

On the relationship between Non-exponential Relaxation and Molecular Stiffness in Aromatic Model Compounds.

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Abstract

The α relaxation of a series of ether-ketone model compounds was studied to quantify the effect of molecular stiffness on the KWW stretching exponential. The obtained values decrease with increasing stiffness and are within the theoretical bounds predicted for systems with spatial dimensionality varying from 2 to 1.

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In complex systems, like glass-forming liquids, the relaxation function $\phi(t)$ of a property follows a characteristic non-exponential pattern which can be expressed by the empirical Kohlrausch-Williams-Watts (KWW) function ¹: $\phi(t) \propto \exp[-(t/\tau_{kww})^\beta]$, where τ_{kww} is a characteristic relaxation time, and β varies between 0 and 1. The stretching exponential parameter, β , serves to characterize the width of the continuous spectrum of relaxation times. In particular, the non-exponential behaviour constitutes one of the most striking features of the α relaxation appearing above the glass transition temperature (T_g) in complex liquids ².

Currently, the broad spectrum of reported experimental values of β for many glass-forming substances ³ can be envisioned from several viewpoints. Some authors like, Götze et al. ⁴ and Böhmer et al. ⁵, indicate that KWW equation is a convenient empirical representation and β is a phenomenological parameter. Ngai et al. ^{6, 7} relates the degree of intermolecular coupling with the spectral width of the relaxation function expressed by β . On the other hand, Phillips ^{8, 9, 10} regards β as an intrinsic property of a system depending explicitly on the dimensionality d of its configuration space according to: $\beta = d/(d + 2)$. The effects of a possible spatial constraint on the effective dimensionality d are accounted for by the heuristic relationship: $d = \{d\} - \bar{d}$. Here, $\{d\} = nd_b$, with d_b being the bare dimensionality for unhindered diffusion of n particles, and \bar{d} is a correction due to constraints imposed by long-range forces, conservation conditions or internal structural effects ^{8, 9, 10}. For systems with short-range forces, like a mixture of soft spheres,

a value of $\beta=3/5$ is predicted. This implies $\{d\}=3$, $\bar{d}=0$ and $d=3$. For systems with long-range interactions, like those with Coulomb forces between charged particles, predictions offer a value of $\beta=3/7$ ($\{d\}=3$, $\bar{d}=3/2$ and $d=3/2$). Finally, for systems with two spatial constraints, like spin glasses, $\beta=1/3$ ($\{d\}=3$, $\bar{d}=2$ and $d=1$)⁷⁻⁹. The above author postulated that an unavoidable distribution around these three fixed theoretical situations provides the observed broad distribution of experimental β values. In the light of these arguments, the lower value $\beta = 0.42 \approx 3/7$ reported for polypropylene glycol¹¹ compared to $\beta = 0.6 \approx 3/5$ for its lower molecular weight homologue, propylene glycol, can be reasonably explained by the presence of long-range spatial constraints caused by interchain entanglements which set up above a critical entanglement length⁷⁻⁹. A similar argument was earlier used in a series of narrow polystyrene fractions to account for the decrease of β from 0.63 to 0.47 as the molecular weight increases from $M_n=9 \cdot 10^3$ g/mol to $M_n=233 \cdot 10^3$ g/mol¹². Here, it could not be excluded that the small but finite polydispersity of the polystyrene fractions ($M_w/M_n < 1.06$) might have affected the β values derived from these latter studies¹².

In macromolecular systems, in addition to chain length and polydispersity, chain stiffness is another molecular factor affecting β . There is now qualitative experimental evidence available suggesting that β tends to decrease the higher the intrinsic chain stiffness and the stronger the interchain interaction^{13, 14}.

The present communication aims to present a quantitative evaluation regarding the

effect of molecular stiffness over the KWW stretching exponential of the α relaxation, as derived from dielectric spectroscopy experiments. To isolate chain stiffness from other intermolecular factors, the study was performed on chemically homogeneous, i.e. strictly monodisperse, low molecular weight ether-ketone model compounds (fig.1, tab 1) of poly(aryl-ether-ketone-ketone) (PEKK). The synthesis of the model compounds has been described elsewhere ¹⁵. Glassy specimens were prepared for dielectric measurements by quenching from the molten state between two gold coated metallic plates ¹⁵. Complex dielectric permittivity $\epsilon^* = \epsilon' - i\epsilon''$, was measured over a frequency range $10^{-2}\text{Hz} < F < 10^5\text{Hz}$ by using an Stanford lock-in amplifier SR830 with a dielectric interface and control temperature unit from Novocontrol.

