

Influence of diamine structure on the low temperature dielectric relaxation of some poly(ether imide)s

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ABSTRACT: Broadband dielectric relaxation spectra are reported on a range of poly(ether imide) polymers in which the chemical structure of the diamine used to create the polymer is systematically varied with the anhydride structure based on 2,2-bis-[4-(3',4'-dicarboxyphenoxy)phenyl]hexafluoroisopropylidene dianhydride. In all the polymers examined, a dipole relaxation was observed below room temperature. The magnitude and activation energy associated with the relaxation process varied with the chemical structure reflecting the effects of steric hindrance on the conformational change associated with the N—C and C—O—C linkages. Values of the activation energies varied between 29 and 34 kJ/mol⁻¹, and are consistent with the observed relaxation being associated with constrained local oscillatory motions of small elements of the polymer backbone. The glass transition temperatures of these polymers are in the range 195–243°C and are associated with the large scale motion of the polymer backbone. Changes in the backbone structure influence the extent of inter chain–chain interaction and are reflected in the amplitude of the relaxation process and the high frequency limiting dielectric permittivity ϵ_{∞} values which are important when these polymers are used in thin film electronic applications. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41684.

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INTRODUCTION

In previous papers, the broadband dielectric relaxation of poly(ether imides) containing a range of different structures in ether segment have been presented.^{1–3} In the case of the poly(ether imide)s containing ethyleneoxide with varying chain length, the low temperature dielectric spectrum changes as the molecular weight increased. For the shortest chains, a single broad relaxation was observed which became resolved into two separate processes when the chain length was increased. A study of polyimides obtained using bis(ether anhydride)s with 3- or 4-phthalimide moieties showed dipolar relaxations occurring at low temperatures associated with local motions of the chain backbone.³ The low temperature relaxation allows the polymer to undergo small scale local conformational change which imparts to the materials advantageous impact properties. Using a hindered diamine it was possible to explore the effects of variation of the ether segment on the low temperature process. Analyses of the dielectric data indicate that the dipole relaxation arises from a cooperative process which involves small scale oscillatory—libration motions about the C—O—C linkage. Rotation about

the N—C bond in this series of polymers was inhibited by the presence of ortho-methyl groups in the phenyl group connected to the imide ring. Small differences were observed in the nature of the relaxation process which can be attributed to the effects of steric constraints on the C—O—C bond movement and the extent to which chain–chain interactions influence chain packing. This latter effect influences the high frequency limiting values of the dielectric permittivity ϵ_{∞} which is important in many electronic applications.

In this study, we explore the effects of varying the structure of the diamine in a series of poly(ether imide)s. The poly(ether imides) investigated in this article were produced by the synthetic route summarised in Figure 1 where R₁ is held constant and R₂ is varied. By systematically changing the nature of the diamine it is hoped that a more detailed understanding of the effects of local structure on the properties of these important polymers can be obtained.

The ether element in this series of copolymers is held constant and was created from 2,2-bis-[4-(3',4'-dicarboxyphenoxy)phenyl]hexafluoroisopropylidene dianhydride (R₁), Figure 2.

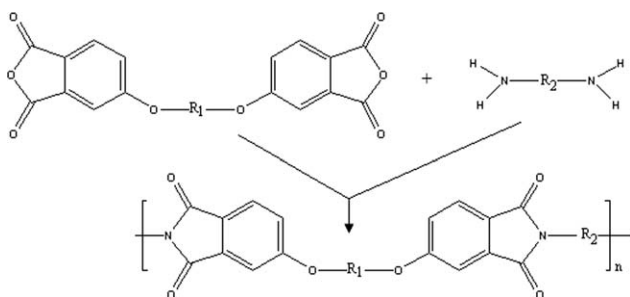


Figure 1. Schematic of the synthetic route used in the production of the poly(ether imide)s.

Changing the nature of the groups which form the backbone structure can introduce steric hindrance influencing the contour which the chain can adopt, which in turn will influence chain mobility and packing density. The intrinsic flexibility of the chain has been shown to influence physical properties such as the impact strength and elongation strength.⁴

Dielectric studies of polyimides carried out at high temperatures are dominated by the effects of ionic migration making investigation of the T_g process very difficult.^{4–11} In many applications

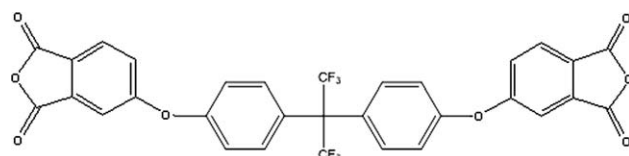


Figure 2. Structure of 2,2-bis[4-(3',4'-dicarboxyphenoxy)phenyl]hexafluoro-isopropylidene dianhydride.

where polyimide films are used at ambient temperatures, the physical properties are influenced by lower temperature relaxation process and their characterisation is the objective of this study. This article is restricted to a discussion of the low temperature dielectric behaviour of these materials.

