Relaxation Behaviour in Model Compounds of Poly(aryl-ether-ketone-ketone) as Revealed by Dielectric Spectroscopy.

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Abstract

The relaxation behaviour of a series of ether-ketone oligomers, considered as model compounds of poly(ether-ketone-ketone), was studied by means of dielectric spectroscopy. The dynamics of the α relaxation of ether-ketone model compounds as compared with that of poly(aryl-ether-ketone-ketone) PEKK (50/50), shows up differences which can be attributed to the variation of inter and intra molecular correlations with the chain length. Model compounds exhibit a nearly similar degree of cooperativity regardless the differences in T_g values. The PEKK(50/50) polymer exhibits stronger cooperativity than the oligomers suggesting that in poly(ether-ketone-ketone)s molecular motions above T_g extend to more than one monomeric unit.

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1.Introduction

The glass transition is commonly associated with the onset of liquid-like mobility at the length scale of relevant molecular units. For low molecular weight substances these elements are individual molecules and for flexible-chain polymers they are statistical chain segments. The cooperativity of molecular motions appearing in glass forming liquids and polymers at temperatures above the glass transition temperature, T_g , is strongly dependent on the molecular structure and , therefore, on the chain flexibility^{1,2}. Until now, the dynamics of rigid and semirigid polymers has not received so much experimental attention as that of flexible polymers³. In the case of semirigid polymers, a chain backbone can be considered as a sequence of rigid virtual bonds with essentially unhindered intermolecular rotation around more flexible units acting like molecular swivels⁴.

The preparation of oligomers with a well defined molecular architecture is a promising approach to understand some of the physical properties of polymers^{5,6}. In particular, the study of the dynamics of oligomeric compounds has been shown to be very valuable when compared with the molecular motions in polymeric systems⁷⁻¹⁰. Additionally to the degree of cooperativity², the length scale of the molecular motions⁹ occurring below and above T_g is a topic in which the study of model compounds with well defined molecular architecture can be of great interest.

Semirigid polymers like poly(aryl-ether-ketone)s have found a great variety of applications due to their high thermal stability, enhanced chemical resistance and outstanding mechani-

cal properties¹¹. Oligomers of poly(aryl-ether-ether-ketone) (PEEK) and poly(aryl-ether-ketone-ketone) (PEKK), have been used as model compounds to study crystalline structural phase transitions of these polymers¹²⁻¹⁴. However no comparison has been done, so far, between the dynamics of the α relaxation of a poly(aryl-ether-ketone) and that of model compounds with average molecular lengths comparable to those of the repeating unit.

In this work we have synthesized and studied the properties of a series of well defined ether ketone oligomers which can be envisioned as model compounds of PEKK. Our aim is to investigate the molecular dynamics of the α relaxation of these semirigid polymers by means of dielectric spectroscopy.

2. Experimental Part

2.1. Materials

1,3-bis(4-phenoxybenzoyl)benzene (EK1, fig. 1a), was synthesized by a Friedel-Crafts reaction according to a previously described procedure^{13,15,16}. EK2 (fig. 1a) was prepared, by a similar method, by reaction of EK1 with benzoyl chloride in the presence of aluminium chloride.

EK3 (fig. 1a) was prepared by a multistep procedure: First, 4-methylbenzophenone was prepared from reaction of toluene and benzoyl chloride in the presence of aluminum chloride using dichloroethane as solvent. The product, 4-methylbenzophenone, was recrystallized in hexane with a yield of 70 %. 4-benzoylbenzoic acid was obtained by oxidation of 4-methylbenzophenone with sodium permanganate in a mixture of pyridine and water (1:2 v/v). This product was recrystallized in a mixture of water/ethanol (1:1 v/v) with a yield

of 80 %. The corresponding acid chloride was obtained by reaction of the acid with tionyl chloride and subsequent recrystallization in n-pentane. Finally, EK3 (fig. 1a) was obtained by reaction of EK1 with this latter compound . EK3 was washed with N-methyl pyrrolidone and N,N'-dimethylformamide rendering a yield of 60 %.

