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Dielectric investigations on secondary relaxation of polyarylates: comparison of low molecular models and polymeric compounds

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This paper focuses on the secondary relaxation (γ-relaxation) behaviour of a set of polyarylates and of the corresponding model systems composed of a single repeat unit and end-groups. The common feature of the compounds is that they contain short dipolar groups (O, C=O, CO–O, SO_2) between successive phenyl units. The method of analysis was dielectric spectroscopy. The aim of the investigations was to characterize the motions connected with this relaxation and their dependence on the chemical structure. It was found that all systems display γ-relaxations which have many features in common, such as for instance the activation energy. Yet differences also exist, for instance in terms of the relaxation strength and the relaxation time distribution, which reveal the impact of the actual chemical structure on the relaxation behaviour. The general conclusion is that the γ-relaxation has to be connected both with inter- and intramolecular motions, the correlation length of which cannot be much larger than the scale set by a single repeat unit.

(Keywords: polyarylates; γ-relaxation; dielectric investigation)

INTRODUCTION

Secondary relaxation processes taking place within the glassy state strongly affect macroscopic properties[1,2]. These relaxations lead, for instance, to stepwise variations of elastic moduli, dielectric constants or thermal expansion coefficients. Of particular interest is that the width, the strength and the frequency range of such transitions have been related to the ductility of main chain polymers. Polycarbonate (PC) of bisphenol A is a prominent example of the case where the 'local' γ-relaxation has been made responsible for the strong ductility of PC.

The molecular origin of secondary relaxations and in particular of that responsible for ductility has been and is still the topic of controversy. The view that seems to emerge currently is that it is not uniquely the phenyl π-flip which is the origin of this relaxation in phenyl ring-containing main chain polymers and the source of energy dissipation. Based on dielectric, dynamic mechanical, n.m.r. studies, neutron scattering, etc., the conclusion seems to be that the γ-relaxation involves, at least in PC, cooperative intramolecular and intermolecular motions[3,4]. The extent of correlation is still a matter of discussion. Floudas *et al.*[5] concluded, based among other things on consideration of density fluctuations, that the scale of the motion should not amount to more than the length of one monomer unit. The exact type of motion is not known; it may be rather complex involving small-angle fluctuations, conformational changes, motions controlled by a molecularly heterogeneous packing, etc.

Based on the results described so far, the expectation is that polymers containing phenyl rings along the chain backbone connected by short groups such as oxygen etc. should display secondary relaxations that have many features in common – at least on a qualitative level – due to the common mechanism. The expectation is even that model systems, the chemical structure of which corresponds approximately to that of the monomers, should also display such a relaxation, again with features similar to the ones observed for the polymers. On the other hand, the expectation is that the particular chemical structure of the polymers and model systems should give rise to differences in the relaxation properties on a quantitative scale, due to the presence of different intra- and interchain contributions.

It was the purpose of the investigation reported in this contribution to learn more about the character of the secondary relaxation in polymers carrying phenyl rings along the chain backbone and in particular about the impact of the chemical structure on this character. We have consequently selected for the investigations polyarylates containing O, C=O, CO–O–, SO_2 groups between successive phenyl units and we have, in addition, considered model systems composed of one repeat unit and end-groups. The method of analysis is primarily dielectric spectroscopy. The comparison of the results obtained for the various polymers and the corresponding model systems should allow us to draw conclusions with respect to the nature of the secondary process and its dependence on chemical structure, chain length, etc.