EXPERIMENTAL

Synthesis of Precursor Materials

The bis(ether anhydride) of 2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]hexafluoro-isopropylidene was synthesized by a standard procedure described previously.^{12–15} The synthesis involved a nitrodisplacement reaction between 4-nitrophthalimide and 4,4'-(hexafluoroisopropylidene)diphenol (bisphenol AF) obtained from Aldrich. The resulting tetranitrile was characterized by

Table I. Description of the Diol and Amines used to Create the Poly(Ether Imide)s Used in this Study

HO-R1-OH		Nomenclature
		2,2-bis(4'-hydroxyphenyl) Hexafluoropropane
H ₂ N-R ₂ -NH ₂		
	D1	1,4-bis(4'-aminophenoxy)benzene
	D2	1,4-bis(4'-aminophenoxy)-2-methylbenzene
	D3	1,4-bis(4'-amino-2'-fluorophenoxy)benzene
	D4	1,4-bis(4'-amino-2'-methylphenoxy)-2,3,5-trimethylbenzene
	D5	1,3-bis(4'-aminophenoxy)benzene
	D6	1,4-bis(4'-amino-3'-methylphenoxy)benzene
	D7	1,4-bis(4'-aminophenoxy)-2,3,5-trimethylbenzene
	D8	1,2-bis(4'-amino-3'-methylphenoxy)-3,5-ditertbutylbenzene

Table II. Physical Characteristics of the Poly(Ether Imide)s Studied in this Paper

Polymer	D1	D2	D3	D4	D5	D6	D7	D8
T_g [°C]	215	213	198	241	195	232	243	227
Density [g.cm ³]	1.379	1.362	1.412	1.299	1.378	1.347	1.323	1.234

elemental analysis and melting point. Elemental analysis: Calc. for $C_{31}H_{14}N_4O_2F_6$: C, 63.27%; H, 2.39%; N, 9.52%; Found: 63.36%; H, 2.31%; N, 9.58% Yield, 97.6%; MPt., 233–234°C. The tetranitrile was hydrolysed to tetraacid and dehydrated to the dianhydride which was characterized similarly. Elemental analysis: Calc. for $C_{31}H_{14}O_8F_6$: C, 59.24%; H, 2.24%; Found: C, 59.31%; H, 2.19%; Yield, 96%; MPt, 232.0–232.5°C. The structures of the diamines investigated in this article are presented in Table I.

Synthesis of Polyimides. The polyimides were prepared by a conventional, two-stage solution polymerization and imidization process, as described previously.¹² The synthesis involved 1 mmol of diamine being dissolved in 5 cm³ of *N*-methylpyrrolidinone at room temperature and an exact stoichiometric equivalence of dianhydride, Table I added with stirring. After standing overnight, the mixtures formed a highly viscous solutions of poly(amic acid)s which was chemically imidized by the addition of 2 cm³ of an equivolume mixture of acetic anhydride and pyridine at room temperature. After leaving for several hours, the resulting polyimides were isolated by precipitation into methanol. The high-molecular weight polyimides were washed with boiling precipitant to remove residual solvent. Thin films of the polymers were produced by slow solvent evaporation from polymer solutions (3 wt %) in dichloromethane in flat bottomed Petri dishes (Anumbra). The transparent, yellow films, thickness 30–60 μm, were annealed for 3 days at 120°C under vacuum to remove moisture. These films were used for the dielectric analysis.

Density and Differential Scanning Calorimetry Measurements

Densities of the cast polyimide films were determined by a flotation method at 25°C using a saturated aqueous solution of K_2CO_3 . The density of the salt solution was measured using an Anton Parr DM60 oscillating digital density meter connected to a DM601 density measuring cell. Measurements were performed in triplicate and the densimeter was thermostated at $25 \pm 0.1^\circ C$. Glass transition temperatures were determined using a Perkin Elmer DSC-2 with a heating rate of 10°C min under nitrogen.

Dielectric Relaxation

Dielectric measurements were carried out using a broadband dielectric spectrometer operating between 0.1 and 6.5×10^4 Hz.¹⁶ To achieve maximum electrical contact, aluminum electrodes were coated onto the polymer films using an Edwards E306A coating system. The temperature was controlled by a Linkam CI93 computer interface and a Linkam LNP pump with a liquid nitrogen cooling system. Spectra were recorded at intervals of 10°C from -140 to $-60^\circ C$. The frequency dependent permittivity $\epsilon'(\omega)$ and dielectric loss $\epsilon''(\omega)$ were fitted to the Havriliak–Negami¹⁷ eq. (1) allowing calculation of the α and β distribution parameters and the characteristic relaxation time τ :

$$\epsilon(\omega)^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{\left(1 + (i\omega\tau)^{1-\alpha}\right)^\beta} \quad (1)$$