In order to perform dielectric measurements of the oligomers, the synthesized samples were brought above their calorimetric melting temperatures, then confined between two circular gold-plated metallic blocks of 2 cm in diameter and finally quenched in ice water. The specimens' thickness was kept constant by using Teflon spacers. The resulting samples were amorphous. This procedure is commonly used to measure low molecular weight materials¹⁰ and introduces an error¹⁷ of $\approx \pm 20\%$ in the absolute value of $\Delta\epsilon$.

A PEKK (fig. 1b) specimen was synthesized at DuPont, with a para/meta phenyl isomer ratios (T/I)T/I ratio of 50/50 and $M_n \approx 5870$ g/mol and $M_w \approx 23800$ g/mol¹¹. Amorphous films were obtained by press molding from the melt and subsequent quenching under pressure between two cold metal blocks. Polymer films with circular gold electrodes (2 cm in diameter) were prepared by sputtering the metal onto both free surfaces. The specimens were placed between two gold-plated stainless steel electrodes.

2.2. Techniques

Thermal analysis of the samples was carried out by Differential Scanning Calorimetry (DSC), using a Perkin-Elmer DSC4 device at a heating rate of 20 K/min under nitrogen. The temperature was calibrated using Indium standards. Samples of typically 5 mg were encapsulated

in aluminum pans. In order to obtain amorphous specimens, the encapsulated samples were brought above their calorimetric melting temperatures and they were subsequently quenched on ice water.

Complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$, was measured covering a frequency range 10^{-2} Hz $< F < 10^5$ Hz by using an Stanford lock-in amplifier SR830 with a dielectric interphase and control temperature unit from Novocontrol. To analyze the shape and temperature evolution of the α relaxation the phenomenological Havriliak-Negami (HN) formulation was used, including a conduction term^{18,19}. According to this approach, the dielectric loss, ϵ'' , exhibits a frequency dependence of the type:

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty) r^{-c} \sin(c\psi) + \frac{\sigma}{\epsilon_{vac}\omega^s} \quad (1)$$

with:

$$r^2 = 1 + 2(\omega\tau_0)^b \cos(b\pi/2) + (\omega\tau_0)^{2b} \quad (2)$$

and:

$$\tan\psi = \frac{(\omega\tau_0)^b \sin(b\pi/2)}{1 + (\omega\tau_0)^b \cos(b\pi/2)} \quad (3)$$

where $\omega = 2\pi F$, ϵ_0 and ϵ_∞ are the relaxed($\omega=0$) and unrelaxed($\omega=\infty$) dielectric constant values, τ_0 is the central relaxation time of the relaxation time distribution function and b and c ($0 < b, c < 1$) are shape parameters which describe the symmetric and asymmetric broadening

of the relaxation time distribution function, respectively¹⁸. Eq. 1 leads to the a Debye single relaxation time equation when $b=c=1$. Here, σ is related to the direct current electrical conductivity, ϵ_{vac} is the vacuum dielectric constant and s depends on the nature of the conduction mechanism. A value of $s<1$ is associated to a non-ohmic transport¹⁹.

Molecular modeling was performed by means of the program Cerius2, v3.5. The Dreiding 2.21 force field was used. Structures were minimized until the energy difference between two structures was less than 10^{-4} . Calculations were run on a Silicon Graphics Indigo R-10000 workstation.

3. Experimental Results

3.1. Differential Scanning Calorimetry

The DSC traces for the quenched EK oligomers are shown in fig. 2. The glass transition of the samples appears as discontinuous steps in the heat flow accompanied by a peak characteristic of a physical aging process (inset fig. 2). Upon heating, EK2 and EK3 exhibit sharp exotherms indicating the onset of a cold crystallization process. At higher temperatures, EK2 and EK3 show endothermic peaks which suggests the melting of the previously formed crystals. Both, the crystallization rate and the melting temperature also increase with the increasing molecular length. The thermal behaviour followed by the polymer (see fig. 2) is qualitatively similar to that found in the oligomers though shifted to higher temperatures. The T_g values for oligomers and polymer are presented in table 1