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EXPERIMENTAL

The four amorphous aromatic polymers investigated here and the four corresponding model compounds are shown in *Figure 1*. They are polyarylates, which constitute a class of high-performance materials[6–9]. The model systems are composed of one repeat unit of the polymers and an end-group. The dielectric measurements covered the frequency range from 20 Hz to 1 MHz; we used a Hewlett-Packard impedance analyser (HP 4284A). A nitrogen gas heating system and the fact that the measurements were fully computer controlled ensured a precision of 0.2 K in the temperature for a temperature range of 100–470 K. The samples were kept between two electrodes (diameter 20 mm) with a separation of about 100 μm for the polymers and 50 μm for the model compounds. The separation was maintained by spacers. To ensure a homogeneous thin film with perfect electric contact in the condenser, the samples were heated to above the glass transition temperature before the upper electrode was brought in contact with the samples. Because the materials degas in the liquid state within a short time interval, the samples prepared in this way were dry. We also investigated polymeric films prepared from solution. To obtain a perfect electric contact we sputtered both sides of the film and the electrodes with a gold layer.

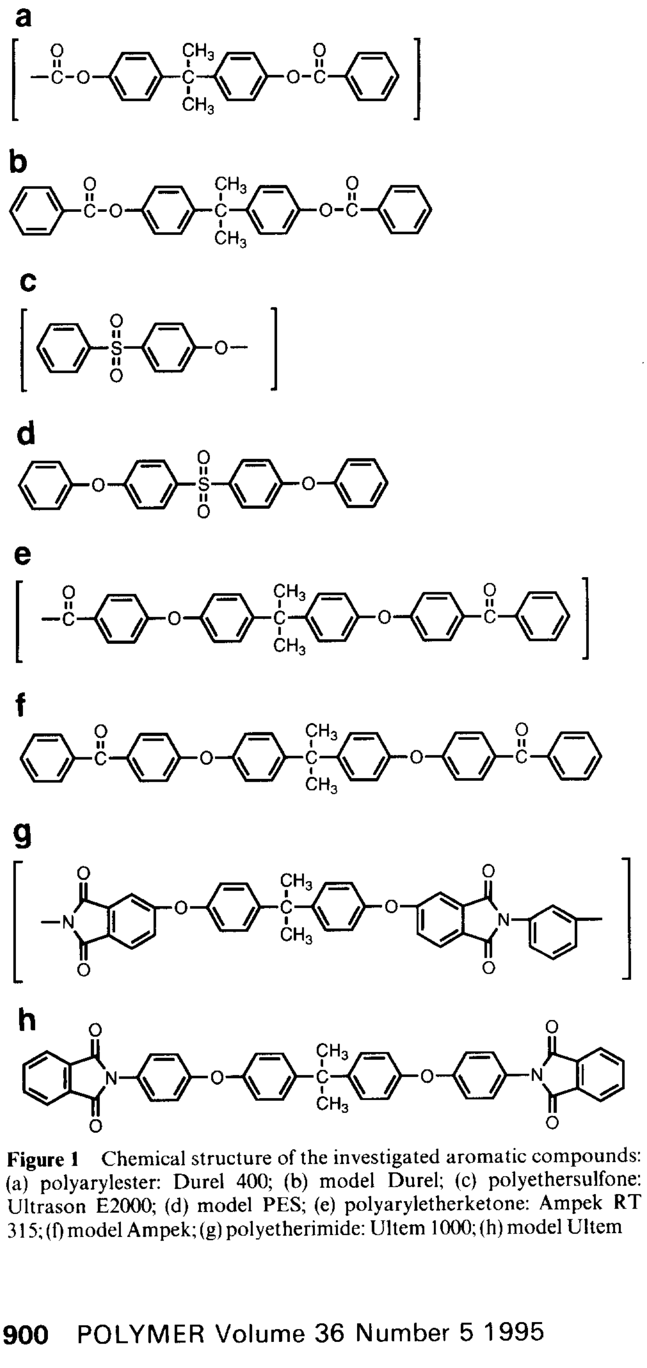

Figure 1 Chemical structure of the investigated aromatic compounds: (a) polyarylester: Durel 400; (b) model Durel; (c) polyethersulfone: Ultrason E2000; (d) model PES; (e) polyaryletherketone: Ampek RT 315; (f) model Ampek; (g) polyetherimide: Ultem 1000; (h) model Ultem

RESULTS AND DISCUSSION

The dielectric investigations reveal clearly that all compounds studied, i.e. the polymers and the corresponding model systems, display secondary relaxation processes. It furthermore seems that these processes have many features in common. One observation is, for instance, that the relaxation happens in about the same frequency range for a given temperature for all polymers and model systems. For the following discussion we will call this process γ-relaxation. The features common to all samples will be represented first and these features will be demonstrated using the results obtained for the polyarylate Durel and its model system.

