Dielectric relaxation of liquid crystalline side-chain poly(vinyl ether)s

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Dielectric permittivity and loss have been measured over the frequency range 10^{-2} Hz–10 kHz between 100 K and 350 K for samples of two mesomorphic side-chain poly(vinyl ether)s, poly(4-(11-(vinyloxy)undecyloxy)-4-ethoxyphenylbenzoate) (P-EtO) and poly(4-(11-(vinyloxy)undecyloxy)-4-cyanophenylbenzoate) (P-CN) of different degree of mesogen group orientation. X-ray scattering showed that P-EtO was in a semicrystalline state below 345 K, whereas P-CN displayed a tilted smectic structure at temperatures lower than 315 K. Four relaxation transitions were found in P-EtO: α, the glass–rubber transition occurring at 290–300 K, and three subglass processes referred to as β, γ and δ. P-CN exhibited only three dielectric processes, α, β and γ. The low temperature process, δ, was absent in P-CN and could be assigned to torsion about the pendent phenyl–carbon–ether–oxygen bond. Subglass processes β and γ exhibited an Arrhenius temperature dependence with activation energies of 60–105 and 32 ± 2 kJ mol^{-1}, respectively. The activation energy of the γ process was insensitive to morphology and it was assigned to local motions in the spacer group. The activation energy of the β process varied considerably among the studied polymers with higher values for the highly ordered P-EtO than for P-CN. It is suggested that the β process leads to reorientation of the carboxylic group in the phenyl benzoate moiety.

(Keywords: liquid crystalline polymers; poly(vinyl ether); mesogen group orientation)

INTRODUCTION

The dielectric relaxation of liquid crystalline side-chain polymers has recently received some attention[1–13]. Interest in this group of polymers is motivated by their potential use in optronics and electronics. The focus of this paper is the dielectric relaxation in subglass processes of partially crystalline or smectic polymers showing smectic (S_A) mesomorphism at higher temperatures. Data obtained by n.m.r.[14], small-angle neutron scattering[15] and thermal analysis[16] provide evidence in favour of a two-phase morphology. The smectic layers with the mesogens, which at lower temperatures may crystallize, organize in stacks together with the more disordered domains essentially consisting of the backbone chains sandwiched between the crystalline lamellae. The spacer group decouples the main chain from the mesogen and allows it to attain an anisotropic 'random' chain conformation[15]. Evidence for limited interpenetrating flexible-chain and mesogenic components has been presented[15,17]. The molar mass dependence of isotropization of different side-chain oligomers and polymers was found to depend on the chain structure[17]. It was shown that the order within the smectic layers and the penetration by the flexible backbone chains of the smectic layers was not appreciably affected by changes in molar mass in polysiloxanes or in polymethacrylates whereas in poly(vinyl ether)s a reduction in order of the smectic layers was recorded for the high molar mass systems[17].

Five dielectric relaxation processes were found in a series of isotropic side-chain phenylbenzoate-containing polyacrylates and polymethacrylates, oligomethylene spacers with two to six carbons, and methoxy, n-butoxy and cyano end groups[4]: a high temperature relaxation (δ) with an activation energy (ΔE) of 150 kJ mol^{-1}, a glass–rubber transition (α) exhibiting Williams–Landel–Ferry (WLF) temperature dependence and three subglass processes referred to as β ($\Delta E = 50$ kJ mol^{-1}), γ_1 ($\Delta E = 35$ kJ mol^{-1}) and γ_2 ($\Delta E = 24$ kJ mol^{-1}). It was proposed[4] that the subglass processes were due to reorientation of the ester group of the mesogen (β), motions within the oligomethylene group causing reorientation of the surrounding ether dipoles (γ_1) and torsion about the bond between the outer phenylene carbon and the end group (γ_2). These findings were further substantiated in later work[10] on combined main-chain and side-chain polymers.

Pranoto *et al.*[5] studied isotropic and oriented samples of polysiloxanes with phenylbenzoate as mesogen, a six carbon methylene spacer, and methoxy, cyano or chlorine end groups and observed that the β process ($\Delta E = 51$ kJ mol^{-1}), ascribed by the authors to reorientation of the ester dipoles, was strongest for the samples in which the mesogens were oriented perpendicular to the direction of the applied electric field. The β process was broad and followed the symmetric Cole–Cole equation. The glass–rubber transition (α) and the δ relaxation appearing at high temperatures was also reported[5]. The extensive work of Williams *et al.*[6–8,11,12] has shed more light on the α and δ processes.

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This paper presents data from dielectric relaxation measurements of side-chain poly(vinyl ether)s, focusing on the subglass processes. No dielectric relaxation measurements have been reported on these polymers. Samples with different mesogen group orientations and of different crystallinities have been studied. It was anticipated that the data would provide information not only about the nature of the relaxation processes but also about the orientation of the relaxing dipoles.