The phenomenological Havriliak-Negami (HN) formulation in the form $\epsilon'' = -Im[\epsilon^*] = -Im[\epsilon_\infty + (\Delta\epsilon) \cdot [1 + (i\omega\tau_0)^b]^{-c}]$ was used to analyze the relaxation curves as describe elsewhere ^{15, 16, 17, 18}. Fig.2(upper) shows dielectric loss data for the three investigated systems at T=313 K, T=343 K and T=368 K for EK1, EK2 and EK3 respectively. The continuous lines indicate the best fit to the HN equation (tab.1). For the sake of comparison, in order to build up a master plot, the relaxation curves were normalized by the maximum value of ϵ'' and shifted in the frequency axis to achieve a common frequency of maximum loss value of 1 Hz. Frequency-to-time domain conversion was accomplish by inverse Laplace transformation of the $\epsilon''(\omega)$ values generated from the best HN fits by using a subroutine based on the Hagenah procedure ^{17, 18}.

Fig. 2(lower) shows by the continuous lines the best fit to the KWW equation of the frequency-time converted data. The apparent broadening of the relaxation spectra, in order $EK1 < EK2 < EK3$, can be quantitatively accounted for by the KWW eq.1 with decreasing exponent β (table 1). Similarly to the case of the narrow polystyrene fractions¹², the experimental values of β for the model compounds change continuously in the interval from 0.65 to 0.49 with no evidence for preference of one of the theoretical values, $\beta=3/5$ or $3/7$, expected for systems in which the relaxation is dominated by short-range or by long-range interactions respectively⁸. It can be seen (tab. 1), however, that the β values tend to decrease with increasing chain stiffness as expressed through the mean length of the virtual bond^{19, 20}: $\langle l \rangle = L/(n + 1)$. Here, L is the molecular contour length¹⁵ (i.e. that corresponding to its full extension)(tab. 1), and n is the number of intramolecular swivels permitting unhindered internal rotation. This value remains the same ($n=3$) regardless of the chemical structure of the model compounds corresponding to two oxygen bridges and one intramolecular "kink" at the central meta-phenyl moiety (Fig.1). Therefore, the molecular stiffness expressed through $\langle l \rangle$ ¹⁵ increases substantially in the sequence $(\langle l \rangle_{EK3}) > (\langle l \rangle_{EK2}) > (\langle l \rangle_{EK1})$. As shown in fig.3, there is a linear dependence of β with the reciprocal molecular stiffness given by the following empirical relation: $\beta = 0.308 + (0.197)/\langle l \rangle$. Although this empirical relationship, restricted to the three investigated samples, must be treated as a mathematical description, a tentative discussion of the physical implications can be attempted. In fact, $\beta = 0.308$ can be regarded

as the effective lower limit for the infinitely stiff model compound in a fully extended rod-like conformation. This is achieved, in practice, by a fully aromatic, all-para molecule with $L > 10$ nm and $n = 0$. This value is close to the stretched exponent $\beta = 1/3$ expected for a system with a spatial dimensionality $d = 1$ ⁸. Within this context, the increase of molecular stiffness would be equivalent to the decrease of its spatial dimensionality. In fact, the fractal dimensionality of a polymer chain decreases from 2, for a flexible chain in an unperturbed coiled conformation, to 1 for a stiff, rod-like chain²¹. It is noteworthy that $\beta = 1/3$ can also be regarded as a theoretical lower limit corresponding to a random walk on the fractal structure of a percolating cluster in a closed space²².