Figure 2 displays the dependence of ε′ and ε″ on the frequency for a selected set of temperatures for Durel and *Figure 3* the same data for the model system. The close resemblance between the relaxation behaviour of the polymer and the model system, which carries specific end-groups, is obvious. This seems to indicate that the γ-relaxation cannot involve processes happening on a scale which is much larger than the one defined by the dipole-carrying groups located between the neighbouring phenyl rings. A similar conclusion can be drawn from a comparison of the relaxation behaviour of the different polymers.

A second feature which is common for all samples is that the temperature–relaxation time dependence

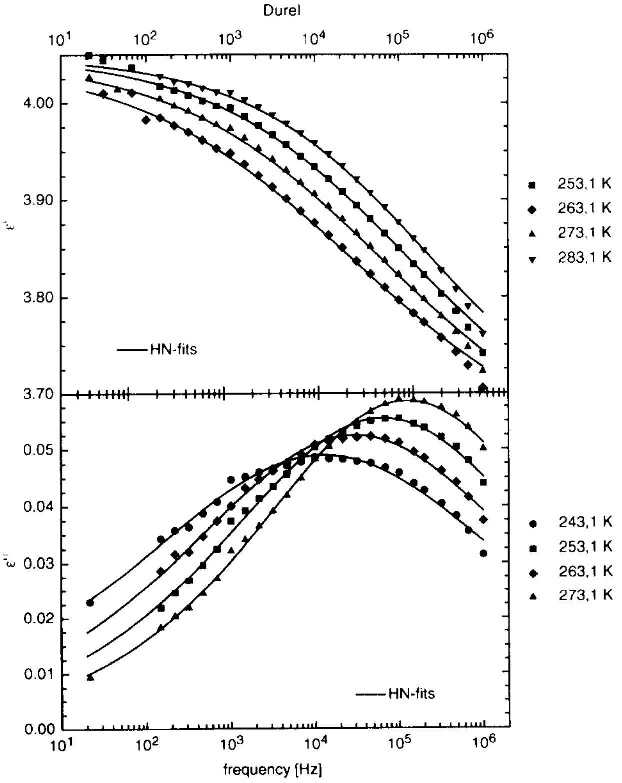

Figure 2 Durel 400: frequency and temperature dependence of the real part ε′ and the dielectric loss ε″ – experimental results and Havriliak–Negami fits; ε′ and ε″ *versus* frequency (log scale)