3.2. Dielectric Spectroscopy

Dielectric loss data, $\epsilon''(F)$, measured in the available frequency window for the EK1, EK2 and EK3 oligomers are shown in fig. 3 at different temperatures as a function of the frequency. In all cases, ϵ'' measurements were taken at $T > T_g$ in order to focus on the α relaxation process. The highest measured temperature was chosen to prevent cold crystallization of the samples. As expected, the α relaxation manifests itself, for all systems, as a maximum in $\epsilon''(F)$. As the temperature increases the frequency of maximum loss, F_{max} , shifts towards higher values. At low frequencies the relaxation is accompanied by a remarkable increase of $\epsilon''(F)$ due to a dc-conductivity contribution. $\text{Log}_{10}F_{max}$ values for the investigated oligomers have been represented in fig. 4 as a function of the reciprocal temperature. In all cases, the temperature dependence of F_{max} clearly exhibits a non-Arrhenius behaviour. As illustrated in fig. 4, , the experimental results can be described by a Vogel-Fulcher-Tamann (VFT) function of the type:

$$\text{Log}_{10}F_{max} = \text{Log}_{10}F_0 - \frac{A}{T - T_0} \quad (4)$$

The corresponding VFT parameters are shown in table 1. To reduce the effect of fitting over a limited frequency range a value of $\text{Log}_{10}F_0 \approx 13$ was assumed according to a recent proposal²⁰. This assumption does not affect the quality of the data fit into the VFT equation but reduces the dispersion among fitting parameters which exhibit an accuracy of $\approx \pm 15\%$ for A and $\text{Log}_{10}F_0$ and $\approx \pm 5\%$ for T_0 . There is an evident dependence of the T_0 with

molecular weight which somehow mimics the observed increase of T_g . The strong-fragile scheme proposed by Angell¹, allows one to classify glass forming systems on the basis of the temperature dependence exhibited by the viscosity or the relaxation time. Within this scheme, the fragility of a system has been defined by the degree of departure from the Arrhenius behaviour exhibited by the relaxation time of the α relaxation process^{1,2,21}. The strength parameter, $D=2.303A/T_0$, characterizes the fragility. The corresponding values are shown in tab. 1

At each temperature, ϵ'' values were fitted according to eq. 1 and the result of this treatment is presented in fig. 3 by the continuous curves. The separate contribution of both, the relaxation and the conduction process has been also represented. Due to the small conductivity contribution in case of EK3 the conductivity term was ignored in this case. From the analysis of the experimental dielectric curves the characteristic parameters of eq. 1 such as $\Delta\epsilon=\epsilon_0 - \epsilon_\infty$, b , c , τ_0 , σ and s are obtained. Table 2 shows these parameters for selected temperatures of fig. 3 at which the relaxation process is centered around the middle of the experimental frequency window. Inspection of table 2 shows that the oligomers exhibit a clear non-Debye behaviour, $b<1$ and $c<1$ over the whole investigated temperature range.

Dielectric loss data for PEKK (50/50) are shown in fig. 5 at different temperatures, $T>T_g$, as a function of the frequency. The α relaxation is broader as compared with that of the oligomers specially with the EK1 one though presents similar characteristics. The corresponding F_{max} values for the polymer have been included in fig. 4. Here, it is also evident that F_{max} exhibits VFT behaviour with parameters represented in table 1. Fitting, in this

case, of the ϵ'' values to eq. 1 give rise to the continuous lines represented in fig. 5. Table 2 shows the parameters at a selected temperature for which the relaxation time is comparable with that of the oligomers. The values of the dielectric parameters of PEKK are in agreement to previous reported data²²⁻²⁴. For the polymer, both, broadening and asymmetry become higher than for the oligomers as revealed by the lower values of the b and c shape parameters.

4. Discussion

4.1 Dependence of T_g on the molecular structure.

As mentioned in the introduction, a virtual bond can be defined for semirigid systems as a stiff chain fragment within the limits of which no internal rotation is possible. For the model compounds investigated, the intermolecular conjugation between the phenylene moieties and the carbonyl groups hinders the internal rotation between the ether linkages, the latter acting like molecular swivels. The mean length of the virtual bond can be estimated from the following simple expression^{4,25}:

$$\langle l \rangle = \frac{L}{n_s + 1} \quad (5)$$

where L is the chain contour length (i.e. that corresponding to its full extension), and n_s is the number of intramolecular swivels. Calculations performed by using Cerius2 (see experimental) of the full extension configuration (L) for the oligomers and for the repeat unit of the polymer are shown in table 1. It can be easily verified in our case that the number of intermolecular