EXPERIMENTAL

Poly(4-(11-(vinyloxy)undecyloxy)-4-ethoxyphenylbenzoate), denoted P-EtO, and poly(4-(11-(vinyloxy)undecyloxy)-4-cyanophenylbenzoate), referred to as P-CN, were prepared by electroinitiated cationic polymerization. The initiation system was identical to that used for photoinitiated polymerization in previous work[18]. Initiators were phenacyltetramethylenesulfonium hexafluoroantimonate and phenothiazine in molar ratios with respect to the monomers of 1:250 and 1:25. Polymerization was performed in the cell later used for the dielectric measurements. The mixture of the monomer and the initiators was melted into the cell and heated to a temperature above the isotropization temperature. The temperature was then lowered and the monomer turned smectic (S_A) and became highly oriented from contact with the rubbed polyimide film. A sinusoidal a.c. voltage of 10 V (rms) and 100 Hz was applied inducing further alignment of the monomer as assessed by polarized microscopy. The frequency of the a.c. voltage was then lowered and at ~1 Hz the polymerization was initiated. The polymer, denoted PLAN, was highly ordered and transparent. Overall isotropic samples (ISO) were prepared by heating the PLAN samples above their clearing temperatures and then cooling them slowly to room temperature. A P-EtO sample denoted QUENCH was produced by heating the isotropic sample to 373 K, keeping it at that temperature for 2 min and finally quenching it in liquid nitrogen. The repeating units of the polymers are shown in *Figure 1*.

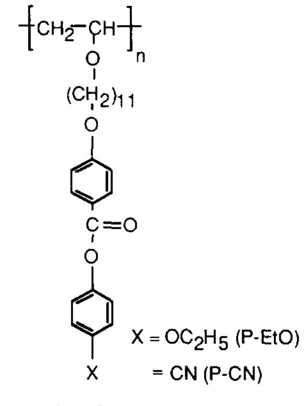

Figure 1 Repeating units of the polymers studied

Table 1 Thermal transitions in the polymers studied[18–20]

	Thermal transition temperatures (K) and enthalpy changes (kJ mru^{-1})[a]	
Polymer	Heating[b]	Cooling[b]
P-EtO PLAN	$G310C_B340(4.6)S_A409(4.7)I$	
P-EtO ISO	$G310C_B339(5.0)S_A407(5.0)I$	$I396(4.5)S_A330(4.7)C_B310G$
P-CN PLAN	$S_C316(3.8)S_X353(12.9)S_A436(1.8)I$	
P-CN ISO	$S_C309(0.9)S_X349(12.5)S_A427(2.0)I$	$I423(1.4)S_A305(13.0)S_C$

[a] mru, mole repeating units

[b] G, partially glassy state; C_B, crystal B; S_C, smectic C; S_A, smectic A; S_X, ordered smectic phase; I, isotropic melt

It is known from parallel work[19] that the polymers are atactic with a 50/50 mixture of *meso* and *racemic* dyads according to ^{13}C n.m.r. The number-average molar mass, expressed in polystyrene equivalents, of samples polymerized under conditions similar to those used in this study amounted to 13 000 to 15 000 for poly(4-(11-(vinyloxy)-undecyloxy)-4-methoxyphenylbenzoate) and 35 000 to 45 000 for P-CN[18,19]. The uniformity index ($\bar{M}_w/\bar{M}_n$) of polymers produced under these conditions was equal to 2 ± 0.3[18,19]. Phase transition data from d.s.c. are presented in *Table 1*. The structural assignments were made by X-ray diffraction and polarized light microscopy. A detailed presentation of these data is made in a parallel paper[20]. Crystal B which is a subgroup of smectic B was indicated by the presence of three orders of reflections of the sharp low angle reflection associated with a considerable regularity of the layer spacings, the presence of a single sharp wide-angle reflection and by additional findings made by polarized light microscopy[20]. P-EtO, independent of degree of orientation, contains a significant fraction of crystal B (width of wide-angle peak: 0.005 rad), ~50% according to X-ray data[20] at temperatures lower than 345 K. The P-CN samples gave no Bragg-like wide-angle reflections at temperatures lower than 310 K and, from an analysis of the diffraction pattern from the oriented sample, it was concluded that the polymer possessed a tilted smectic structure (S_C)[20]. The P-EtO samples exhibited a glass transition at 310 K (*Table 1*).

X-ray diffraction work presented in reference 19 confirmed that the P-EtO PLAN had a high degree of orientation of mesogenic groups in the film plane. Values for the order parameter between 0.90 and 0.95 were obtained from the azimuthal-angle-intensity scans[19]. P-CN possessed a S_C structure at room temperature and thus the order parameter based on i.r. dichroism of the cyano stretching band (2250 cm^{-1}) amounted to 0.70 which is lower than in the case of P-EtO[21]. The spacer group orientation of this particular polymer was also measured from the C–H stretching bands and typical order parameter values were 0.3–0.4[21].