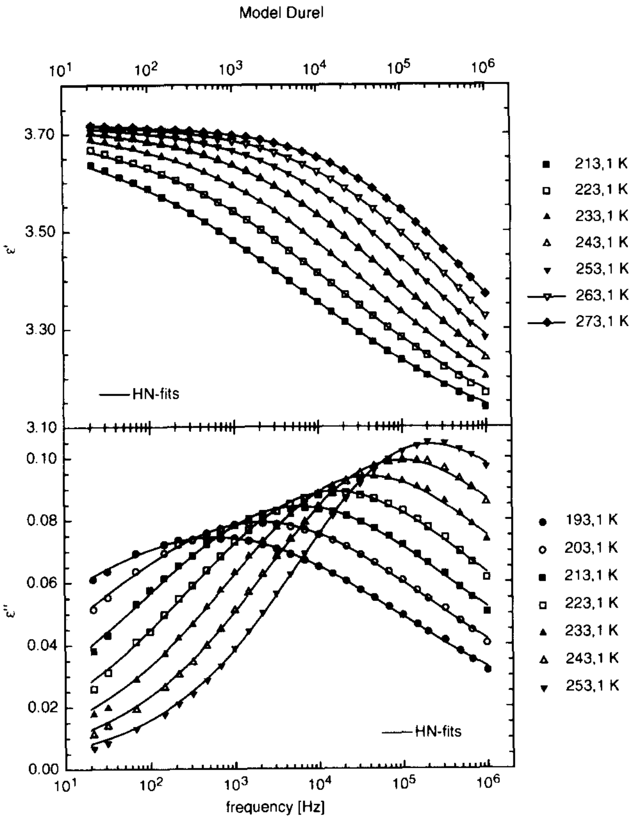

Figure 3 Model Durel: frequency and temperature dependence of the real part ε' and the dielectric loss ε'' – experimental results and Havriliak–Negami fits; ε' and ε'' *versus* frequency (log scale)

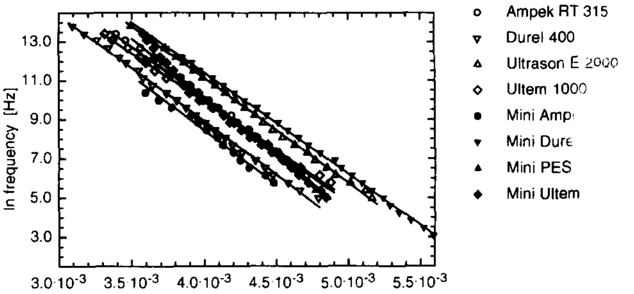

Figure 4 Arrhenius plot: activation diagram for the secondary relaxation of the eight investigated compounds showing ln frequency *versus* the reciprocal of temperature

corresponds to an Arrhenius type

$$\ln(\nu_{\mathrm{max}}) = \ln(\nu_0) - E_a/RT$$

as is apparent from *Figure 4*, which contains the results for all polymers and model systems studied. The activation energy amounts in all cases to 46 ± 3.5 kJ mol^{-1} and in addition we find that the prefactors $\ln(\nu_0)$ (32.1 ± 2) are also very similar, as apparent from *Table 1*. This means that the absolute values of ν_{max} for a given temperature vary only in narrow intervals. The variation furthermore is not a regular function of the chemical structure or of whether a polymer or model system is considered.

The features described so far are not only characteristic of the polyarylates and the model systems. Similar results have been reported for polycarbonate. Polycarbonate has the advantage that the number of investigations on its dynamic properties and the number of techniques employed to study the dynamic properties are very large. This allows us to draw some conclusions beyond those possible on the basis of the results presented so far.

The n.m.r. studies, for instance, have revealed the presence of a phenyl ring flip as a prominent mode of motion and that this process is related to the secondary relaxation of polycarbonate. The activation diagram and the corresponding activation energy are very similar to the ones observed for the polyarylates and the model systems. So the conclusion might be that we are actually observing in all cases relaxation properties which are controlled by an identical process, namely the phenyl ring flip. The assumption at this point is that predominantly the phenyl ring flips are the origin of the γ-relaxation. This is appropriate in view of the similar chemical structures of the systems considered in this contribution. The close neighbourhood of the phenyl rings and the dipoles which couple to the dielectric properties favour this interpretation. The process causing the γ-relaxation would thus be assumed to be a local one, involving only the phenyl ring and the neighbouring dipolar group in the chain backbone. However, data reported in the literature based, for instance, on neutron scattering are not in all cases in accordance with this interpretation. Investigations of other groups indicate that the phenyl flip is not of paramount importance for the secondary relaxation[5]. The authors conclude that the phenyl flip can be considered only as an indicator of the mobility of the molecule. Studies on liquid crystal materials containing an ester group between two phenyl rings[10,11] lead to a similar conclusion. The temperature range and the activation energy of dielectric relaxation correspond to those of the phenyl flip, but a molecular correlation cannot be established. Considering this fact, the results obtained for the polyarylates containing different dipolar groups in the neighbourhood of the phenyl groups, that the relaxations are characterized by the same activation energy, are more than unexpected. This result provides a new element in the discussion about the interrelationship between the phenyl flip and the secondary dielectric relaxations.