swivels remains the same regardless of the chemical structure of the oligomers. Two oxygen bridges and one intramolecular kink at the central meta-phenyl moiety make $n_s = 3$ for each oligomer. Therefore, the chain stiffness, as expressed through $\langle l \rangle$ dramatically increases as $EK3 > EK2 > EK1$ (See table 1). This effect strongly influences the T_g values of the model oligomers which tend to linearly increase with $\langle l \rangle$ (see table 1). This effect has been also reported for polymeric systems^{11,26}. In particular, it was pointed out that T_g values of pol(aryl-ether-ketone)s exhibit a strong dependence on the percentage of rigid phenyl-carbonyl linkages present in the polymer backbone¹¹.

The considerably higher T_g value of PEKK (50/50), essentially having a similar chemical structure to that of the oligomers, does not follow the linearity observed for the oligomers if one considers $\langle l \rangle$ referred to the monomer unit (tab. 1). Here, certainly a chain-length effect will tend to increase the T_g value²⁷.

Finally, we wish to point out that recent work relates molecular structure and dynamics near T_g (cooperativity) with the occurrence of the low van der Waals peak (LVDW) as detected by X-ray scattering²⁸. The appearance of this peak has been associated to the existence of side groups of sufficient length to provide regions of short chain packing which may diffract coherently. In the present study, neither the model compounds nor the polymer exhibit such a peak^{11,14,22}. This is due to the absence of side groups in our samples.

4.2 Dependence of the shape parameters on the chain length.

Schönhals and Schlosser have proposed that the shape parameters, which characterize the dielectric α relaxation in the frequency domain, can be related to the molecular dynamics at the glass transition provided that the molecular mobility is controlled by inter and intramolecular interactions²⁹. In this model, the b and c HN parameters are related to two new, so called, scaling parameters of the α relaxation m and n by $m = b$ and $n = b \cdot c$. This model relates m to large scale motions while n is controlled by small scale motions. Experimental support of the model has been provided by different dielectric spectroscopy techniques^{7,8}. In particular it was shown that $m \leq 1$ and $n \leq 0.5$ for polymer materials²⁹.

In our case, the m and n parameters are shown in fig.6 for the investigated model compounds and for the polymer as a function of their corresponding F_{max} values. The scaling parameters m and n exhibit a clear molecular weight dependence decreasing upon going from EK1 to PEKK (50/50). The model compounds exhibit a non-Debye behaviour although both, m and n values are systematically higher than those for the polymer. According to the model, a m decrease with molecular weight is expected to be due to the increase of intermolecular correlation²⁹. As regards the n values, only the lowest molecular weight investigated oligomer, EK1, exhibits $n > 0.5$. The value of $n = 0.5$ can be interpreted on the basis of an interchain damped diffusional propagation of orientation along the chain³⁰. Unexpectedly for the oligomeric samples EK2 and EK3 the values of n are below the polymer limit. This indicates that a strong hindering of the intrachain diffusion process appears with a

relatively moderated increase of molecular weight. This process can undoubtedly be affected by the increase in chain rigidity pointed out above. When comparing monodisperse compounds with polymers one should consider the effect of polymer polydispersity which, in principle, may broaden the segmental relaxation spectrum in the polymer as compared with that of the oligomer. However, in our case, the polymer sample with a polydispersity $M_w/M_n \approx 4$ exhibits values $m < 1$ and $n < 0.5$ over the whole investigated temperature range similar to previously reported data on poly(ether-ketone) specimens with polydispersities ranging from 2.4 up to 3.2^{11,22,31,32} indicating that polydispersity is not the main source of broadening. Experiments performed in flexible polymers and their corresponding low molecular mass oligomers nearly show a similar behaviour though some differences are evident. Experiments in poly(propylene glycol), poly(vinyl acetate) or poly(p-chlorostyrene) performed in a dynamic range comparable to the one investigated here, have shown a stronger temperature dependence of both m and n parameters⁷. The smaller temperature dependence of the shape parameters exhibited for the oligomers and the polymer reported here can be ascribed to the inherent higher chain rigidity of our samples.

