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Dielectric relaxation behaviour of fluorinated aromatic poly(ether)s and poly(ether ketone)s

A.A. Goodwin[a,]*, J.R. Atkinson[b], J.N. Hay[b], F.W. Mercer[c]

[a]*Materials Engineering, Monash University, Clayton, Victoria 3168, Australia*
[b]*Metallurgy and Materials, Birmingham University, Birmingham B15 2TT, UK*
[c]*Research and Development, Raychem Corporation, Menlo Park, CA 94025, USA*

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Abstract

Eight amorphous, thermoplastic aromatic poly(ether)s and poly(ether ketone)s, some containing fluorine, were investigated by dielectric relaxation spectroscopy over the frequency range 20–10^5 Hz and the temperature range −130–300°C. For the polymers containing perfluorophenylene units, three relation processes were observed; one corresponding to the glass transition (α-relaxation), and a further two sub-T_g secondary process (β- and γ-processes). For polymers without perfluorophenylene units, a β-process was not detected. The sub-T_g transitions followed Arrhenius behaviour and were sensitive to polymer structure and chain flexibility. The sub-ambient relaxation exhibited a strong dependence on absorbed moisture. The polymers containing perfluorophenylene units showed a significant decrease in dielectric permittivity at 100 kHz and this was attributed mainly to a reduced electronic polarisability. The α-relaxation strength of the perfluorinated polymers, which arises from dipolar motions, was also reduced. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorinated polymers; Dielectric relaxation spectroscopy; α-relaxation

1. Introduction

Aromatic thermoplastic polymers are generally characterised by excellent thermal, mechanical and electrical properties, and can be melt processed into a wide range of articles [1]. Such polymers are commonly used to insulate current carrying cables due to their relatively low dielectric constant and processing characteristics. In the electronics industry, however, the small size-scale of components and the desire for faster signal processing is placing greater demands on the properties of polymer dielectric interlayers, such that insulators are required with dielectric constants below those achievable with conventional thermally stable polymers [2]. Polyimides have proved good candidates for use as dielectric materials in these applications as a result of their ease of processing from solution, high thermal stability and good electrical performance. The fluorination of these polymers affects a number of properties, e.g. moisture absorption, optical properties and dielectric constant [3]. The glassy state dielectric constant is lowered since the incorporation of fluorine increases the fractional free volume, lowers the electronic polarisability (providing the fluorine substitution pattern is symmetric) and increases the hydrophobic character of the polymer [4]. Studies on aromatic polyimides and partially fluorinated aromatic polyimides have shown that moisture absorption and dielectric constant are directly related to the total imide content of the polyimide [5]. Dielectric constants as low as 2.7 (at 10 kHz) and equilibrium water uptake as low as 0.7 wt% were achieved by fluorinating both dianhydride and diamine units, and these minimum values were obtained with 20 wt% fluorine. The pattern of fluorine substitution is important in determining the dielectric constant since the dipole orientation increment due to asymmetric substitution is often large enough to overcome the decrease in electronic polarisation caused by the fluorine, and it has been shown that the primary factor in reducing the dielectric constant is the elimination of water from the polymer [4].

Qualitatively similar results have been reported for fluorinated thermoplastic poly(ether)s and poly(ether ketone)s containing hexafluoroisopropylidene (HFIP) and perfluorophenylene units [6,7]. The amorphous nature of these polymers renders them soluble in aprotic solvents and allows for film casting from solution. These polymers are being investigated as candidates for micro-electronic applications, as the absence of polar imide groups and presence of

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* Corresponding author.

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symmetric substituted fluorine leads to a reduction in water uptake to 0.1 wt% with a corresponding decrease in the room temperature dielectric constant to around 2.5.

In this paper, we report the dielectric behaviour of a series of non-crystallising aromatic poly(ethers)s and poly(ether ketone)s containing cyclic 2,2′-biphenyl, HFIP (6F), perfluorophenylene and oxadiazole groups, to learn of the effects of fluorination and chemical structure on dielectric properties over a wide temperature range. The dielectric parameters obtained within the α-relaxation region will be compared with those obtained from ambient temperature studies and will be discussed in terms of electronic and dipolar polarisability. The secondary relaxation behaviour of these polymers will also be reported.

2. Experimental

2.1. Materials

Details of the synthetic methods used to prepare the polymers can be found elsewhere [8]. Weight average molecular weights varied between 38 000 g/mol and 102 000 g/mol with polydispersities in the range 2.1 to 3.0 [9]. Tough, transparent films for analysis were prepared by solution casting or compression molding, and scanned by d.s.c. to determine the glass transition temperature. Polymer structures are shown in Fig. 1.

2.2. Dielectric relaxation spectroscopy

Dielectric relaxation data were obtained using a Polymer Labs DETA system which incorporated a parallel plate cell arrangement and computer-controlled furnace. To ensure good electrical contact between the electrodes and sample, the polymer films were sputter coated with a thin layer of gold. The main parameters of interest were dielectric constant, ϵ', and dielectric loss, ϵ'', which were determined over the frequency range 20–10^5 Hz at temperatures between −130°C and 300°C. Experiments were carried out in both temperature scanning and isothermal modes in an inert atmosphere of nitrogen gas.

2.3. Curve fitting

Non-linear least-squares fitting of the dielectric loss data was accomplished with PeakFit 4.04 software (Jandel Scientific) which utilises the iterative Marquardt–Levenberg fitting algorithm. The confidence intervals for the model parameters were determined at the 95% limit and a graphical pre-fitting method was used to manipulate the fitting function on the screen to match the experimental data prior to fitting.

3. Results and discussion

In this section, we will compare values of dielectric relaxation strength, $\Delta\epsilon$, with ambient permittivity, ϵ', and it is worth noting the differences between the parameters. Relaxation strength is estimated by fitting a suitable function to isothermal loss data to obtain values of the relaxed and unrelaxed permittivity which are not accessible within the experimental frequency range. This procedure is performed on data obtained at temperatures above the glass transition temperature and is thus dominated by dipole orientation polarisation. Ambient permittivity for glassy polymers is, on the other hand, a single low frequency measurement which is considered to be mainly due to electronic polarisation, since dipolar units are mainly immobile in the glass state. It should be noted, however, that some authors consider ϵ' to also consist of contributions from atomic and dipole orientation polarisation. This would indeed be the case for those polymers which possess γ and β processes, e.g. polyimides.