where ϵ_0 and ϵ_∞ are respectively the complex and limiting low- and high-frequency permittivities and were estimated using plots Cole–Cole plots in which the dielectric permittivity $\epsilon(\omega)'$ is plotted against the dielectric loss $\epsilon(\omega)''$. Values of ϵ_0 and ϵ_∞ are obtained as the intercepts of the curves with the permittivity axis. Values of α and β are frequency-independent, dimensionless constants characteristic of the number and breadth of the relaxation processes involved. For an ideal dipole relaxation process $\alpha = 0$ and $\beta = 1$ and is observed with free rotational of an isolated dipole. The variation of the characteristic relaxation time, τ as a function of temperature was used to calculate the apparent activation energy using the Arrhenius equation.

Polymer Characterization

Gel permeation chromatography was carried out on the polymers using DMF/LiCl(0.1 M) as eluant and a molecular weight 66 kg mol⁻¹ with reference to polystyrene standards indicating that a high degree of conversion had been achieved with this polymerization method.¹² Thermogravimetric analysis indicated that the polymers were stable up to a temperature over 400°C.

RESULTS AND DISCUSSION

Glass Transition Temperature

The thermal characteristics of the polymers used in this study are summarized in Table II.

The values of T_g for these polymers are consistent with values for poly(ether imide)s containing flexible back bone structures and the introduction of steric hindrance in certain cases raises the T_g whilst in others the pendant groups appear to have a lesser effect on T_g . The lowest value of T_g is observed with D5 in which there will be less steric constraints with regard the rotation of the central 1,3 substituted phenyl group. The introduction of the fluorine atoms in the α positions next to the central 1,4 substituted phenyl ring in D3 gives rise to a T_g which is only slightly higher than that for D5. D1 and D2 exhibit comparable values of T_g indicating that the methyl substitution in the ortho position on the phenyl of the central phenyl ring appears to have little effect. D8 with ortho and para tertiary butyl substitution on the central phenyl ring increases the T_g in comparison with D5. However, the highest values of the T_g are observed with D6, D4, and D7. D6 is ortho methyl substituted next the imide ring whereas D4 is meta methyl substituted to the phenyl rings connected to the imide ring and trimethyl substituted in the central phenyl ring. Removal of the methyl groups in the phenyl rings connected to the imide ring in D7 leads to a further rise in the T_g and would allow conjugation across the N–C bond. The highest value is observed in D7

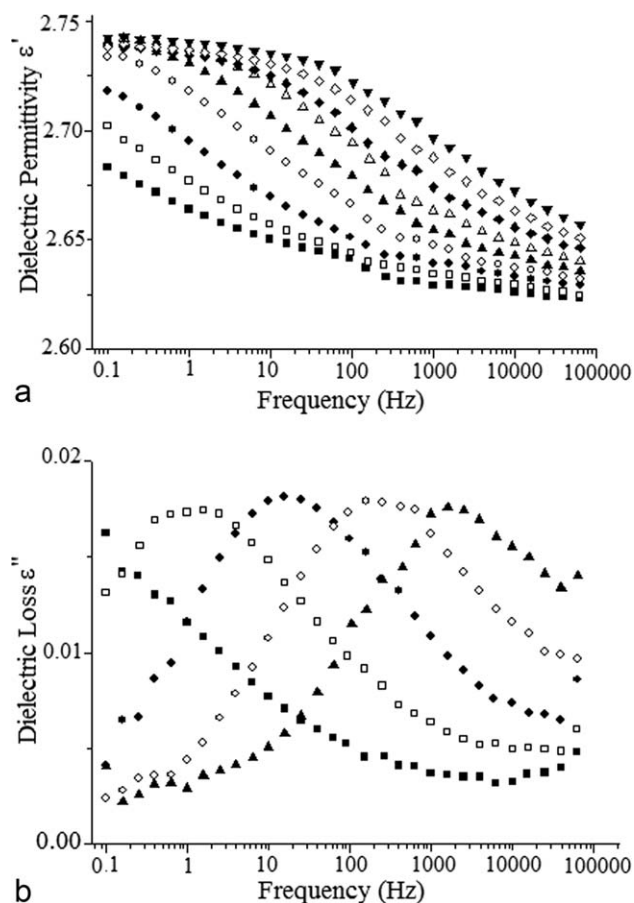


Figure 3. Dielectric permittivity (ϵ') (a) Key: ■—140°C, □—130°C, ●—120°C, ◐—110°C, ▲—100°C, △—90°C, ◆—80°C, ◇—70°C, ▼—60°C and dielectric loss (ϵ'') (b) for poly(ether imide) D1, Key: ■—140°C, □—120°C, ●—100°C, ◐—80°C, ▲—60°C.

which is trimethyl substituted in the central phenyl ring but not in the rings next to the imide ring and similar extended conjugation may be invoked. The T_g processes are connected with the polymer backbone achieving a high degree of flexibility and the values observed reflect both the effects of intramolecular and intermolecular interactions.