The dielectric measurements were made on 25 μm thick samples (dimensions 10 mm × 10 mm) held between two glass plates coated with conductive indium–tin oxide and rubbed polyimide films of submicrometre thickness placed between the conductive indium–tin oxide layers and the polymer (Y type electric cell, EHC Co. Ltd, Japan). The polyimide film showed no measurable dielectric loss in the temperature and frequency range used in this study. The capacitances of the empty cell and of the cell filled with CCl_4 agreed to within 5% with values predicted from cell geometry and the dielectric permittivity of CCl_4.

The dielectric apparatus was an IMASS TDS time domain spectrometer equipped with a Hewlett Packard Series 300 computer. The time domain spectrometer is based on a design by Mopsik[22]. At time $t=0$ a step voltage of 10 or 100 V was applied between the indium–tin oxide layers. This induced a charge $Q(t)$ to flow through the sample and the complex capacitance was obtained as a function of frequency by a numerical Laplace transform, based on a cubic spline, of the time domain capacitance data. The latter covered a time period of 1 min and frequency domain data were obtained from 10^{-2} Hz to 10 kHz. All measurements were carried out by first cooling the sample to 100 K and then heating it while making measurements at progressively higher temperatures. Temperature equilibrium was established prior to each measurement.

RESULTS AND DISCUSSION

The P-EtO samples displayed four dielectric relaxation processes, in this paper referred to as α, β, γ and δ in order of descending temperature (*Figures 2* and *3*).

The γ process appearing at 130 K (10 Hz) was significantly weaker and broader than the higher temperature β process which peaked at 220 K (10 Hz). Both these relaxation processes appeared in the whole measured frequency–temperature range studied. The α process showing a maximum intensity at 300 K (4.5 Hz) in *Figure 2b*), was partly hidden by the pronounced increase in dielectric permittivity and loss appearing at higher temperatures caused by the Maxwell–Wagner–Sillars polarization. For this reason, no detailed analysis of the α process was possible. The calorimetric data presented in *Table 1* showing the presence of a second order transition at 310 K, suggested that the α process is due to the glass–rubber transition. The dielectric α process is very weak with a relaxation strength of $<10\%$ of the β process which indicates that P-EtO is highly ordered. The high frequency (4.5 kHz) data presented in *Figure 2c* show the presence of a fourth process (δ). Comparison is here made with dielectric loss data for poly(*p*-ethoxy styrene)[23]. There is a resemblance between the δ shoulder of P-EtO and the low temperature relaxation peak of the structurally similar poly(*p*-ethoxy styrene), the latter relaxation being assigned to torsion about the pendent ether bond[23]. The δ process only was observed in the very highest frequency data, so that no further detailed analysis was possible.

A comparison between *Figures 2d* and *3b* shows that the unrelaxed, low temperature dielectric permittivity of the oriented P-EtO sample is 20% greater than that of the corresponding isotropic sample. The relaxation processes β and γ are also stronger in the oriented P-EtO