3.1. Electronic polarisation

Table 1 presents the dielectric permittivity, ϵ', of each polymer measured at 100 kHz and 25°C. Prior to each measurement, the sample was thoroughly dried under vacuum to lessen the influence of absorbed moisture on the permittivity. Since all the polymers have glass transition temperatures greatly in excess of room temperature, we make the assumption that dipolar motions are severely restricted and that the measured value of ϵ' arises from the electronic polarisation of the sample. We can see by comparing the data for **1** with **2** and **3** with **4**, that hexafluoro substitution of the cyclic biphenyl group results in a modest decrease in ϵ', but that values remain above 3. If we then compare **1** with **7** and **2** with **8** we see that incorporation of perfluorinated groups reduces the permittivity to values below 3.0. However, while the trend in ϵ' with weight percent fluorine is generally decreasing, it is not perfect. This is because of other structural features which influence ϵ' and make exact comparisons difficult. For example, although **5** has the highest fluorine content of 43%, it has the highest permittivity (2.61) amongst the perfluorinated polymers. The cause of this may be the absence of the polar carbonyl unit which would otherwise restrict electron motions. Polymer **6**, which has a fluorine content of 24%, shows the lowest recorded ϵ' value of 2.10, and it is worth noting here that St. Clair et al. [10] have reported that the incorporation of bulky side groups, in addition to fluorine-containing monomers, is an effective method for reducing chain-to-chain electronic interactions and ambient polarisability. Comparisons between the observed permittivity of **3** and **4** and the other polymers is also difficult since both contain a polar oxidiazole unit. In addition to the potential effects of chemical structure and water content on electronic polarisation, there is also the possibility of changes in free volume occurring with changing structure influencing ϵ', and although we have made no attempt to alter our data to account for this factor, other authors have reported a correlation [4].

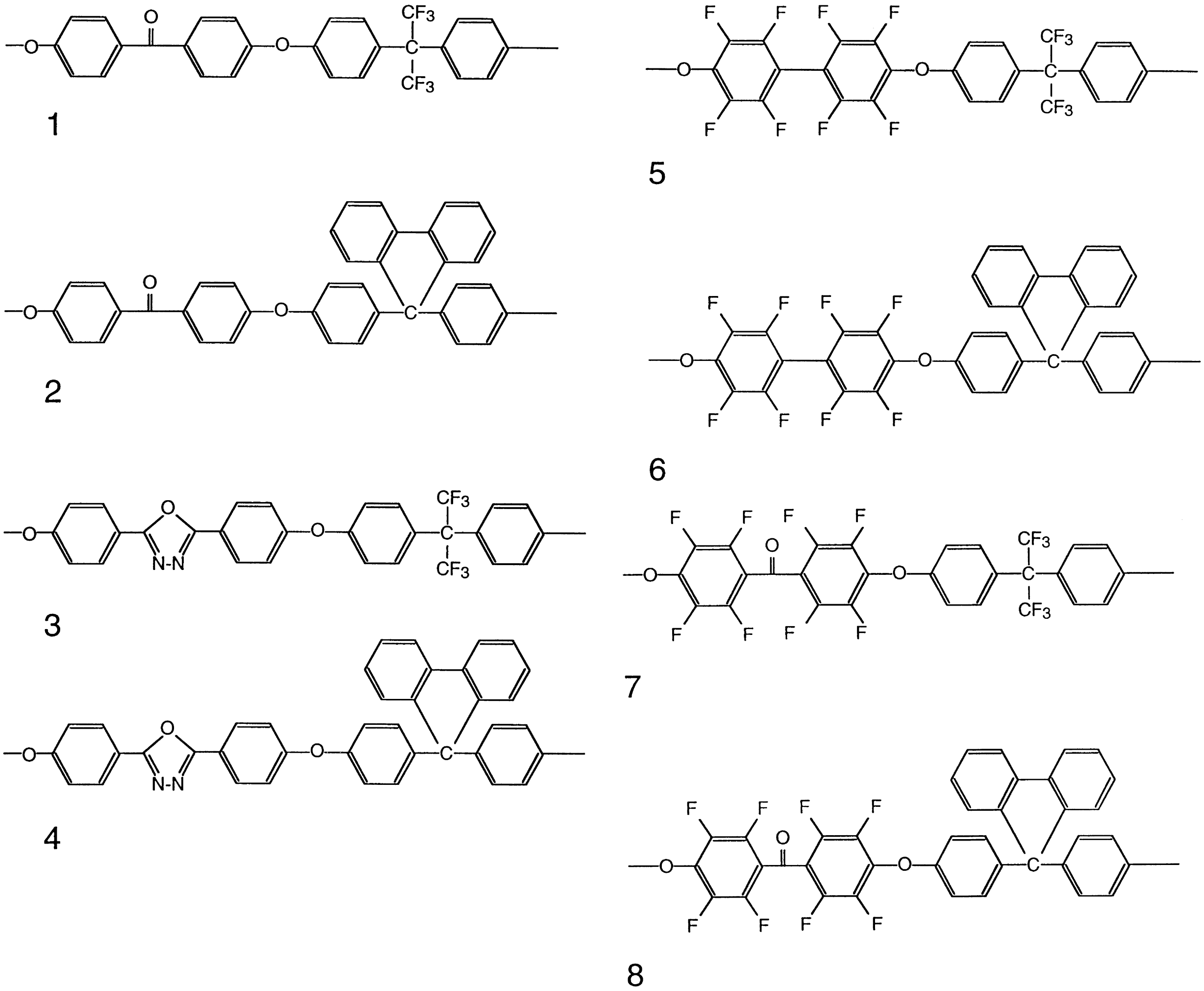

Fig. 1. Chemical structures of aromatic poly(ether)s and poly(ether ketone)s.