The higher extreme corresponding to $\beta = 1$ (Debye-like relaxation) can be expected for an aromatic compound with $\langle l \rangle = 0.29$ nm which is a value close to the diagonal dimension of the benzene molecule. The latter can be regarded, formally, as a starting member of a homologous series of fully aromatic chains. It is important to remark that the above generalizations only apply for aromatic oligomers with a molecular contour length L well below the entanglement length, L_{cr} , above which the kinetic free volume fraction at T_g becomes the key factor controlling the β exponent of long-chain polymers^{23, 24}. It is worth to emphasize that upon going from EK1 to EK3 the molecular length increases up to almost the double (tab.1). It is known that size chain plays a very important role on end-to-end chain dynamics giving rise to significant effects on the dielectric normal-mode relaxation²⁵. However the effect on the segmental relaxation, responsible of the dielectric

α relaxation, is almost negligible^{25, 26}.

In summary, the experimental values of the KWW stretching exponential, β , for aryl-ether-ketone-ketone model compounds are within the theoretical limits predicted for systems of spatial dimensionality varying from 2 to 1. These values exhibit a smooth decrease with increasing molecular stiffness as expressed by the effective length of the virtual bond. According to obtained results, the lower limit, $\beta = 0.308 \approx 1/3$ equals the expected value for a fully aromatic all-para compound in a rod-like conformation having a spatial dimensionality $d=1$. The upper limit, $\beta=1$, would correspond to the value for an aromatic molecule with the virtual bond as short as the diagonal size of benzene.

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Table 1: T_g , $\Delta\epsilon$, b , c , τ_0 , values obtained from the fitting of HN equation and β , τ_{KWW} from the KWW equation at the temperatures reported in the second column. L is the molecular contour length[15]

sample	T_g	T(K)	$\Delta\epsilon$	b	c	$\tau_0(s)$	β	τ_{KWW}	L(nm)
EK1	297	313	7.7	0.95	0.59	$2 \cdot 10^{-3}$	0.65	$9.9 \cdot 10^{-4}$	2.33
EK2	333	343	6.1	0.89	0.51	$5.2 \cdot 10^{-3}$	0.53	$1.9 \cdot 10^{-3}$	3.26
EK3	353	368	1.16	0.87	0.48	$3.2 \cdot 10^{-3}$	0.49	$1.1 \cdot 10^{-3}$	4.24

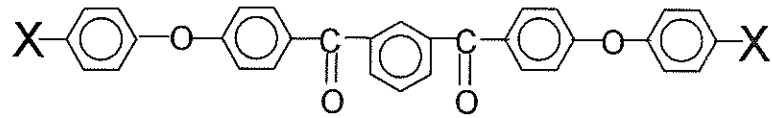
Legends to the figures.

Figure 1: Generalized Chemical Scheme of the EK model compounds.

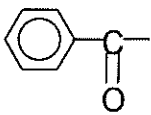
Figure 2: (upper) Normalized dielectric loss, ϵ'' , for the model compounds for the α relaxation process. The continuous lines represent the best fits to the HN relaxation function. (lower) Normalized $\phi(t)$ functions corresponding to the different model compounds. The continuous lines represent the best fits of the calculated data by the KWW function.

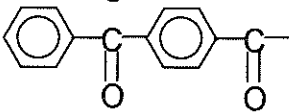
Figure 3: Dependence of β stretched exponential with the reciprocal value of the virtual bond

EK



EK1 X= H

EK2 X= 

EK3 X= 

(a)