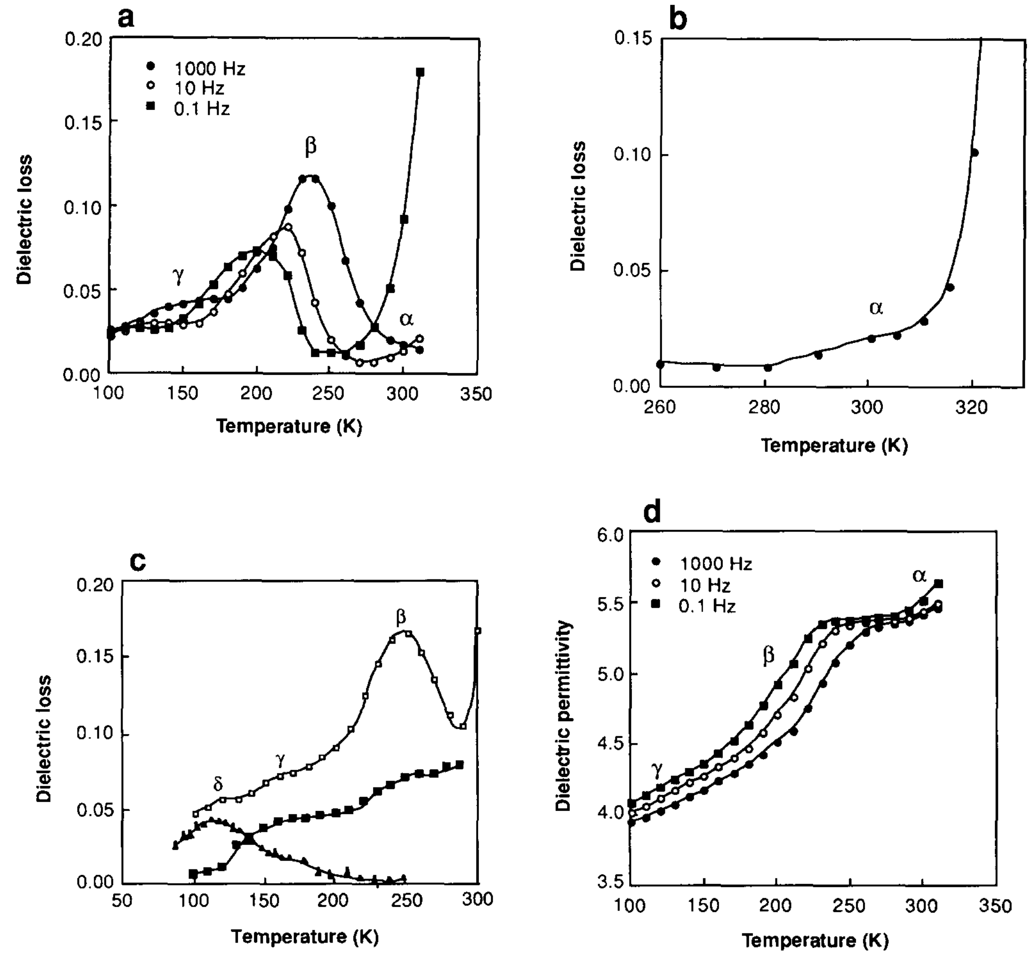

Figure 2 Dielectric relaxation of P-EtO PLAN (except for c): (a) dielectric loss at the frequencies shown as a function of temperature; (b) dielectric loss at 4.5 Hz as a function of temperature showing the α loss process; (c) dielectric loss of P-EtO ISO (□), P-CN ISO (■) and poly(*p*-ethoxystyrene) (▲) at 4500 Hz as a function of temperature showing the δ process[23]; (d) dielectric permittivity at the frequencies shown as a function of temperature

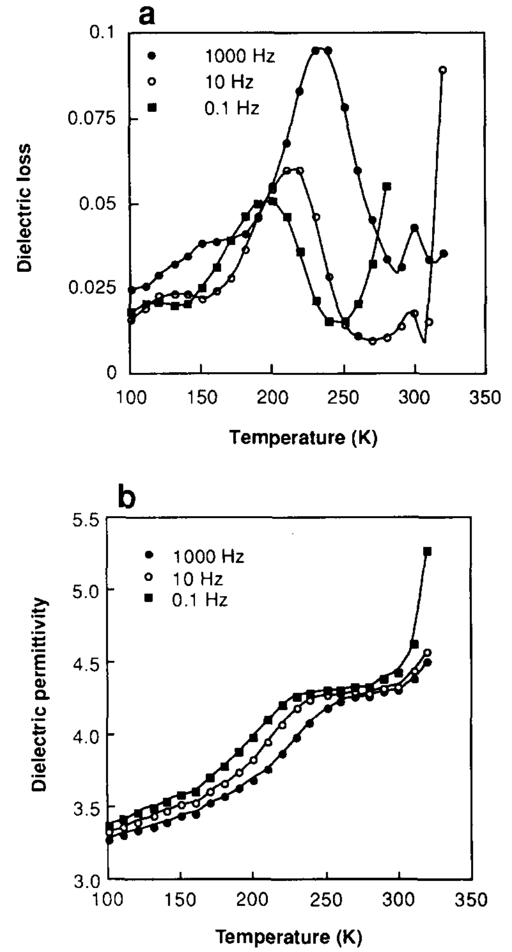

Figure 3 Dielectric relaxation of P-EtO ISO: (a) dielectric loss at the frequencies shown as a function of temperature; (b) dielectric permittivity at the frequencies shown as a function of temperature

sample (PLAN) than in the corresponding isotropic samples (ISO and QUENCH). The relaxation behaviour of P-EtO QUENCH was very similar to that of P-EtO ISO and for that reason is not shown.

P-CN exhibited only three relaxation processes, α, β and γ, according to the previous notations for P-EtO (*Figures 4* and *5*). The low temperature process (δ) was not present in P-CN which was clear from the low high frequency dielectric loss at 100 K (*Figure 2c*). This was true of both the oriented and isotropic specimens. The β and γ loss processes of P-EtO and P-CN were similar in both their temperature position and the relative sizes of the loss peaks. The intensities of the loss processes (β and γ) as judged from the heights of the loss peaks were, however, significantly lower for P-CN than for P-EtO. The unrelaxed dielectric permittivity was 20% lower for the oriented P-CN sample (PLAN) than for the isotropic equivalent, which is clearly different from the behaviour of the P-EtO samples (cf. *Figures 2d*, *3b*, *4b* and *5b*). Similar observations have been made in low molar mass cyano-containing liquid crystalline compounds[24] and may be explained by the fact that the cyano group is very polar so that the unrelaxed dielectric permittivity should be higher in the dipole direction, i.e. it should be higher in the isotropic sample with 1/3 of the cyano dipoles in the direction of the electric field than in the sample with planar orientation with ideally no cyano dipoles along the electrical field. The increase in unrelaxed low temperature dielectric permittivity with increasing planar orientation in P-EtO is consistent with earlier data on main-chain polyesters[25] and these findings can be rationalized in that the polarizability of the aromatic rings (dominant effect) and ester groups is directed perpendicular to the mesogens[25,26]. In the samples with planar orientation of the mesogens, the dipoles are predominantly oriented parallel to the electrical field yielding a higher unrelaxed low temperature dielectric permittivity. These effects should also be present in P-CN but the counteracting effect of the cyano groups is dominant in this polymer.