Dielectric Measurements

Previous dielectric studies^{1–11} and observations by Coleman and Koros¹⁸ and Mi *et al.*¹⁹ have proposed that small scale local motions are a controlling factor in influencing the gas permeability and influence the elongation and fracture characteristics of the materials.²⁰ To characterise the local chain dynamics in these polyimides, dielectric measurements were carried out over the frequency range 10^{-1} to 10^5 Hz and over a temperature range from -160 to -20°C , and the variation of the dielectric permittivity and dielectric loss as a function of temperature recorded. The film studied had been dried in vacuum for 3 days at 120°C . All the polymers exhibited dielectric relaxations within the frequency–temperature range studied. The analysis for the poly(ether imide) D1 will be discussed in detail and those for the remainder will be summarised in terms of their Cole–Cole plots in the next section.

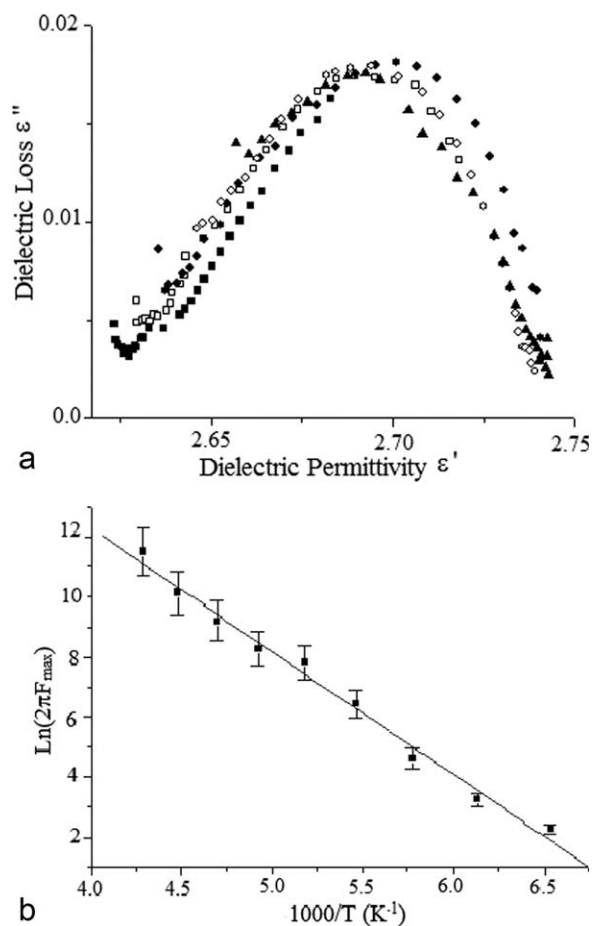


Figure 4. Cole–Cole Plot for poly(ether imide) D1 (a) Key: ■—140°C, □—120°C, ●—100°C, ◐—80°C, ▲—60°C, Arrhenius energy plot for poly(ether imide) D2 (b).

Dielectric Characterization of D1

The dielectric permittivity and loss for poly(ether imide) D1 are presented in Figure 3.

In the temperature range -140 to -60°C ; a single dielectric relaxation is observed in the frequency range 10^{-1} to 10^5 Hz. The dielectric loss peaks are significantly broader than those associated with a single dipole relaxation process. Cole–Cole plots, Figure 4(A) in which the dielectric loss ($\epsilon''(\omega)$) is plotted against the dielectric permittivity ($\epsilon'(\omega)$) and values of ϵ_0 and ϵ_∞ were estimated from the intercept with the permittivity axis., Figure 3.

The curves obtained at various temperatures superimpose onto a single curve indicating that the amplitude of the dipole relaxation is essentially temperature independent. The dielectric data can be fitted to the Havriliak–Negami eq. (1) using values of α and β of 0.59 and 0.3 respectively. For the ideal dipole relaxation, the values of α and β should be 0 and 1. The significant deviation from ideal behaviour indicates that the dipole relaxation probably involves coupled rotation of more than one chemical bond in the polymer backbone. Normally such coupled motions are associated with the glass transition process but in the case of the polyimides, the main backbone is