In the following we will report features of the relaxation process observed for our systems which are not in accordance with the assumptions that the γ-relaxation is connected only with intrachain motions involving just the phenyl ring and the neighbouring group.

Table 1 Activation energies of the secondary relaxation

	E_a (kJ mol^{-1})	$\ln \nu_0$ (Hz)
Durel	46.7	31.3
Model Durel	43.1	32.1
Ultrason	44.6	32.6
Model PES	48.0	33.1
Ampek	45.9	32.2
Model Ampek	46.5	30.8
Ultem	42.8	30.5
Model Ultem	50.1	34.2

The width of the relaxation time distribution

One of such features is that this relaxation displays a rather broad width in the frequency domain. A purely local intrachain process should have a restricted width since all neighbourhoods of the relaxing groups should be quite similar. To analyse the width of the distribution we fitted the relaxation data to the empirical Havriliak–Negami expression[12–14]:

$$\varepsilon^* - \varepsilon_\infty = \frac{(\varepsilon_0 - \varepsilon_\infty)}{[1 + (i\omega\tau_{HN})^{1-\alpha}]^{\beta}}$$

where the broadness and the asymmetry of the relaxation time distribution are represented by the parameters α and β respectively. The relaxation time distribution $G(\ln\tau)$ is given by

$$G(\ln\tau) = \frac{1}{\pi} \times \frac{(\tau/\tau_{HN})^{\beta(1-\alpha)}\sin\beta\theta}{\{(\tau/\tau_{HN})^{2(1-\alpha)} + 2(\tau/\tau_{HN})^{(1-\alpha)}\cos\pi(1-\alpha) + 1\}^{\beta/2}}$$

where θ stands for

$$\mathrm{arctg}\left[\frac{\sin\pi(1-\alpha)}{\{(\tau/\tau_{HN})^{(1-\alpha)}\cos\pi(1-\alpha)\}}\right]$$

A Debye-like relaxation characterized by a single relaxation time is represented by a value for α of 0 and β of 1. Furthermore, a value for β of 1 indicates a symmetric relaxation distribution. *Figures 2* and *3* display the fits of this expression to the experimental data. It is obvious that the fit is satisfactory; the parameters α and β obtained for different temperatures are given in *Table 2*. It is sufficient to state here that the relaxation is indeed broad. *Figure 5* displays, for instance, in terms of the corresponding Cole–Cole plot the broad character of the relaxation. The relaxation time distributions are shown in *Figure 6* for Durel and model Durel. A broad distribution is thus a feature common to the polymeric and the model system.

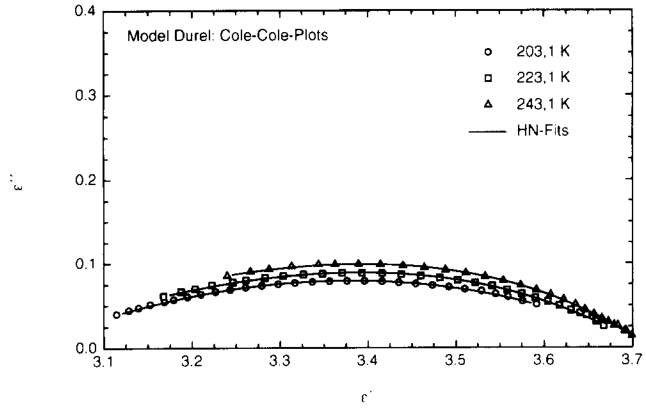

Figure 5 Model Durel: characterization of the relaxation process – Cole–Cole plots showing experimental results and Havriliak–Negami fits for different temperatures; ε'' *versus* ε'