3.2. α-relaxation

d.s.c. and dynamic mechanical glass transition temperatures are listed in Table 2. The relationship between T_g and polymer structure in these materials has been briefly discussed previously [9] and it is of note to report that the slight relative decrease in T_g of the polymers containing perfluorophenylene substitution is consistent with previous studies on fluorinated polyimides [11], and probably arises from a combination of both fluorine-induced increase in free volume and decrease in the strength of inter-chain interactions. The temperature dependence of dielectric loss of **6** and **7** scanned at various frequencies is shown in Fig. 2. The relatively strong peak in ϵ'' corresponds to the glass transition, and this is preceded in both cases by a low intensity, broad transition, this being more prominent in **6**. A comparison of the dielectric α-relaxation results for all samples is shown in Fig. 3 as a plot of the temperature dependence of log τ, where log $\tau = 1/2\pi f_{\max}$, where $f_{\max}$ corresponds to the temperature of the peak maximum. The frequency and temperature location of the loss peaks shows good agreement with those previously measured using dynamic mechanical analysis [9], as can be seen in Table 2 where the glass transition temperature of each polymer, measured by three different techniques, is listed. The variation in T_g with technique for individual polymers is accounted for by the different effective frequencies of measurement. Although the temperature dependence of the relaxation time exhibits the usual curvature associated with the dynamics of the α-relaxation, we can make an approximate comparison of the activation energy for the glass transition process by fitting the data to the Arrhenius

Table 1
Dielectric permittivity, ϵ', of poly(ether)s and poly(ether ketone)s measured at 100 kHz and 25°C

Polymer	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
ϵ'	3.20	3.31	3.04	3.19	2.61	2.30	2.38	2.26

Table 2
Glass transition temperatures (°C) of poly(ether)s and poly(ether ketone)s measured by different techniques

Polymer	d.s.c. T_g	Dynamic mechanical T_g(1 Hz)	Dielectric T_g(1 kHz)
1	159	173	196
2	234	249	266
3	192	206	210
4	267	282	300
5	167	182	190
6	248	262	269
7	149	160	184
8	216	236	261

d.s.c. and dynamic mechanical values are taken from Ref. [9]

equation. Activation energy values between 450 − 600 ± 35 kJ/mol were found, but no clear trend between polymer structure and rotational barriers was apparent from these data. The high values of activation energy are due to the rigid aromatic nature of the polymers. Isothermal dielectric studies were also carried out at a range of temperatures, and a typical result is shown in Fig. 4 for **1**. The steep upturn at low frequencies is caused by ionic conduction and can be subtracted from the dielectric loss due to dipole motions as previously described [12]. The latter can be fitted to the Havriliak–Negami equation [13] given by:

$$\epsilon * = \epsilon_u + \frac{(\epsilon_r - \epsilon_u)}{[1 + (i\omega\tau)^{\beta}]^{\alpha}} \tag{1}$$

where $(\epsilon_r - \epsilon_u) = \Delta\epsilon$ is the relaxation strength, and β and α represent transition broadness and skew, respectively. The loss curves can also be fitted to the Kohlrausch–Williams–Watts (KWW) function [14]:

$$\phi(t) = \exp(-t/\tau)^{\beta} \tag{2}$$

where τ is a characteristic relaxation time and β is a broadness parameter. The temperature dependence of the isothermal relaxation broadness as described by the KWW parameter is shown in Fig. 5, in which the isothermal temperature is normalised by subtracting the d.s.c. T_g value to account for the different glass transition temperatures. The spectral broadness does not vary as a strong function of temperature for any of the polymers, which is in good agreement with a previous study on poly(arylene ether)s with similar structures to those studied here [15]. In that study, the authors used the Havriliak–Negami expression to obtain the distribution of relaxation times which were found to vary by only a few percent for polymers containing various bisphenol and phenolphthalein units. Such small differences in the values were attributed to the structural similarity of each polymer. By contrast, the values of β in Fig. 5 show a significant variation between polymers, although the data do not point towards a simple, empirical relationship between polymer structure and relaxation width.

Fu et al. [15] also used an empirical model to investigate

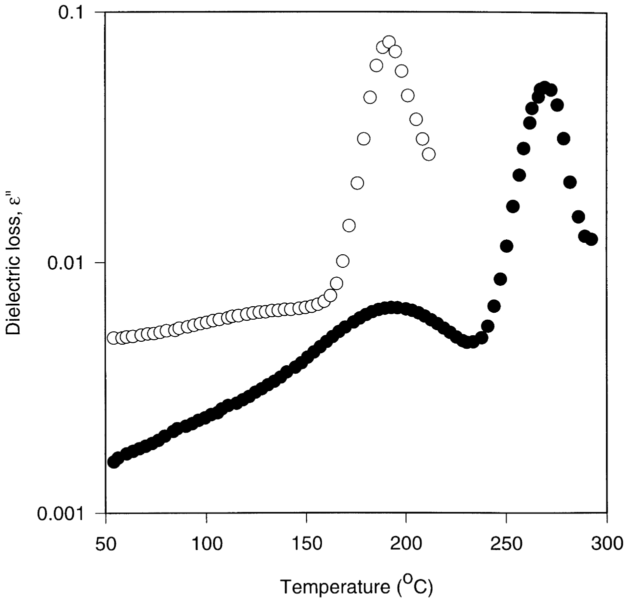

Fig. 2. Temperature dependence of dielectric loss: (●) **6** at 1 kHz; (○) **7** at 250 Hz.