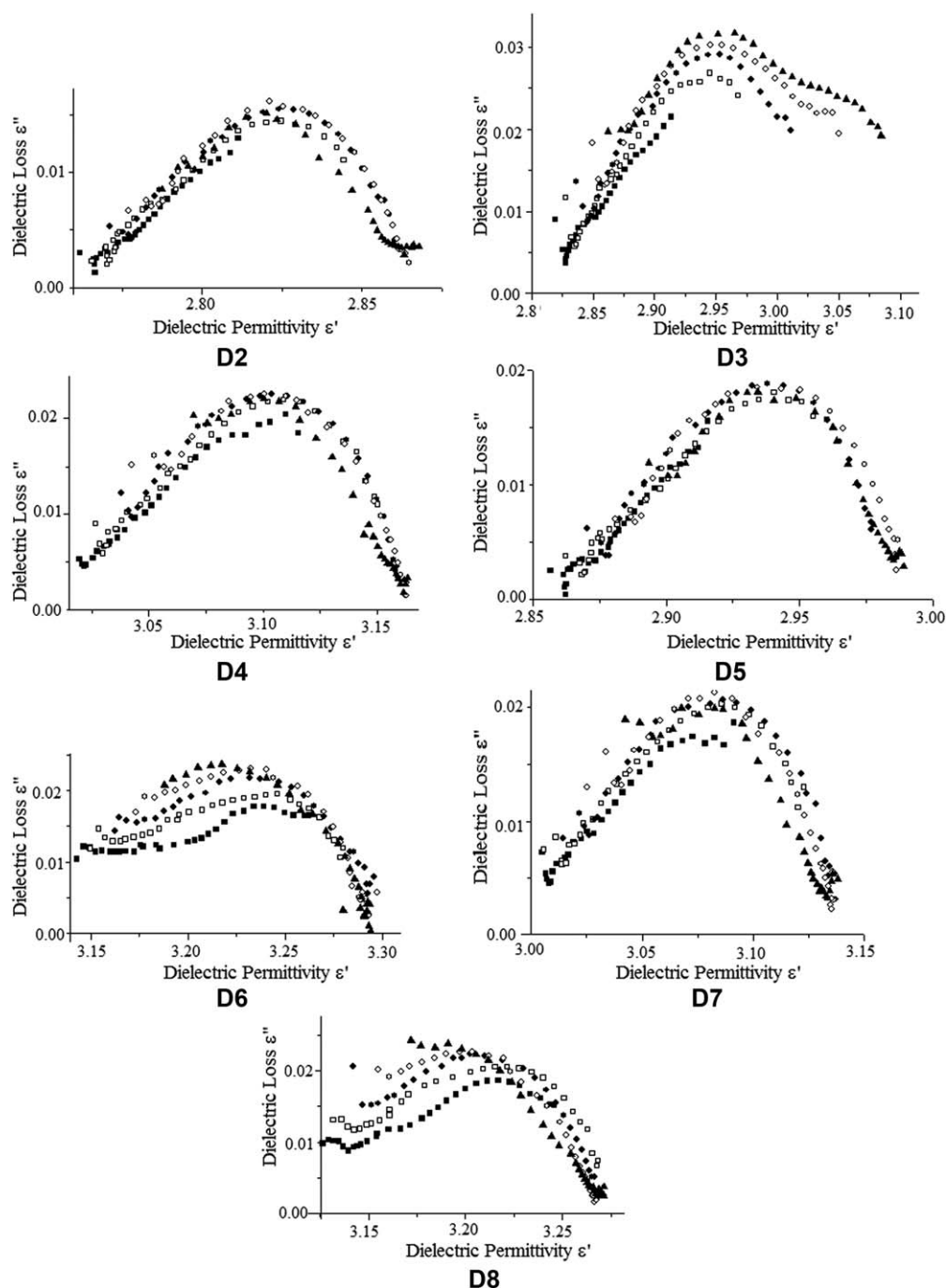


Figure 5. Cole–Cole plot for poly(ether imide)s D2–D8, Key: - \blacksquare —140°C, \square —120°C, \bullet —100°C, \circ —80°C, \blacktriangle —60°C.

assumed to be rigid and the dipole relaxation process must be assumed to be the result of local perturbations of the backbone structure and involve oscillatory—librational motion rather than full scale conformational changes of the whole polymer backbone.^{21,22} The central 2,2-bis(4'-hydroxyphenyl) hexafluoropropane will adopt a conformation which influenced by the hexafluoropropane bridge which twists the neighbouring phenyl groups out of plane but will fix the conformation of this element. Molecular motion is possible to a limited extent about the —O— bond linking this group to the phenyl imide structure but this will be common to all the polymers.

Fitting the data to eq. (1) allows calculation of the dipole relaxation time— τ . The variation of the relaxation time with temperature obeys a good linear relationship and conforms to an Arrhenius type of relationship, Figure 3(B), indicating that the relaxation is a thermally activated process and having an activation energy of $34.1 \pm 1.4 \text{ kJ mol}^{-1}$. This value for an activation energy for dipole rotation is significantly lower than that usually associated with the glass transition process, however, is higher than that for simple conformational change involving a single bond which typically has a value of approximately 10–15 kJ mol^{-1} .^{21,22} As with the glass transition temperature, high value

Table III. Parameters Obtained from Analysis of the Dielectric Curves Using eq. (1)