4.3 Dependence of cooperativity on the molecular weight.

As shown in fig. 4, the experimental F_{max} values can be described by the VFT equation. Angell has proposed that fragility is connected with the topology of the potential energy associated to the available configurations which, upon increasing temperature throughout T_g , are supposed to be modified giving access to a different set of configurational states. In

another approach Ngai et al.², associated fragility with the strength of the correlation between non bonded species which these authors related to the cooperativity of the motion. Here, the fragility of a system can be related to both, the energy barrier of rotation per mole and the configuration entropy of the smallest rearranging region, as considered by Adam and Gibbs in their theory of relaxation³³. From the VFT parameters given in tab. 1 one can estimate values for the kinetic free volume fraction at T_g as $f_g^K = (T_g - T_0)/(2.303A)$ and for the cooperativity parameter of the Adam-Gibbs model as $z_g = T_g/(T_g - T_0)^{33,34}$. This calculation leads an almost constant value of $f_g^K = 0.03 \pm 0.002$ for all the studied systems, while z_g tends to smoothly increase with chain stiffness (see tab. 1). The highest value of z_g for the high molar weight polymer, PEKK(50/50) seems to be reasonable insofar as the onset of segmental motions at T_g would require higher cooperativity due to interchain entanglements.

The cooperativity of chemically identical systems having only differences in molecular weight should be similar considering that the changes in configurational entropy should be equivalent. Experiments performed in polymers with different molecular weights in the range comprised between 10^3 g/mol and 10^5 g/mol, have shown the validity of this prediction². However, experiments in oligomers are not similarly documented. In order to discuss the dependence of cooperativity with molecular weight we have represented F_{max} values as a cooperativity plot in fig. 7. Here $\text{Log}_{10}F_{max}$ has been represented as a function of a normalized T^*/T parameter by taking T^* as the temperature at which the average relaxation time defined as $\tau = (2 \cdot \pi \cdot F_{max})^{-1}$ equals to 10 seconds in accordance with previous studies². From this plot one sees that EK2 and EK3 exhibit a small increase of fragility, characterized in this plot

by a slightly higher slope as $T^*/T \rightarrow 0$, as compared with that of EK1. This finding correlates with the relative decrease of D and increase of z_g upon comparing EK1 with EK2 and EK3 (see tab. 1). Hence, this indicates that oligomers having similar chemical structure show, above T_g , similar dynamic features in terms of cooperativity ($\Delta z_f \approx 0.6$; $\Delta D \approx 2$ regardless the very different T_g values $\Delta T_g \approx 56$ K). Previous studies have shown comparable dynamics in polymeric samples differing in molecular weight².

PEKK (50/50) exhibits a stronger F_{max} normalized temperature dependence as compared to the oligomers, suggesting a higher degree of cooperativity. This can be understood by considering the expected increase of intermolecular steric interferences in the polymeric sample relative to the oligomeric ones. Moreover, this effect indicates that in poly(ether-ketone-ketone)s the molecular motions above T_g may extend to several monomeric units.

Let us discuss the relation between fragility and cooperativity in a more quantitative manner in the light of the empirical relation $M = M_0 - 320\beta$ (where $M_0 = 250 \pm 30$) between fragility and α -relaxation broadening as proposed by Böhmer et al.²¹. Within this scheme, fragility is characterized in terms of a steepness index M defined by the slope of curves in fig. 7 when $T^*/T \rightarrow 0$ that we calculated by the empirical equation²¹ $M = 16 + 590/D$ (table 1). Here, the α -relaxation broadening is characterized by the stretching exponent β corresponding to the Kohlrausch-Williams-Watts (KWW) function which describes the relaxation function in the time domain. As discussed previously²², from the b and c parameter of the HN analysis we obtain the values of β (table 1) by pure imaginary inverse Laplace transformation and subsequent fitting of the time domain relaxation function to a KWW stretched exponential.

As predicted by Böhmer et al. the obtained β values decrease linearly with increasing steepness index M . Absolute values, especially in EK1, are placed above the empirical upper limit $(M_0 + 30)^{21}$. Due to the empirical character of the above equations it is not surprising that the extension of relaxation measurements to new rigid and semirigid polymers and oligomers might give rise to a modification of the empirical parameters which define the equations. Additional measurements in other semirigid systems are required to further elucidate this point.