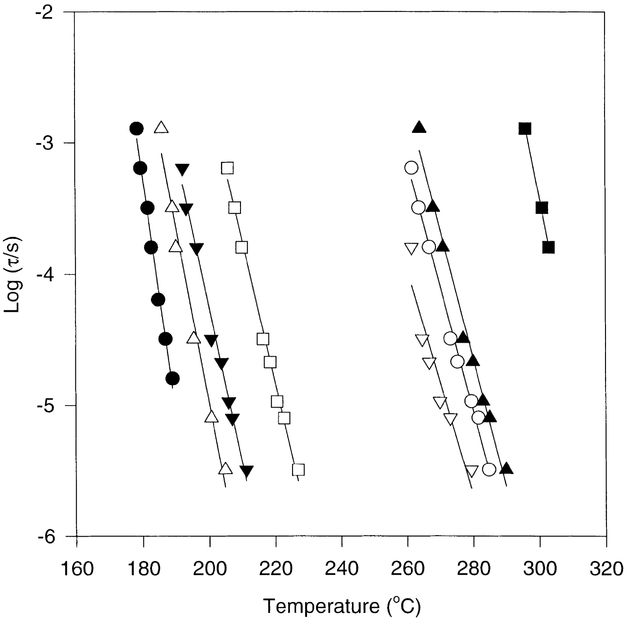

Fig. 3. Temperature dependence of the α-process relaxation time. (●) **1**; (○) **2**; (□) **3**; (■) **4**; (△) **5**; (▲) **6**; (▼) **7**; (▽) **8**. Solid lines are fits to Arrhenius equation.

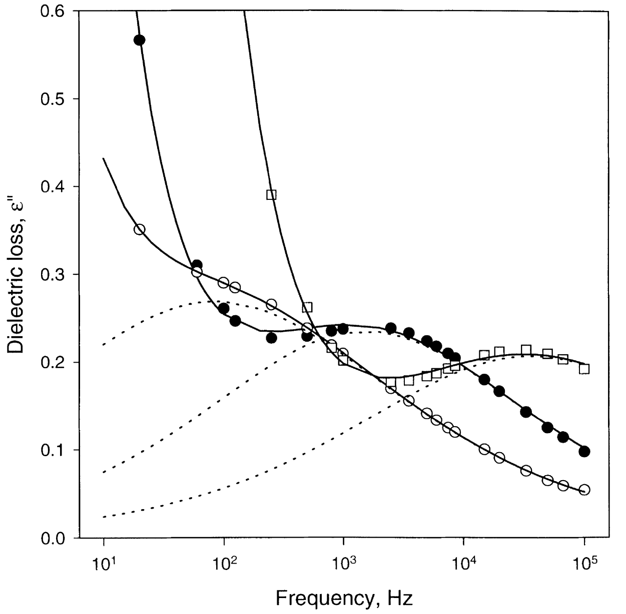

Fig. 4. Frequency dependence of dielectric loss for **1**. (○) 174°C; (●) 177°C; (□) 180°C. Solid lines are summation of conductivity and dipolar loss. Dashed lines are fits to Havriliak-Negami equation.

the inter-molecular and local segment dynamics, and this showed that polymers containing HFIP units experienced a greater extent of inter-molecular coupling as well as greater hindrance to the local segment motions. To investigate this further in our systems, we plot log (relaxation time) against the inverse of the experimental temperature, normalised by the calorimetric glass transition temperature, for **1** and **8** to give the cooperativity plot shown in Fig. 6. It has previously been shown for many polymers [16] that the steepness of the time/temperature dependence is closely related to the extent of inter-molecular cooperativity which in turn is related to chemical structure. Generally, polymers with rigid, inflexible backbones experience a greater coupling of segmental motions and this leads to steeper cooperativity plots. Fig. 6 compares the cooperativity behaviour of a smooth polymer backbone (**1**) with that of a more rigid structure containing a cyclic biphenyl unit in addition to perfluorophenylene units (**8**). Polymer **1** exhibits Arrhenius behaviour, while the relaxation time behaviour of **8** is curved, which indicates the increased cooperative nature of segmental motions. Coupling in this polymer would be expected to be reasonably strong due to the bulky cyclic biphenyl group which would create a significant amount of steric hindrance amongst neighbouring chains. In general, it was found that the polymers containing cyclic biphenyl were more coupled than those without, and that the steepness of the cooperativity plot was largely unaffected by the presence of aromatic fluorine. Another measure of coupling relates to the broadness of the relaxation process, since this can be related to the greater range of environments in which segmental motions occur. This can be quantified by the parameter β, where a smaller value of β is associated with greater broadness and hence coupling. For the polymers studied here, the broadness of the α-relaxation shows no correlation with the steepness of the cooperativity plots, and it is currently unclear as to why this should be.

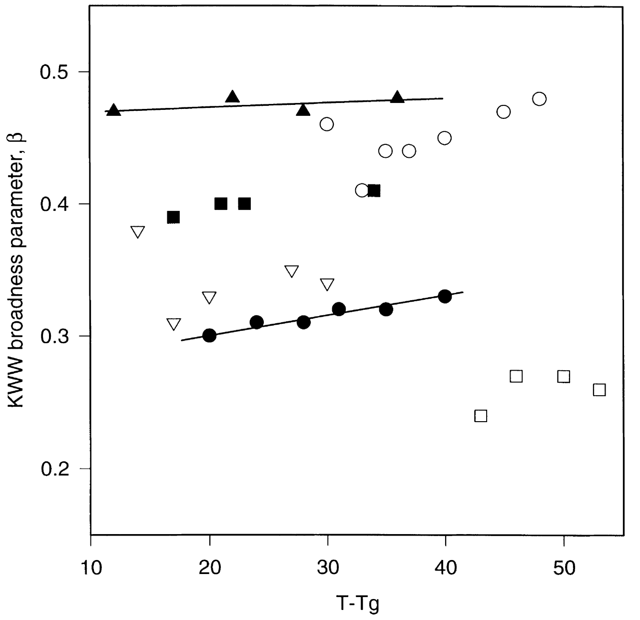

Fig. 5. Temperature dependence of KWW broadness parameter, β. (●) **1**; (○) **2**: (▽) **3**; (▲) **5**; (■) **6**: (□) **7**. Solid lines are linear fits to data for **1** and **5**.