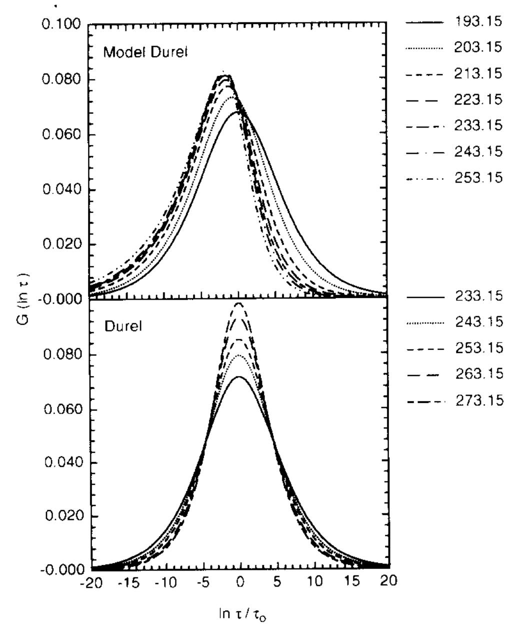

Figure 6 Model Durel and Durel: relaxation time distribution $G(\ln\tau)$ *versus* $\ln(\tau/\tau_0)$ for different temperatures

Table 2 Havriliak–Negami parameters α and β for Durel and model Durel

Temperature (K)	Durel α	Durel β	Model Durel α	Model Durel β
188.15			0.74	1.0
193.15			0.74	1.0
198.15			0.73	0.94
203.15			0.70	0.79
208.15			0.68	0.71
213.15			0.65	0.60
218.15			0.63	0.52
223.15			0.62	0.51
228.15			0.60	0.46
233.15	0.73	1.0	0.6	0.46
238.15	0.72	1.0	0.56	0.37
243.15	0.70	1.0	0.57	0.42
248.15	0.70	1.0	0.56	0.39
253.15	0.68	1.0	0.54	0.35
258.15	0.67	1.0		
263.15	0.66	1.0		
268.15	0.65	1.0		
273.15	0.64	1.0		
278.15	0.63	1.0		
283.15	0.62	1.0		

The dependence of the width on the temperature

A second indication of the effect of intermolecular interactions is that a symmetric and strong broadening occurs as the temperature is decreased for both systems. This behaviour is very similar to that of the secondary relaxation of PC[15,16]. This temperature effect points directly to an intermolecular contribution to the relaxation behaviour.

The effect of chemical structure on the relaxation time distribution

The variation of the chemical structure of the backbone using different neighbouring groups does not lead to significant changes in the relaxation properties. We thus conclude that the intramolecular interactions in the polymeric system do not predominantly determine the relaxation; this fact confirms the dominant influence of the intermolecular interactions.

Symmetry of the relaxation time distribution

The distributions of polymer and low molecular mass model systems are clearly characterized by different symmetries at higher temperatures. An interesting feature is that the relaxation time of Durel shows a symmetric distribution for all temperatures whereas the relaxation time distribution of model Durel shows an asymmetric character (*Figure 6*). We propose an interpretation of these results based directly on the chemical structure (*Figure 1a, b*). In contrast to the polymeric systems the model systems possess phenyl groups at the end of the molecules. These phenyl groups obviously experience smaller hindrance. This motion leads to a shift to smaller relaxation times and thus to an asymmetric relaxation time distribution.