Polyimide	α	β	Loss (max)	$\epsilon_0 - \epsilon_\infty$	ϵ_0	ϵ_∞
D1	0.59	0.3	0.018	0.125	2.75	2.625
D2	0.61	0.31	0.015	0.107	2.875	2.768
D3	0.42	0.45	0.029	0.220	3.05	2.825
D4	0.58	0.32	0.022	0.15	3.17	3.02
D5	0.62	0.32	0.019	0.144	3.00	2.856
D6	0.48	0.3	0.022	0.15	3.30	3.15
D7	0.53	0.35	0.021	0.13	3.14	3.01
D8	0.50	0.35	0.022	0.16	3.275	3.125

of activation energies can be associated with conformational a change which involve cooperative motion of more than one chemical bond. The motion will not correspond to the free internal rotational which is associated with the T_g and may be assumed to be a form of oscillatory—librational motion.

Dielectric Characterization of Poly(ether imides) D2–D8

Isothermal dielectric measurements were carried out on the poly(ether imides) listed in Table I over a temperature range from -140 to -60°C and over a frequency range from 10^{-1} to 10^5 Hz. and the Cole–Cole plots are presented in Figure 5.

The relaxations are very similar to those observed for poly(ether imide); however, there are clear differences arising as the structure is changed. Analysis of the relaxation curves using the Havriliak–Negami eq. (1) gave values of α and β parameters listed in Table III.

The variation in α and β parameters reflect the extent to which the processes deviates from ideal and changes with the structure of the polymer. The activation energies obtained from analysis of the Arrhenius energy plots Figure 6 are summarised in Table IV.

The values of the activation energies obtained are similar implying a commonality in the nature of the process being observed and the values suggest a cooperative relaxation process. The main difference which is observed between the dielectric behaviour in these polymers is their A factors which changes the location of the process on the temperature axis.²²

The A factor is a measure of the differences in the way in which energy can be coupled into the element undergoing the relaxation and therefore is a reflection of the extent to which the other elements of the chain are able to interact and will be influenced by the packing density.

The Cole–Cole plot for poly(ether imide) D2 is similar to that for D1 indicating that methyl substitution in the central phenyl ring is having little effect on the dielectric relaxation process. D4, D5, and D7 all exhibit similar shapes of relaxation process with small differences in the distribution parameters and the activation energies, despite very significant changes in the steric interactions involved in the central phenyl group, Table I. D3 shows evidence of a second higher temperature relaxation process. In D3, the ortho positions to the central phenyl ring structure contain fluorine atoms. If we assume that the bond linking the imide ring to the phenyl is conjugated and imparts rigidity

to the backbone, then at low temperature different isomeric forms can be created as shown in Figure 7.

Whilst similar isomeric structures can be proposed for the other poly(ether imide)s differences in the relaxation behaviour is only observed in D3. Fluorine undergoes a strong repulsive interaction and this reflected in the values of the total energy calculated for the isomers using molecular dynamic minimisation and give values of D3(A) and D3(B) of 73.87 kcal/mol and D3(C) and D3(D) of 74.13 with differences in the dipole/dipole contribution to the total energy of -2.95 and -2.60 . The differences in the energies created between these isomeric structures are giving rise to a separation of the dipole relaxation into two processes. Conductivity processes which are thermally activated made it impossible to explore the higher temperature region more extensively.

D6 and D8 both exhibit very broad relaxation processes and correspond to the polymer in which the conjugation between the imide ring and the neighboring phenyl will be reduced by the presence of the methyl group in the ortho position leading to a multiplicity in the possible isomeric structures. The amplitude of the relaxation process appears to vary with temperature which might imply that the nature of the dipole process was itself changing with temperature. It is, however, clear that changes in the structure of this element of the polymer structure is directly influencing the relaxation process but not in a simple manner. Changes in ability of the backbone to alter its conformation will influence the ability for neighbouring chains to interact and this will be reflected in the packing density. The most highly hindered polymer D8 has the lowest density, with the next highest being D4 which has the highly methyl substituted central phenyl ring. D7 which has a similar central structure to D4 but does not have the methyl substitution next to the imide ring has the next highest density. D6 with methyl substitution next to the imide ring twisting the backbone exhibits the next highest density with D1, D2, and D5 having similar values and will have an element of planarity and rigidity imposed by the conjugation of the phenyl with the imide ring. The highest density corresponds to the polymer in which fluorine substitution has taken place ortho to the central phenyl group. The activation energies for the process do not correlate with the variation in the density; D3 having the highest density yet an activation energy of 30.5 kJ/mol, whereas D8 with the lowest density has comparable activation energy of 29.8 kJ/mol. The highest activation energies are observed with D1, D2, and D5 which are high density polymers and most tightly packed polymer systems. It is clear that neither the packing nor steric hindrance are the controlling factors but some combination of these effects influences the ability for the chains to undergo these localised conformational changes.