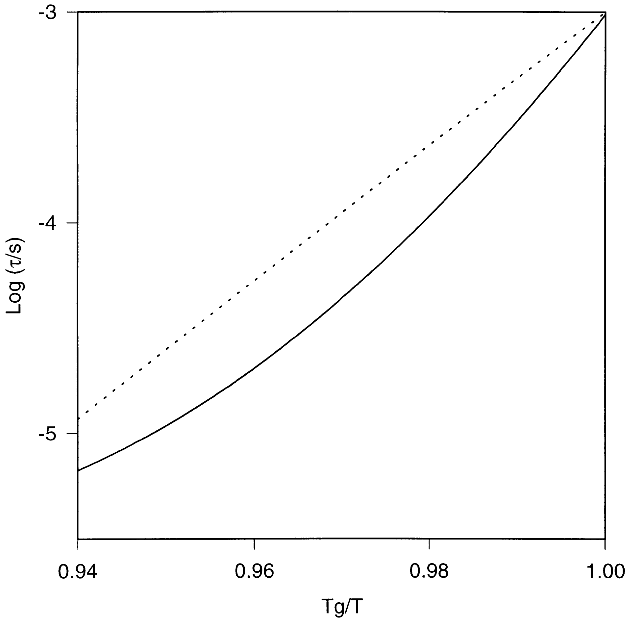

Fig. 6. Cooperativity plot for **1** (dashed line) and **8** (solid line).

3.3. Dielectric relaxation strength, Δε

The dielectric relaxation strength, $\Delta\epsilon$, derived from the HN equation, can be related to the mean square dipole moment through relations such as that derived by Kirkwood [17], which take into account the short-range orientation

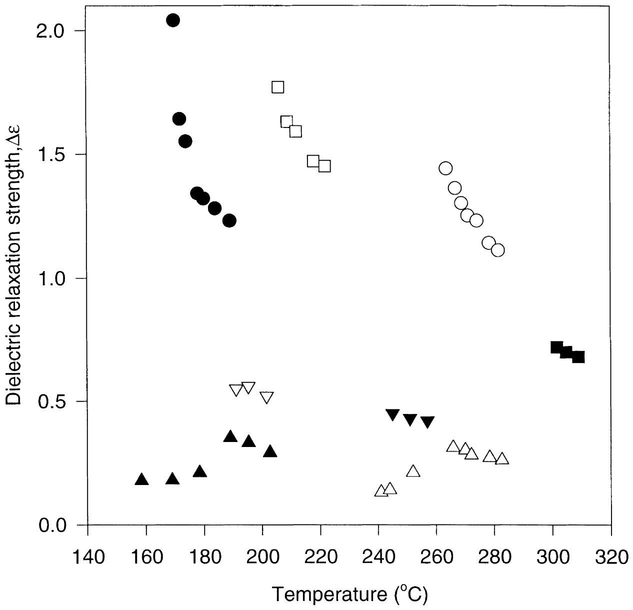

Fig. 7. Temperature dependence of dielectric relaxation strength. (●) **1**; (○) **2**; (□) **3**; (■) **4**; (▲) **5**; (△) **6**; (▽) **7**; (▼) **8**.

correlations between a reference molecule and its nearest neighbours. Fig. 7 shows the temperature dependence of the relaxation strength for each polymer around the α-relaxation region. In general, the value of $\Delta\epsilon$ decreases with increasing temperature beyond the glass transition, which is in line with the predictions of Kirkwood. The initial increase in relaxation strength of **5** and **6** arises because of the influence of the sub-T_g β-transition which is present in the spectra of the polymers containing aromatic fluorine. At temperatures below the glass transition temperature, the β-process relaxes with a relatively small intensity which increases as the glass transition is scanned and large-scale segmental motions are relaxed. According to Williams [18], the dielectric relaxation behaviour of amorphous polymers occurs by partial reorientation (sub-T_g process) and total reorientation (α-process) of a representative dipolar repeat unit. The total dielectric strength is given by the summation of the relaxation strength of each individual process. Fig. 7 shows a qualitatively similar trend to that seen in Table 1, in that the polymers containing perflurophenylene units possess reduced α-relaxation strength. The very lowest values of $\Delta\epsilon$, exhibited by **5** and **6**, compared with the values for **1** and **2**, are caused by the removal of the polar ketone linkage. Polymers **1** and **3** have very similar values, while **2** and **4**, which both contain a cyclic biphenyl group, relax with significantly lower intensity, particularly in the case of **4**. Polymers **7** and **8** both relax with much lower intensity, compared with their non-perfluorinated analogues **1** and **2**. In seeking reasons for the observed behaviour, we should rule out the possibility of changes in the magnitude of the permanent dipole moment due to fluorine substitution, since it is well known that this occurs only in the case of asymmetric incorporation of fluorine. It is worth speculating that the difference in relaxation strength may in part be due to structure-induced changes in the electronic state of the polymers, e.g. dipole–dipole and local field interactions along, and between, polymer chains, as well as to changes in the relaxation behaviour of the polymers through fractional free volume and steric hindrance effects in the rubber state.

3.4. *β-relaxation*

A sub-T_g process which occurs above room temperature has been frequently observed in rigid, aromatic polymers, e.g. polyimides, and its origin has been attributed to numerous mechanisms. Arnold et al. [19,20] used dynamic mechanical analysis and computer simulations to study a number of polyimides, and concluded that the β-process in unoriented films was due to non-cooperative motions in uncrystallised diamines involving the whole unit. With increases in crystallinity and orientation, these motions became more cooperative. The involvement of the dianhydride aromatic imide rings in the β-process with motions in the kHz region has been established by dynamic mechanical, dielectric and solid state ^{13}C n.m.r. studies [21]. In aromatic thermoplastics, e.g. poly(ester amides) and poly(-amides), β-processes which have been observed by both dynamic mechanical and dielectric techniques around and below room temperature have been assigned to motions involving bound water which has formed hydrogen bonds with the amide groups [22] and to motions of non-hydrogen bonded amide groups [23]. This transition is in addition to a γ-transition detected at lower temperatures.