Figure 6 shows the temperature dependence of the central relaxation time (τ) obtained from plots of isochronal dielectric loss *versus* temperature. The two low temperature processes, β and γ, followed the Arrhenius equation. The activation energy of the γ process was very similar, $34 \pm 2\,\mathrm{kJ\,mol^{-1}}$, for all samples studied (*Figure 6* and *Table 2*). The activation energy of the β process varied between $60\,\mathrm{kJ\,mol^{-1}}$ and $105\,\mathrm{kJ\,mol^{-1}}$, with the P-CN samples at the low-value end (60 and $66\,\mathrm{kJ\,mol^{-1}}$) and with the different P-EtO samples varying between $74\,\mathrm{kJ\,mol^{-1}}$ and $105\,\mathrm{kJ\,mol^{-1}}$ (*Table 2*).

The relaxation strengths ($\varepsilon_r - \varepsilon_u$, where ε_r is the relaxed and ε_u is the unrelaxed dielectric permittivity) were

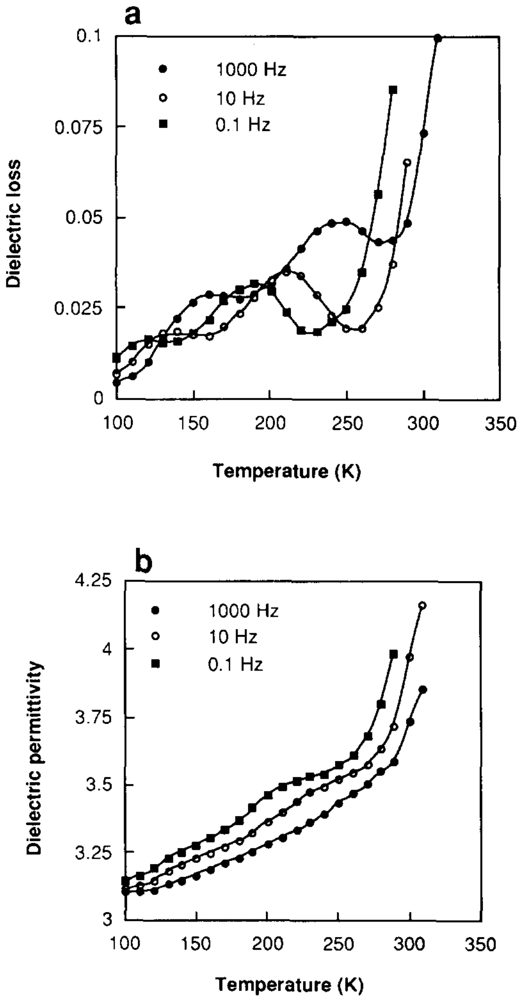

Figure 4 Dielectric relaxation of P-CN PLAN: (a) dielectric loss at the frequencies shown as a function of temperature; (b) dielectric permittivity at the frequencies shown as a function of temperature

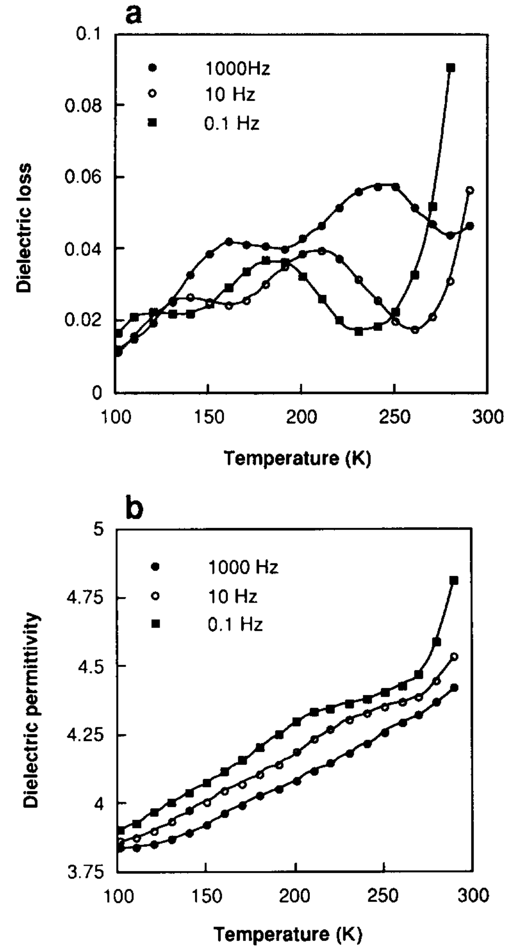

Figure 5 Dielectric relaxation of P-CN ISO: (a) dielectric loss at the frequencies shown as a function of temperature; (b) dielectric permittivity at the frequencies shown as a function of temperature