fig. 1

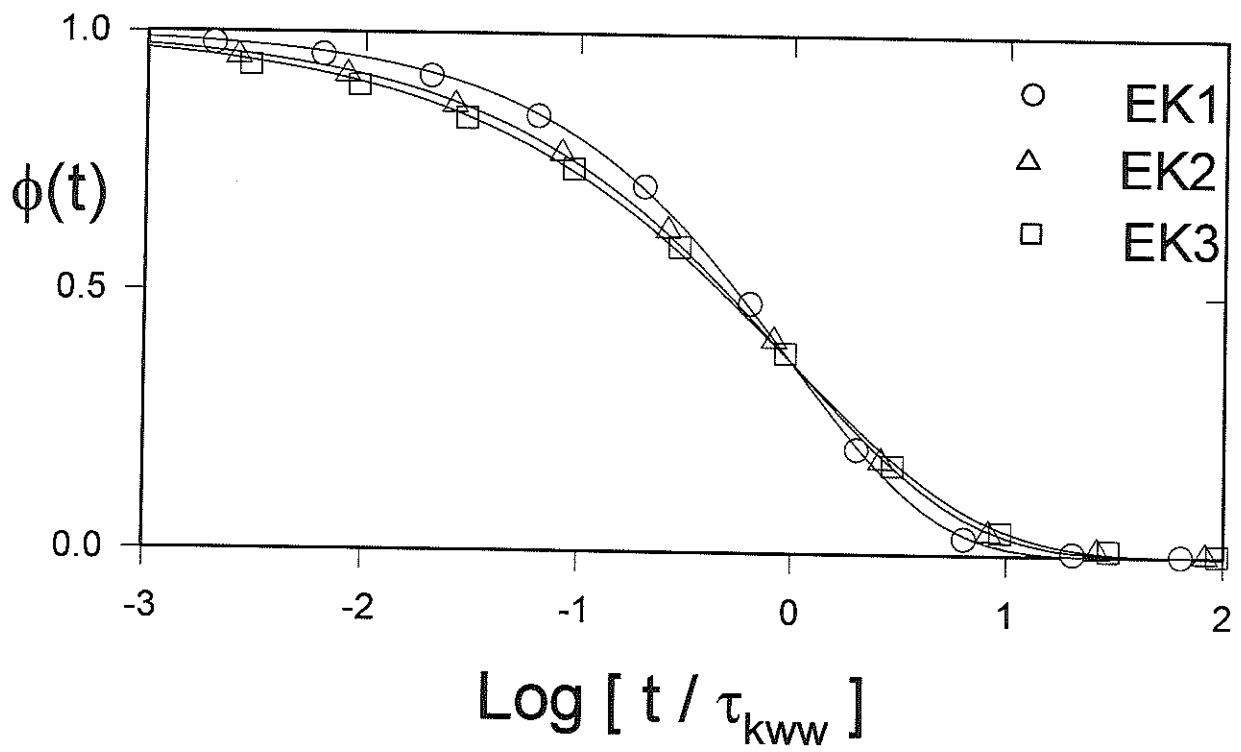
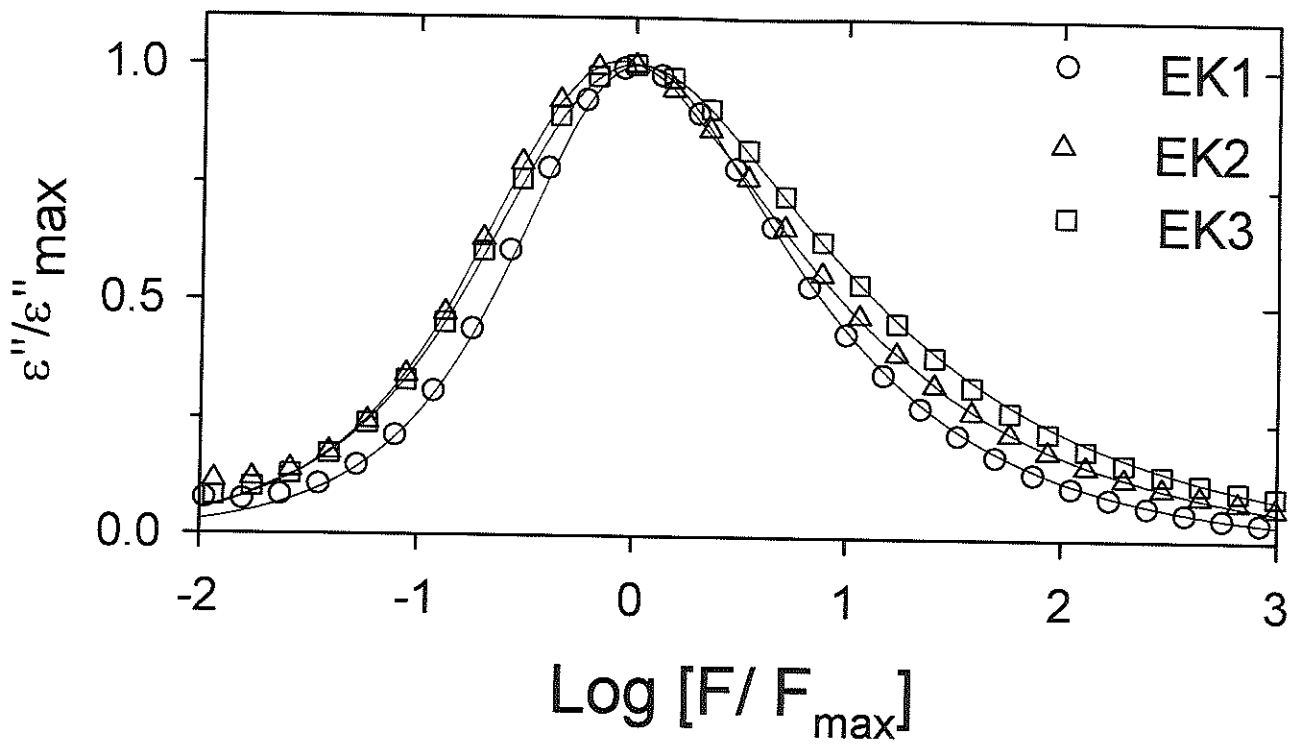