The dielectric data for the polymers shown in Fig. 2 reveal two relaxations which can be more clearly separated into distinct processes by introducing a temperature-dependent term into the HN expression for the higher temperature α-process, and into the Fuoss–Kirkwood (FK) expression for the lower temperature β-process. This is achieved by allowing the relaxation time to vary according to the WLF equation. The FK expression is given by:

$$\epsilon'' = \epsilon''_{\max} \operatorname{sech} m \ln \frac{f_{\max}}{f} \tag{3}$$

where f is the frequency of measurement and m is a parameter ranging from 0 to 1 which characterises the symmetric broadness of the relaxation. The results of this procedure are presented in Fig. 8 which shows the β-transition in both cases to be broad and of low intensity. From isothermal data, average values of the relaxation broadness, using the HN function, were obtained for **5** and **6** equal to 0.45 and 0.34, respectively, which confirms the increased broadness of the β-process, compared with the α-process. It is interesting to note that β-relaxation was detected only in those polymers containing perfluorinated aromatic rings, i.e. **5**–**8**. Previous dynamic mechanical studies on these polymers produced similar findings, with a relatively lower intensity β-process being detected [9], and a weak dynamic mechanical transition located around 100°C was also

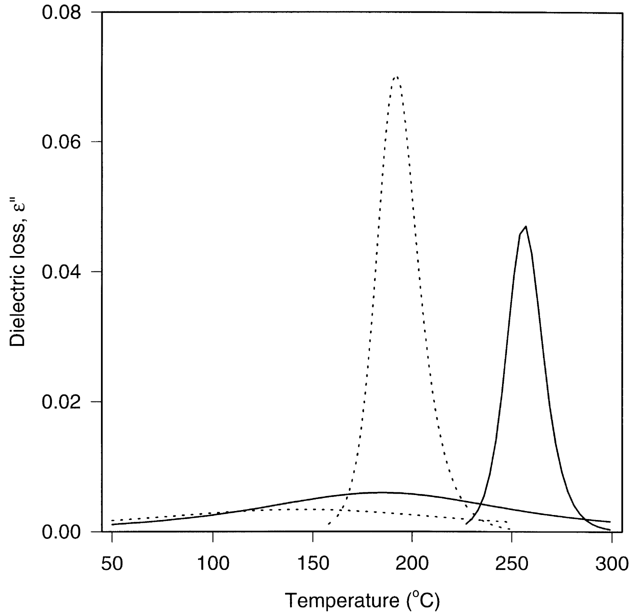

Fig. 8. Data from Figure 2 fitted with temperature-dependent Havriliak-Negami and Fuoss-Kirkwood functions to separate α and β transitions. (———) **6**; (— — —) **7**.

reported for a fluorinated poly(aryl ether) with a T_g of 250°C [24]. The conclusion to be drawn from this is that the aromatic fluorine units are at least partly responsible for the occurrence of this transition, and that although the process is both mechanically and dielectrically active, the greater strength is in the dielectric spectrum. It is unclear as to why the presence of perfluoro units should give rise to an additional relaxation process, since previous studies on the dielectric behaviour of fluorinated polyimides suggest that additional dipole orientation processes occur only when the fluorine is substituted in an asymmetric manner [11]. Another significant effect attributed to the presence of fluorine is the reported increase in both steric hindrance and free volume, and this may have some connection to the observed β-process, particularly when the significant effect perfluoro substitution has on the molecular polarisability is considered. The presence of large substituted groups can also facilitate a β-relaxation, as reported by Han et al. [25] in a dynamic mechanical study of a non-fluorinated polyketone containing phenolphthalein linkages. This is in contrast to the relaxation behaviour of the more common poly(aryl ether ketones), e.g. PEEK, which do not show above-ambient β-relaxations when investigated by either dielectric or dynamic mechanical techniques.

The frequency dependence of the β-relaxation was plotted in an Arrhenius manner, as shown in Fig. 9, and from which the linear behaviour, which is usual for sub-T_g processes, was used to calculate an apparent activation energy, ΔE_{act}. The values for **5**, **6** and **8** are listed in Table 3, along with an estimation of the peak position at 1 kHz of the β-process of each polymer. The peak position increases from 150°C for **5** to 186°C for **6** presumably due to the large cyclic biphenyl group slowing the motions responsible for the process and leading to a requirement for more thermal energy for the process to become kinetically activated at any given frequency. When a flexible ketone linkage is added to **8**, the rate of relaxation increases and the

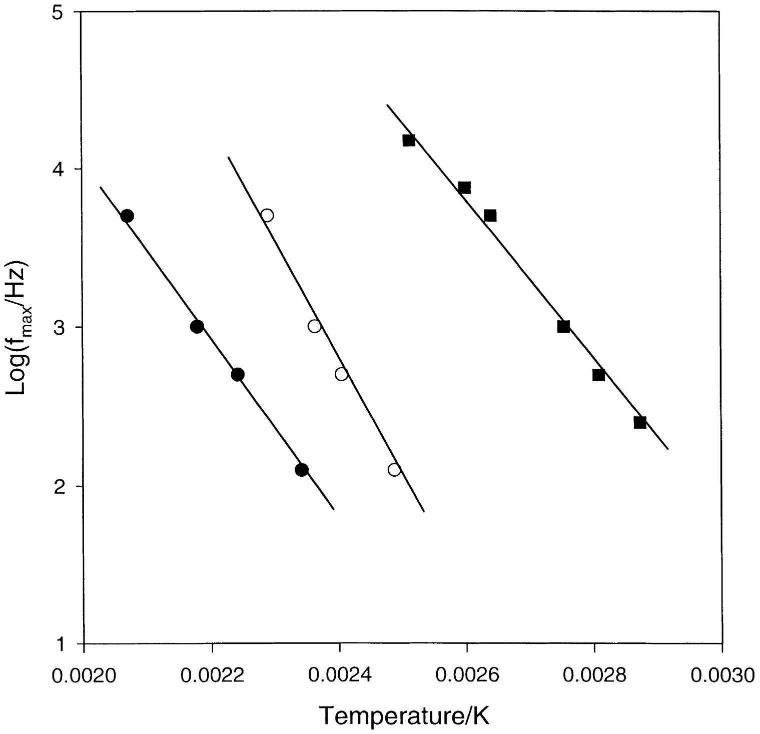

Fig. 9. Arrhenius plot of data from β-relaxation region. (○) **5**; (●) **6**; (■) **8**. Solid lines are fits to Arrhenius equation.