Thus we suggest that the discussed similarities and differences clearly point to a restriction of the extent of the intermolecular and intramolecular correlation. We propose a dominant influence of the intermolecular interactions on the relaxation. Furthermore, we conclude that the scale of the motion should not amount to more than the length of one repeat unit. The asymmetry of the distribution for the model system points to an extent of intramolecular correlation including more than one neighbouring group. These features are characteristic also for all the other compounds considered here, at least on a qualitative basis, yet strong differences exist on a quantitative basis. This is obvious from the data obtained for the parameters α and β. This holds for a comparison between the different polymers and also for a comparison between the polymer and the corresponding model system. The conclusion thus has to be that the γ-process is controlled by motions which have to contain non-local intermolecular and intramolecular components.

The same conclusion can be drawn from a consideration of the strength of the γ-relaxation, defined as $\varepsilon_0 - \varepsilon_\infty$ where ε_0 is the relaxed and ε_∞ the unrelaxed value of ε' (in the neighbourhood of the γ-relaxation). To judge the data obtained on the relaxation strength we have performed calculations on the most favourable configurations of the individual structures considered here and on the corresponding dipole moments, using the semi-empirical quantum mechanical method Mopac 6. *Figure 7* shows as an example the result for the biphenylester as compared with the one for the biphenylether and *Table 3* contains the dipole moments obtained for the different chain segments. The result is that the absolute values of the dipole moments located between consecutive phenyl rings are of the same magnitude in all cases, so one would expect similar relaxation strengths for all polymers and model systems. This is in particular true on the basis of the n.m.r. results, suggesting the presence of phenyl ring flips in all samples. Yet the results do not correspond to this expectation, as

Table 3 Dipole moments for the relevant groups (given by X in phenyl-X-phenyl)

X	μ (Debye)
-CO-	2.97
-CO-O-	2.13
-O-	1.25
$-SO_2-$	5.5

Table 4 Comparison of tan δ and relaxation strength

	Maximum tan δ ($\times 10^{-3}$)	Relaxation strength ($\varepsilon_s - \varepsilon_\infty$)
Durel	10–18.5	0.45
Model Durel	19–33	0.765
Ultrason	2.6–3.5	0.15
Model PES	0.85–1.2	$\ll 0.1$
Ampek	1.25–2	$\ll 0.1$
Model Ampek	1.1–1.9	$\ll 0.1$
Ultem	0.95–1.2	$\ll 0.1$
Model Ultem	0.8–1.5	$\ll 0.1$