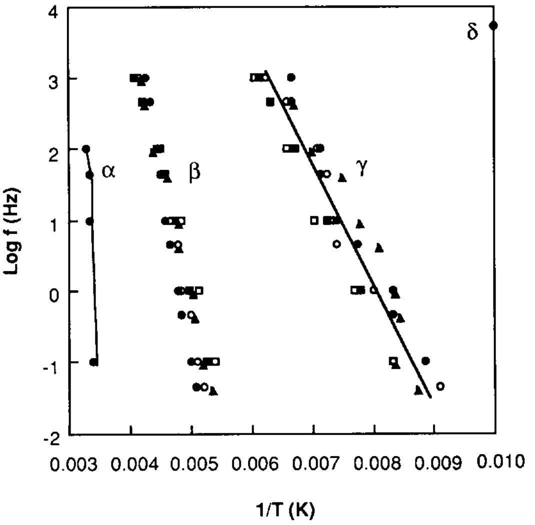

Figure 6 Temperature dependence of relaxation processes as obtained from plots of isochronal dielectric loss *versus* temperature: (●) P-EtO PLAN; (○) P-EtO ISO; (▲) P-EtO QUENCH; (■) P-CN PLAN; (□) P-CN ISO

obtained from Argand plots fitting the Havriliak–Negami equation[27] to the dielectric (ε^*) data:

$$\varepsilon^* = \varepsilon_u + \frac{\varepsilon_r - \varepsilon_u}{[1 + (i\omega\tau)^{\bar{\alpha}}]^{\bar{\beta}}} \tag{1}$$

where ω is the angular frequency, $\bar{\alpha}$ is the symmetric broadening parameter and $\bar{\beta}$ is the asymmetric broadening parameter.

Data for the unrelaxed and relaxed dielectric permittivities obtained from the fitting of equation (1) and adapted to the following linear temperature equations:

$$\varepsilon_u = \varepsilon_u^\circ + k_{1u}T \tag{2}$$

$$\varepsilon_r = \varepsilon_r^\circ + k_{1r}T \tag{3}$$

are presented in *Table 3*. Relaxation strength data were obtained from these polynomial expressions and are presented in *Table 2*. P-EtO showed significantly greater β and γ relaxation strengths for the sample with planar orientation (PLAN) of the mesogens than for the isotropic samples (ISO and QUENCH). The ratio of the relaxation strength values ($\Delta\varepsilon_{PLAN}/\Delta\varepsilon_{ISO}$) amounted to 1.55–1.75 (β at 200 K) and 1.63–1.83 (γ at 110 K). P-CN exhibited the opposite behaviour with lower relaxation strength values for the sample with planar orientation: ($\Delta\varepsilon_{PLAN}/\Delta\varepsilon_{ISO}$) was equal to 0.52 ($\beta$ at 200 K) and 0.38 (γ at 110 K).

The asymmetric broadening parameter $\bar{\beta}$ was in all cases equal to 1. The symmetric broadening factor $\bar{\alpha}$, on the other hand, exhibited different values as shown in *Tables 4* and *5*. The low temperature process (γ) showed

Table 2 Temperature dependence and strength of relaxation processes

Sample	Process	ΔE (kJ mol^{-1})	$\varepsilon_r' - \varepsilon_u'$
P-EtO PLAN	β	105	1.40[a]
P-EtO ISO	β	88	0.90[a]
P-EtO QUENCH	β	74	0.80[a]
P-CN PLAN	β	66	0.32[a]
P-CN ISO	β	60	0.62[a]
P-EtO PLAN	γ	33	0.95[b]
P-EtO ISO	γ	32	0.58[b]
P-EtO QUENCH	γ	36	0.52[b]
P-CN PLAN	γ	35	0.19[b]
P-CN ISO	γ	34	0.50[b]

[a] Relaxation strength at 200 K
[b] Relaxation strength at 110 K

Table 3 Temperature dependence of unrelaxed and relaxed dielectric permittivity[a]