Table 3
β-peak location and apparent activation energy, ΔE_{act} (kJ/mol), for polymers containing perfluorophenylene groups

Polymer	Peak location	ΔE_{act}
5	150	154 ± 8
6	186	112 ± 3
7	125	-
8	90	99 ± 5

Peak location was taken at 1 kHz for **5**, **6** and **8**, and at 250 Hz for **7**

peak thus shifts to the much lower temperature of 90°C. The β-process of **7** merges with the α-relaxation at relatively low frequency and cannot be separated from the α-relaxation above 250 Hz. The apparent activation energy for the process varies from 154 ± 8 kJ/mol for **5** to 99 ± 5 kJ/mol for **8** and is lowest in the polymer containing a ketone linkage, and hence both peak position and apparent activation energy indicate the important role played by the flexibility of the chain and size of the substituted groups in the kinetics of the β-relaxation. The values of ΔE_{act} are typical for a β-process and can be compared with 100–130 kJ/mol for polyimides [26] and 190–210 kJ/mol for aromatic polyamides [23].

3.5. γ-relaxation

Sub-ambient secondary relaxations in rigid aromatic polymers are agreed upon by many authors to be associated with phenyl ring motions [26], and to be influenced by water content, ageing history and morphology [27]. A proton n.m.r. and dynamic mechanical study proposed a two-stage mechanism for the γ-transition [28]; the first stage involving motions of water molecules which is then followed by coupled motions of the polymer chains. In many instances, the γ-transition is bimodal in nature with both components undergoing a loss in intensity with decreases in relative humidity [29]. Further evidence of the influence of absorbed solvents is given in a dynamic mechanical study of PEEK in which the sub-ambient secondary relaxation is significantly changed when the polymer is exposed to water and simple alcohols [30]. The authors state that new relaxation processes occur as a result of motions of the solvent molecules, which are hydrogen bonded to the PEEK chain. It is not clear, however, if this produces a change in the underlying secondary motions of the PEEK backbone. The issue of over what length scale the γ-transition operates has been addressed in a dielectric study of model aromatic compounds and related polymers by Schartel and Wendorff [31], from which it was concluded that sub-ambient secondary relaxations in aromatic polymers are associated with inter- and intra-molecular motions on a length scale equivalent to a single repeat unit.

Fig. 10 shows the temperature dependence of dielectric loss in the γ-relaxation region for **1** and **6** at a frequency of 1 kHz. Due to problems caused by moisture condensing onto the dielectric apparatus at low temperatures, these were the only polymers for which satisfactory and quantative data were recorded, although a γ-process was observed in all polymers. The influence of water on sub-ambient

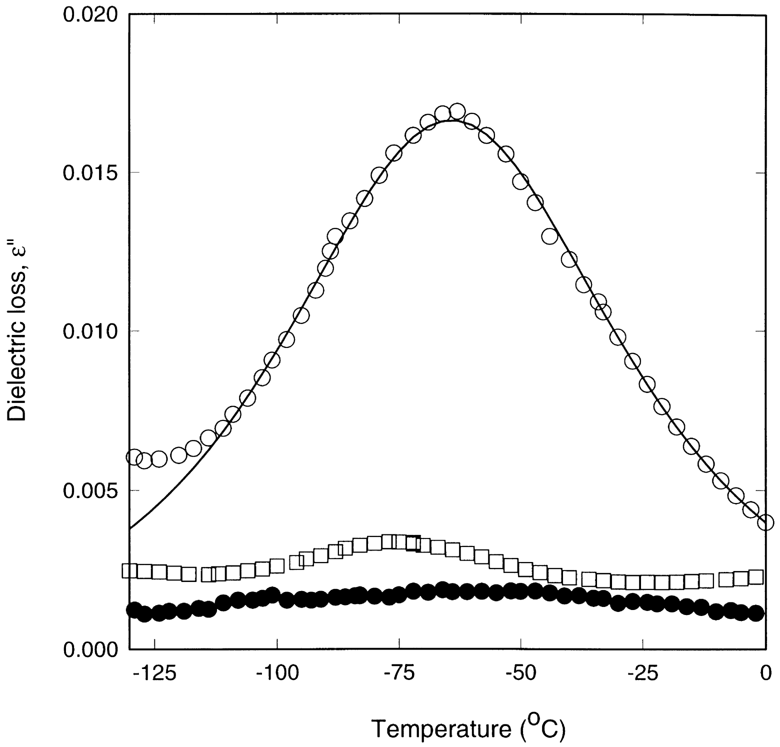

Fig. 10. Temperature dependence of dielectric loss in γ-transition region. (●) **1** [dry]; (○) **1** [wet]; (□) **6** [wet]. Solid line is fit to temperature-dependent Fuoss-Kirkwood equation.

Table 4
Fuoss-Kirkwood analysis of **1** ('wet') in γ-transition region

T(°C)	−70	−66	−63	−60	−57	−54	−50
$\Delta\epsilon$	0.14	0.13	0.13	0.14	0.13	0.13	0.15
m	0.29	0.33	0.34	0.30	0.31	0.32	0.31