5 Conclusions.

The comparison of the dynamics of the α relaxation of ether-ketone oligomers with that of PEKK (50/50) shows up differences which can be attributed to variations of the inter and intramolecular correlation with molecular weight and chain flexibility. The scaling parameters of the dielectric α relaxation, m and n , decrease with increasing molecular weight. The m decrease with molecular weight has been explained as due to an increase of the intermolecular correlation. The observed decrease of n indicates a dramatic hindering to the intrachain diffusion process appearing with moderated increase of molecular weight. Oligomers exhibit nearly similar dynamic features in terms of cooperativity regardless the differences in T_g values. PEKK (50/50) exhibits a stronger cooperativity than the oligomers. Our results point towards the fact that in poly(ether-ketone-ketone) polymers molecular motions above T_g extend to more than one monomeric unit.

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Table 1: Structural and Relaxation Parameters of the EK model compounds and PEKK
(50/50)

	EK1	EK2	EK3	PEKK (50/50)
$T_g(K)$	297	333	353	425
A	667.3	647.0	710.9	611.9
$\text{Log}_{10}F_0$	13	12.9	13	12.9
T_0 (K)	251.7	284.4	303.7	381.3
D	6.1	5.24	5.4	3.7
L	23.3	32.6	42.4	28.4
$\langle l \rangle$	5.8	8.1	10.6	7.1
f_g^K	0.029	0.032	0.030	0.031
z_g	6.5	6.8	7.1	9.7
M	112.7	128.6	125.2	175.4
β	0.65	0.53	0.49	0.41

Table 2: $\Delta\epsilon$, b , c , τ_0 , σ and s values obtained from the fitting of equation 2 to some characteristic temperatures of the investigated systems.

sample	T(K)	$\Delta\epsilon$	b	c	$\tau_0(s)$	σ	s
EK1	313	7.7	0.95	0.59	$2 \cdot 10^{-3}$	$9.4 \cdot 10^{-12}$	1
EK2	343	6.1	0.89	0.51	$5.2 \cdot 10^{-3}$	$5.1 \cdot 10^{-12}$	1
EK3	368	1.16	0.87	0.48	$3.2 \cdot 10^{-3}$	-	-
PEKK(50/50)	438	3.4	0.77	0.46	$2.5 \cdot 10^{-3}$	$8.1 \cdot 10^{-11}$	0.97

Legends to the figures.

Figure 1: Generalized Chemical Scheme of (a) EK model compounds and (b) PEKK (50/50)

Figure 2: DSC scans of EK1, EK2, EK3 and PEKK (50/50). Inset shows an enlarged view of the T_g region. Heating rate: 20K/min

Figure 3: Dielectric loss, ϵ'' , for the model compounds EK1, EK2 and EK3 as a function of temperature (labelled) for the α relaxation process. The continuous lines represent the best fits to the HN relaxation function including the conductivity contribution.

Figure 4: Frequency of maximum loss, F_{max} , values as a function of reciprocal temperature for: $\circ$ EK1, $\triangle$ EK2, $\square$ EK3 and ∇ PEKK (50/50). Continuous line represents the best fit of the experimental data to the VFT equation.

Figure 5: Dielectric loss, ϵ'' , for amorphous PEKK(50/50) as a function of temperature for the α relaxation process. The continuous lines represent the best fits to the HN relaxation function including the conductivity contribution.

Figure 6: Dielectric scaling parameters $m = b$ (hollow symbols) and $n = b \cdot c$ (full symbols) of the α relaxation as a function of the corresponding F_{max} values for $\circ$ EK1, $\triangle$ EK2, $\square$ EK3 and ∇ PEKK (50/50).

Figure 7: Cooperativity plot comparing F_{max} values of model compounds: $\circ$ EK1, $\triangle$ EK2, $\square$ EK3 and polymer (∇ PEKK (50/50)). T^* has been defined as the temperature at which

$$\tau = (2\pi F_{max})^{-1} = 10 \text{ s}$$

EK

EK1

$X = H$

EK2

EK3

(a)

PEKK

(b)

fig. 1

Fig.2

Fig. 3

Fig. 4

Fig. 5

Fig.6

Fig.7