Macromolecules 1992;25:1941.
[16] Chen CL, Lee CL, Chen HL, Shih JH. Macromolecules 1994;27:7872.
[17] Hamerton I, Heald CR, Howlin BJ. Macromol Theory Simul 1996;5:305.
[18] Verot S, Battesti P. Can J Chem 1995;73:581.
[19] Verot S. PhD thesis, Université Claude Bernard, Lyon, 1996.
[20] Boon J, Magré EP. Makromol Chem 1969;3:630.
[21] Galasso V, De Alti G, Bigotto A. Tetrahedron 1971;24:2663.
[22] Smeyers YG, Hernandez-Laguna A. J Chim Phys 1978;1:75.
[23] Pitea D, Ferrazza A. J Mol Struct 1983;92:699.
[24] Baraldi I, Gallinella E, Momicchioli F. J Chim Phys 1986;83:655.
[25] Colquhoun HM, O'Mahoney CA, Williams DJ. Polymer 1993;34:218.
[26] Fleischer EB, Sung N, Hawkinson SJ. Phys Chem 1968;72:4311.
[27] Hoffman R, Swenson JR. J Phys Chem 1970;74:1970.
[28] Grimaud M, Loudet M, Royer R, Pfister-Guillouzo G. Bull Soc Chim de France (Vol. 5–6) 1974:1161.
[29] Rappoport Z, Biali SE, Kaftory M. J Am Chem Soc 1990;112:7742.
[30] Chen CL, Chen HL, Lee CL, Shih JH. Macromolecules 1994;27:2087.
[31] Kricheldorf HR, Bier G. Polymer 1984;25:1151.
[32a] Guggenheim EA. Trans Faraday Soc 1949;45:714.
[32b] Guggenheim EA. Trans Faraday Soc 1951;47:573.
[32c] Smith JW. Macromolecules 1950;46:394.
[33] Diaz-Calleja R, Riande E, San Roman J, Compan V. Macromolecules 1994;27:2092.
[34] Nunes RC, Pinto MR, Saiz E, Riande E. Macromolecules 1995;28:211.
[35] Salom C, Riande E, Hernandez-Fuentes I, Diaz-Calleja R. J Polym Sci B 1993;31:1591.
[36] Diaz-Calleja R, Saiz E, Riande E, Gargallo L, Radic D. Macromolecules 1993;26:3795.
[37] Diaz-Calleja R, Saiz E, Riande E, Gargallo L, Radic D. J Polym Sci B 1994;32:1069.
[38] Momicchioli F, Baraldi I, Bruni MC. Chem Phys 1982;70:161.
[39] Kalika DS, Krishnaswamy RK. Macromolecules 1993;26:4252.
[40] Chao J, Desando MA, Gourlay DL, Orr DE, Walker S. J Phys Chem 1984;88:711.