$\Delta\epsilon$ is dielectric relaxation strength and m is broadness parameter

relaxations is immediately apparent from a comparison of the spectra for **1** which were recorded on 'wet' and 'dry' samples, respectively. Wet samples are defined as those which have been equilibrated in a typical ambient laboratory atmosphere, while dry samples are defined as those which have been heated above the T_g and then cooled within the dielectric cell in a dry, inert atmosphere. That the transition is still present in the 'dry' sample, albeit with a much reduced intensity, is probably due to the difficulty in removing all traces of water due to the rigidity of the polymer chains. Isothermal studies in this temperature range were also conducted and the data were fitted to the Fuoss–Kirkwood equation to give values of m and $\Delta\epsilon$, as shown in Table 4. The much lower intensity of the relaxation process, compared with the β- and α-process, can be seen in the values of $\Delta\epsilon$ which are quite independent of temperature at 0.13–0.15 for the 'wet' sample and are reduced to an average value of 0.07 for the 'dry' sample. These values can be compared with an aromatic polyamide with an equilibrium water content of 5.3 wt% (which is approximately 10 times the equilibrium amount absorbed by **1**) and a relaxation strength for the γ-process of 0.50 [23]. The 'dry' sample also has a broader relaxation as shown by an average value of m equal to 0.25. Good fits to the Arrhenius equation were obtained as shown by Fig. 11 and the values of ΔE_{act} were 54 ± 2 kJ/mol and 67 ± 2 kJ/mol for the 'wet' and 'dry' samples, respectively. These results are in line with those reported by Jonas and Legras [27], who demonstrated that water acts as a plasticiser for the sub-ambient relaxation process in PEEK by decreasing the temperature location and activation energy of the process and increasing the intensity. These effects are observed in both dielectric and dynamic mechanical spectra. The data for **6**, which were recorded for a 'wet' sample, again highlight the effect of water on the intensity of the process. The much lower relaxation intensity of **6**, compared with **1**, may be due to the fact that when immersed in water at room temperature, **6** absorbs an equilibrium value of 0.13 wt% of water compared with 0.55 wt% absorbed by **1**. This large difference in water uptake confirms the greater effectiveness of aromatic fluorine substitution in reducing polarisability and increasing the hydrophobic nature of the molecule. Although there is also the possibility that the different intensities arise from the changing chemical structure, which results in different relaxation mechanisms being responsible for the γ-process in each polymer, it is more likely that the

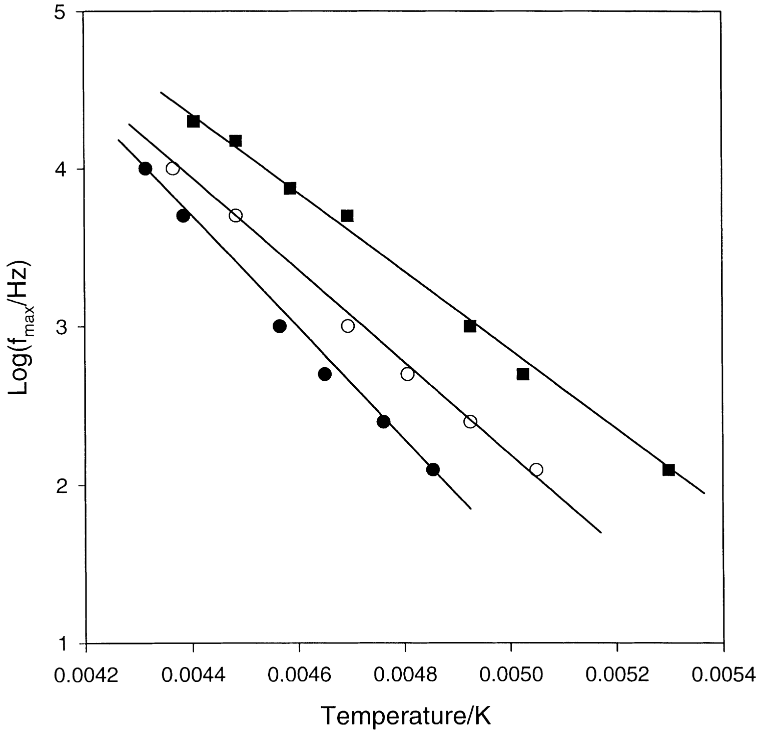

Fig. 11. Arrhenius plot of data from γ-relaxation region. (●) **1** [dry]; (○) **1** [wet]; (■) **6** [wet]. Solid lines are fits to Arrhenius equation.

water content is the most important factor, as has been reported in many previous studies. The fact that the relaxation peak temperature of **6** is located at a slightly lower temperature compared with **1** (− 75°C and − 65°C, respectively) and has a lower value of ΔE_{act} equal to 29 ± 1 kJ/mol, could be attributed to the relative increase in free volume and reduction in chain–chain interactions resulting from the presence of perfluoro units. As has been discussed earlier, these effects are of sufficient magnitude to cause a relative lowering of the glass transition temperature, and it is therefore of no surprise that they can also influence molecular motions responsible for secondary relaxations.

4. Conclusions

This work has investigated the dielectric behaviour of a series of thermoplastic aromatic polymers which contain a variety of substituted groups, with a particular emphasis on the effects of chemical structure on dielectric properties. Polymers containing cyclic biphenyl groups were found to be subject to greater intermolecular coupling, when judged by the steepness of the temperature dependence of the relaxation time. Perfluorophenylene units exerted a significant influence on the dielectric relaxation behaviour in that they were associated with an above-ambient secondary relaxation which was not detected in polymers in which perfluoro substitution was absent. This process, denoted β-relaxation, was well described by the Arrhenius equation, and the location and activation energy was sensitive to chain structure and flexibility. A sub-ambient secondary relaxation, denoted γ-relaxation, which was present in all polymers, also displayed Arrhenius behaviour, and was influenced in its position and activation energy by the polymer structure and flexibility of the backbone. In addition, the location, broadness and strength was very dependent on the water content of the polymer, and this is in line with many other studies of the sub-ambient relaxation behaviour of aromatic polymers.

The dielectric permittivity at room temperature was lowest in the perfluorinated polymers and this seemed to confirm other reports that symmetric fluorine substitution results in a decrease in electronic polarisability. However, the possibility of the γ and β (where present) processes contributing to the dielectric permittivity at room temperature, by allowing local motions of permanent dipoles to occur, should also be considered. Although not able to achieve the maximum extent of dipole orientation under such conditions, it could make a significant contribution. The α-relaxation strength of the polymers, which gives an indication of the dipole orientation polarisability, was also lowest in those polymers containing perfluorophenylene units. It was speculated that structure-induced changes in the electronic and conformational structure of the polymers were responsible for these observations.

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