Sample	Process	ε_u°	k_{1u}	ε_r°	k_{1r}
P-EtO PLAN	β	5.639	−0.0083	6.705	−0.00649
P-EtO ISO	β	3.803	−0.0021	4.325	−0.00016
P-EtO QUENCH	β	3.287	−0.0004	3.732	0.01995
P-CN PLAN	β	3.156	0.0003	3.127	0.00205
P-CN ISO	β	4.488	−0.0031	5.621	−0.00562
P-EtO PLAN	γ	4.148	−0.0069	5.015	−0.00617
P-EtO ISO	γ	3.423	−0.0028	4.002	−0.00274
P-EtO QUENCH	γ	2.916	−0.0005	3.299	0.00071
P-CN PLAN	γ	3.234	−0.0014	3.189	0.00078
P-CN ISO	γ	4.232	−0.0042	4.781	−0.00466

[a] Equations (2) and (3) were fitted to the experimental data

Table 4 Symmetric broadening factor ($\bar{\alpha}$) for β process[a]

Temp. (K)	P-EtO PLAN	P-EtO ISO	P-EtO QUENCH	P-CN PLAN	P-CN ISO
160	0.13	0.13	0.14	–	–
180	0.13	0.15	0.14	0.23	0.15
200	0.13	0.16	0.15	0.23	0.20
220	0.17	0.20	0.20	0.28	0.20
240	0.28	0.33	0.32	–	–
260	0.51	0.59	0.63	–	–

[a] By fitting of equation (1) to experimental data

Table 5 Symmetric broadening factor ($\bar{\alpha}$) for γ process[a]

Temp. (K)	P-EtO PLAN	P-EtO ISO	P-EtO QUENCH	P-CN PLAN	P-CN ISO
100	0.06	0.08	0.08	0.20	0.13
110	0.07	0.09	0.09	–	–
120	0.07	0.10	0.10	0.20	0.13
140	0.10	0.13	0.13	0.20	0.14

[a] By fitting of equation (1) to experimental data

lower $\bar{\alpha}$ values than the β process. A small but significant difference was also noticed between the oriented and isotropic samples of P-EtO, the oriented sample (PLAN) always having the lower $\bar{\alpha}$ value corresponding to the broader relaxation. Both β and γ appear to be narrower in P-CN than in P-EtO.

The molecular interpretation of the dielectric relaxation processes is presented in *Figures 7* and *8*.

The δ process, present only in P-EtO, involves motions of the pendent ethoxy group and torsion about the bond labelled 4. The appearance of a dielectric loss process in poly(p-ethoxy styrene) in the same temperature/frequency domain[23] is strong evidence in favour of this interpretation. The torsion about the same bond in P-CN does not lead to any change in dipole moment and hence the onset of such motion in P-CN is dielectrically inactive.

The γ process involves motion of the spacer group associated with the polar bonds labelled 1 and 2. It is present in both P-EtO and P-CN. The activation energy values obtained for the studied samples is the same, $34 \pm 2\,\mathrm{kJ\,mol^{-1}}$ (*Table 2*). Zentel *et al.*[4] report activation energy values of $35 \pm 10\,\mathrm{kJ\,mol^{-1}}$ for the so-called γ_1 process in phenylbenzoate-containing polyacrylates and polymethacrylates. The γ_1 process was assigned to motion in the methylene spacer group[4]. Semicrystalline, main-chain polyethers displayed a subglass process assigned[28] to motion in the methylene spacer with an activation energy of $50\,\mathrm{kJ\,mol^{-1}}$. Activation energies reported[29] for various polymers with longer oligo-methylene groups are typically in the range of 40–$50\,\mathrm{kJ\,mol^{-1}}$.

The β process is tentatively the result of coordinated torsions either about bonds 2 and 4 or about bonds 3 and 4 (*Figure 7*). The latter coordinated torsions lead to a mirror-imaging of the carboxyl group without any internal change in the surrounding groups (*Figure 8*). The swept-out volume of the motion should also be relatively limited. The intramolecular energy barrier for rotations about bonds 3 and 4 was calculated for oligo-hydroxy benzoic acid[30] and it was concluded that, due to resonance stabilization, the carbonyl group should be planar with respect to the nearby phenyl group, i.e. bond 3 can take two stable angular values, 0 and 180°. These two energetically indifferent rotational isomers are separated by an energy barrier (intramolecular)[31] amounting to $\sim 20\,\mathrm{kJ\,mol^{-1}}$. The energy barrier for torsion about bond 4 is according to the semiempirical AM1 calculations[30] $< 5\,\mathrm{kJ\,mol^{-1}}$, and four different stable conformers are present at torsion angles -135, -45, $+45$ and $+135°$. Thus a $+180°$ torsion about bond 3 coordinated with a $-180°$ torsion about bond 4 (from $+135$ to $-45°$) should give minimum change in the shape (small swept-out volume) and the required dielectric activity. Noticeable is the great variation in activation energy (60–$105\,\mathrm{kJ\,mol^{-1}}$; *Table 2*) among the studied samples. Side-chain phenylbenzoate-containing polyacrylates and polymethacrylates displayed a similar subglass process with reported[4] activation energies between $41\,\mathrm{kJ\,mol^{-1}}$ and $59\,\mathrm{kJ\,mol^{-1}}$. Main-chain polyesters of similar structure, poly(p-hydroxynaphthoic acid (HNA)-*co*-p-hydroxybenzoic acid (HBA)), displayed a subglass process assigned to the HBA moieties with an activation energy[32,33] close to $60\,\mathrm{kJ\,mol^{-1}}$. Terpolymers consisting of HBA, 4,4′-dihydroxybiphenyl and terephthalic acid had a subglass process originating from the HBA groups with an activation energy[34] between $59\,\mathrm{kJ\,mol^{-1}}$ and $71\,\mathrm{kJ\,mol^{-1}}$. Copolymers of HBA and ethylene terephthalate displayed a subglass process assigned to both constituents with an activation energy[35] of $56\,\mathrm{kJ\,mol^{-1}}$. These variations in activation energy illustrate that the intermolecular interaction plays a vital role since the intramolecular barriers should be $< 30\,\mathrm{kJ\,mol^{-1}}$. The activation energy of P-CN is in the same range as the majority of the reported data from phenylbenzoate-containing polymers. P-EtO, the most highly ordered polymer, also showed the highest activation energies, 74–$105\,\mathrm{kJ\,mol^{-1}}$.