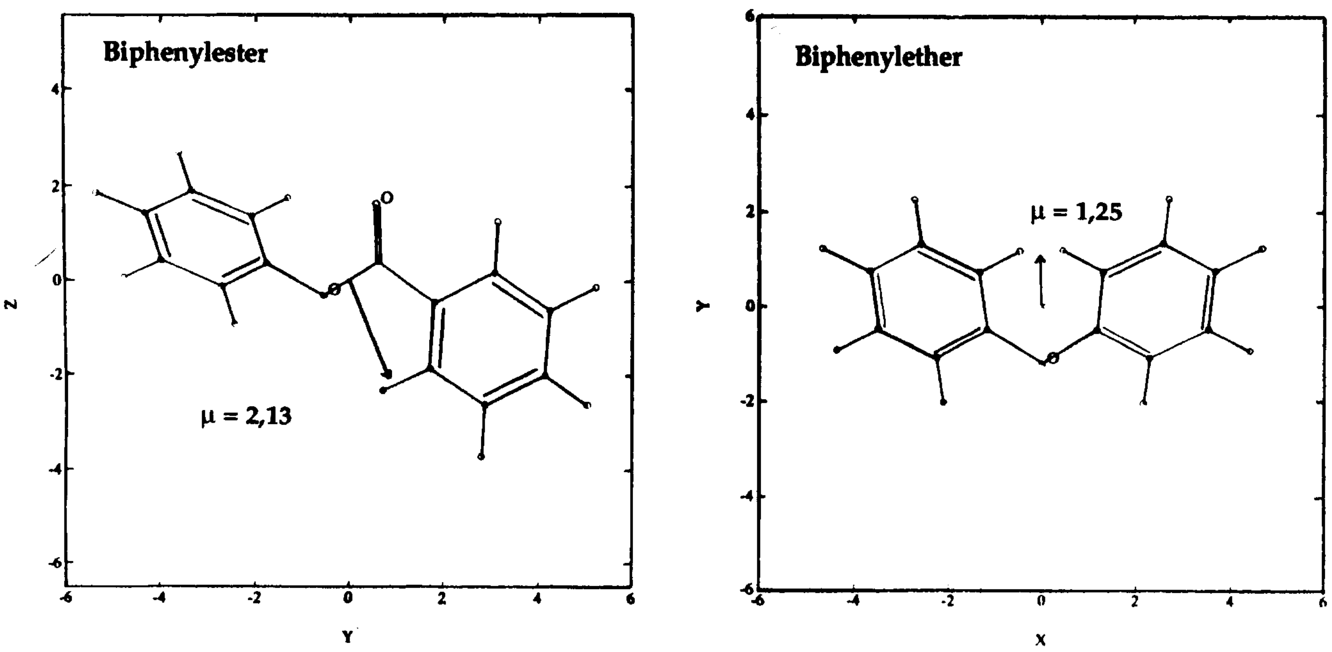

Figure 7 Favourable configurations for biphenylester and biphenylether and dipole moments, results obtained using Mopac 6

is apparent from *Table 4*. It is obvious that the relaxation strength is large for Durel and its model system as compared with all the other samples studied. We therefore have to conclude again that the relaxation processes happen on a scale larger than just the scale defined by a phenyl ring and the neighbouring dipolar groups along the chain backbone.

The different intrachain and interchain configurations apparently give rise to different restrictions with respect to the motion of the dipoles. The ester group in Durel and in model Durel, for instance, is the only group which gives rise to an approximately linear chain segment. It is able to rotate over an appreciable angle without requiring a larger motion of the neighbouring chain units. This interpretation is in agreement with quasistatic simulations of localized motions in PC[17]. A rotation of the ketone, ether and sulfone groups will cause a corresponding motion in the neighbouring groups, so that this motion is strongly hindered and the corresponding relaxation strength is weak.

Finally, a very strong point in favour of the non-local character of the processes causing the γ-relaxation is the strong impact of the presence of water on the relaxation properties. The data reported above were obtained for samples which were carefully dried prior to any dielectric analysis. Samples containing water in a controlled manner display a γ-relaxation, the strength of which is strongly increased, usually by more than an order of magnitude. The activation energy and the frequency range for given temperatures in which the relaxations occur are still the same. We pointed out in earlier publications[6-8] that the presence of water enhances the secondary relaxation strength for polyarylates. The origin of the modification of the dielectric properties by water may be twofold: water acts as a local plasticizer and water provides additional dipoles which contribute to the observed relaxation strength. In any case the conclusion has to be that the γ-relaxation is not only controlled by localized processes involving just a phenyl ring flip coupled to a similar motion of the neighbouring dipoles along the chain backbone.

CONCLUSION

Based on the dielectric relaxation studies performed on a systematic set of polyarylates and the corresponding model systems we have to conclude that the basic motion giving rise to the secondary γ-relaxation is the same in all cases. This is obvious from the fact that the activation energies are identical, that the relaxations happen independently of the length of the molecules and the particular chemical structure in the same frequency range for given temperatures. All compounds are, in addition, characterized by a rather broad distribution of the relaxation time. The comparison between the relaxation behaviour of the particular polymer and its model system shows that the correlation length cannot be much larger than the scale set by the length of the repeat units.

The observations that the relaxation strength depends, at nearly equal magnitude of the dipoles of the relaxing groups, on the chemical structure, that the relaxation time distribution is different for polymer and low molar mass model components and, finally, that the presence of water has a strong effect on the relaxation strength lead us to the conclusion that the γ-relaxation has to involve both intrachain and interchain contributions; the scale of the correlation has been given above.

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