High Frequency Limiting Dielectric Permittivity ϵ_∞

The high frequency limiting permittivity is an important parameter when assessing the dielectric loss characteristics of thin films. The value of ϵ_∞ reflects the atomic and molecular constitution of the polymer and will be influenced by dipole–dipole and dipole–induced dipole interactions which can arise from chain–chain interactions. A plot of ϵ_∞ versus density,

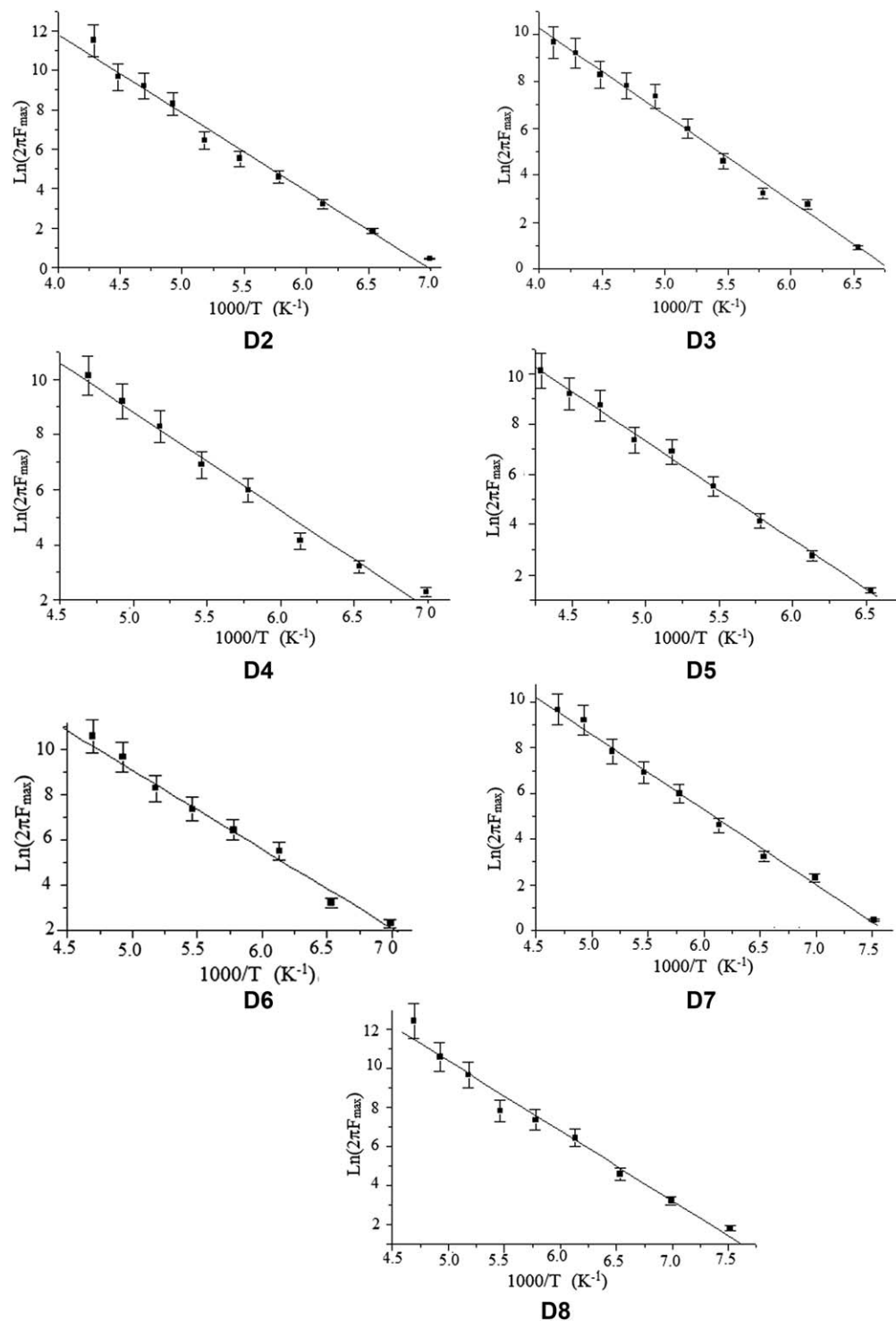


Figure 6. Arrhenius activation energy plots for the relaxation times for D2–D8.