Fig.2

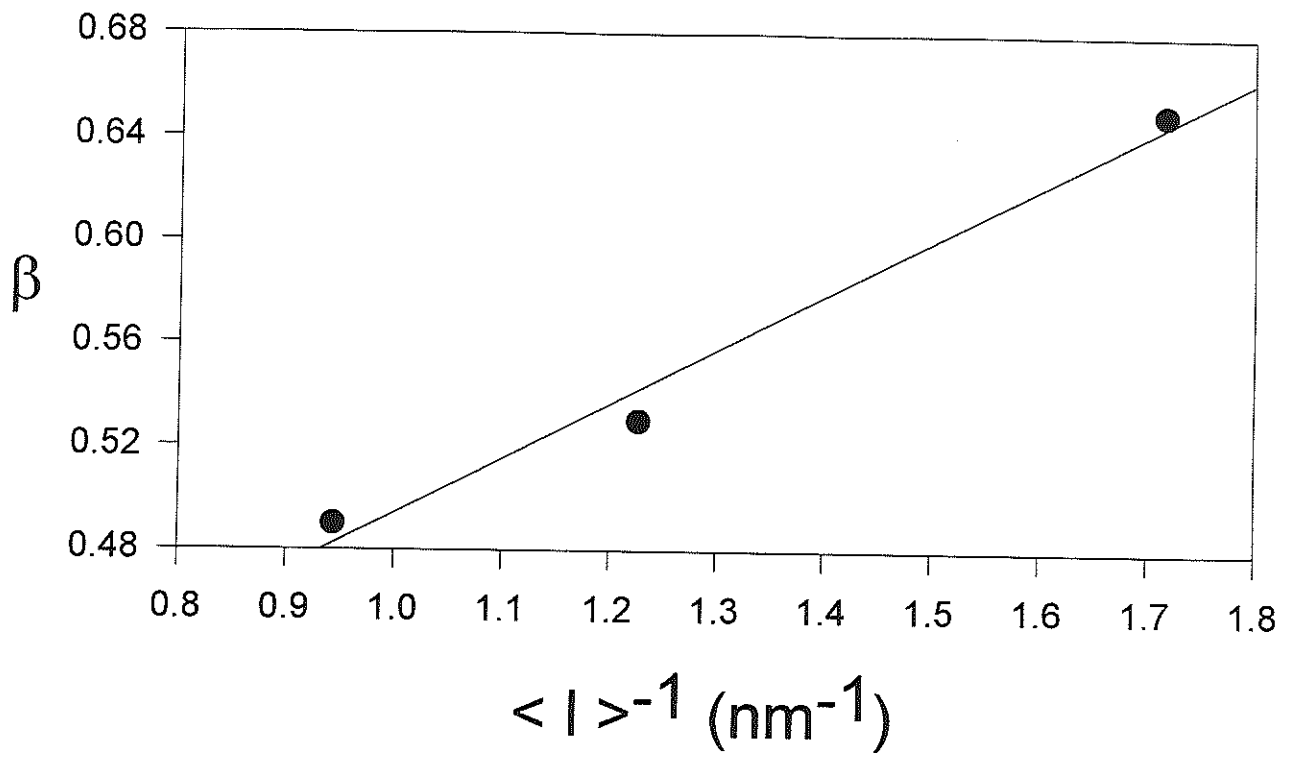


Fig. 3