Table IV. Activation Energies for the Dipole Relaxation Process

Polyimide	D1	D2	D3	D4
Activation energy kJ mol ^o	34.1 ± 1.4	33.0 ± 1.5	30.5 ± 1.1	29.5 ± 1.5
Polyimide	D5	D6	D7	D8
Activation energy kJ mol ^o	32.7 ± 0.7	28.9 ± 1.6	27.3 ± 0.8	29.8 ± 1.6

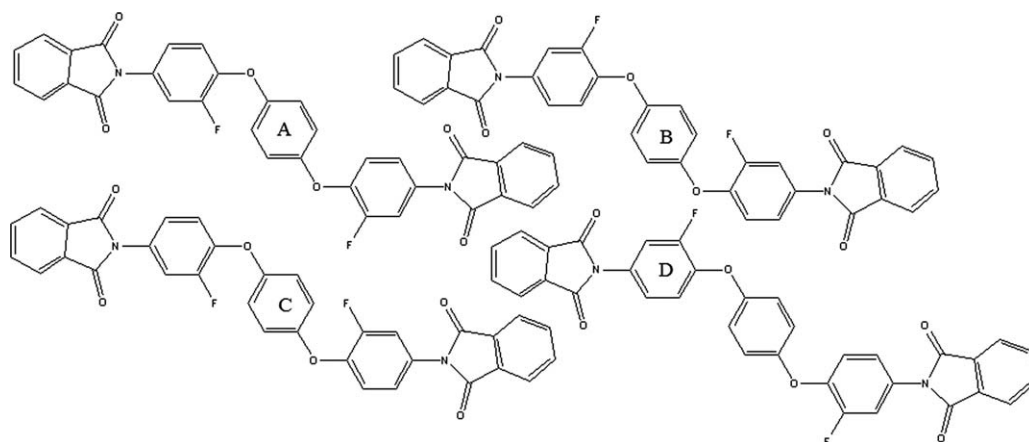


Figure 7. Various possible isomeric forms of the ether segment in D3.

Figure 6 shows that although a general downward trend can be identified with certain members of the series there are two systems which do not follow this trend; D6 and D1. Intuitively we would expect that ϵ_{∞} should increase with the density of the polymers and not decrease as is observed. An upward trend was observed in a previous study of poly(ether imide)s but the fluorine containing polymers showed deviations from the general upward trend. In this series, D1 is the simplest structure and hence should have the lowest values of ϵ_{∞} , however, D5 with an identical atomic composition exhibits a higher value indicating differences in the extent of chain–chain interactions on the value of ϵ_{∞} influencing the observed values. Fluorine has the ability to induce quadrupole interactions and in part may explain the high value observed with D8 (Figure 8).

It is predictable that D8 should have a higher value of ϵ_{∞} as a consequence of the larger number of C–H bonds present in this molecule and the steric hindrance associated with the $(\text{CH}_3)\text{C}-$ entity produces the low density inhibiting chain packing. In D6 a high value of ϵ_{∞} is observed, the density being slightly lower than in D1 but significantly higher than with D8 and the pendant groups have been reduced to two methyl groups in the ortho position to the imide ring. Steric effects would be expected to twist the phenyl ring out of the plane of

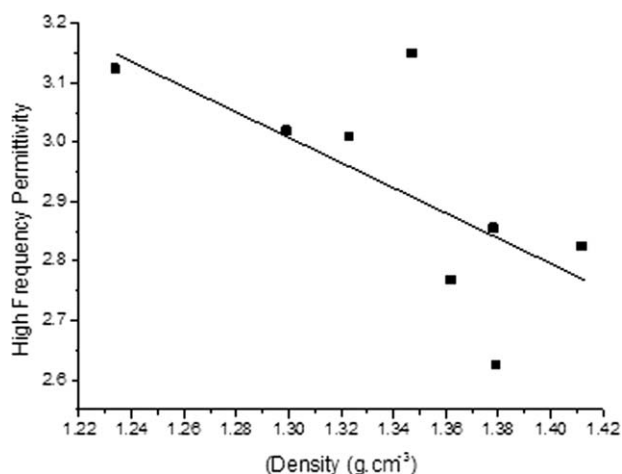


Figure 8. Variation of the high frequency permittivity ϵ_{∞} with density.

the imide ring which will significantly influence the ability for the chains to pack and influence the extent of dipole–induced dipole interaction.

This study indicates that the ability to control the high frequency limiting value of the permittivity of these poly(ether imide)s is not simply a consequence of chemical structure of the polymer but also reflects the extent to which chain–chain interactions are influenced by the flexibility and spacing which results from these changes in chemical structure. Polyimides are used as insulating layers in a number of electronic applications and in high frequency applications these limiting values can significantly influence power dissipation and related processes.

CONCLUSIONS

The poly(ether imide)s investigated in this study illustrate the way in which changing the chemical structure of the central imide block influences the ability of the polymer to undergo local oscillatory motions. These motions will influence the mechanical properties and are sensitive to changes in the conformations adopted by the chain. No simple correlation with changes in the density was observed with either the variation of the T_g , the low temperature relaxation process or values of the high frequency limiting permittivity ϵ_{∞} . In all cases steric interactions are influencing the conformations which will be generated and but will influence the ability of the molecules to pack together as well as controlling the rotational energy profile for the conformational change. The similarity in the activation energies for the dipole relaxation suggest that it is a combination of inter and intra molecular interactions which are influencing these processes.

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