The relaxation strength data can be treated according to the Onsager–Kirkwood–Fröhlich equation[29]:

$$\varepsilon_r - \varepsilon_u = \frac{3\varepsilon_r}{(2\varepsilon_r + \varepsilon_u)} \frac{4\pi N}{3kT}\left(\frac{\varepsilon_u + 2}{3}\right)^2 g\mu_0^2 \tag{4}$$

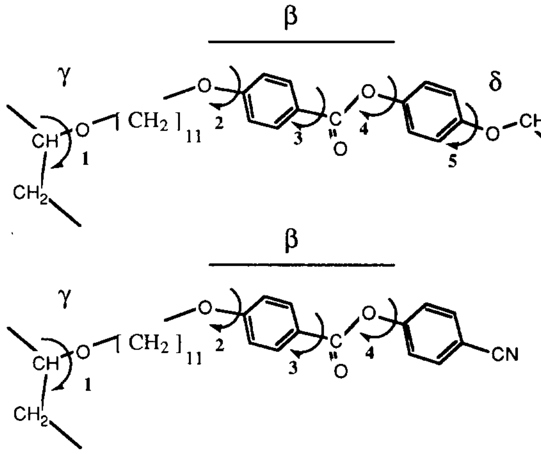

Figure 7 Structural interpretation of dielectric relaxation processes in P-EtO and P-CN

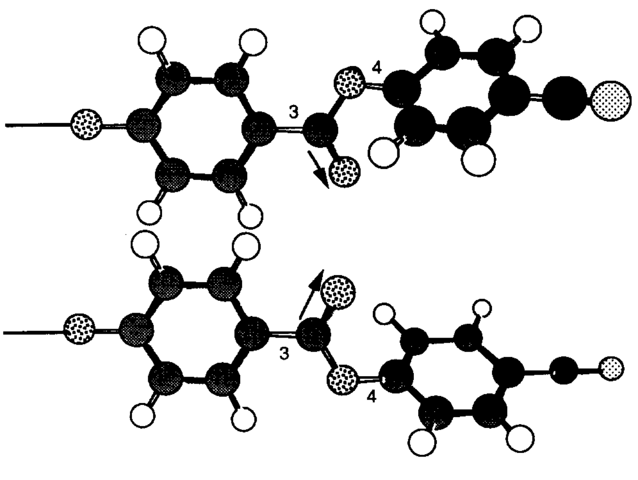

Figure 8 Reorientation of the carboxylic group in the phenyl benzoate moiety

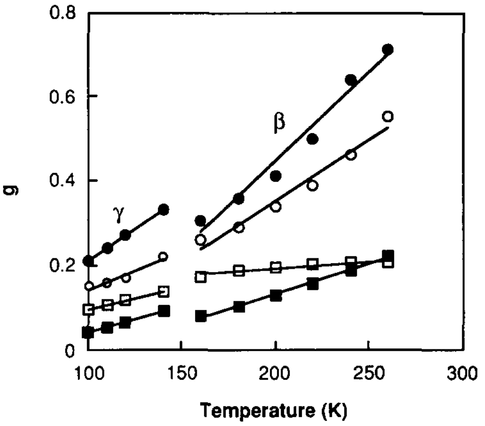

Figure 9 Correlation factor (g) of the Kirkwood–Onsager–Fröhlich equation [equation (4)] as a function of temperature for γ and β: (●) P-EtO PLAN; (○) P-EtO ISO; (■) P-CN PLAN; (□) P-CN ISO

where N is dipole density, μ_0 is the dipole moment, k is the Boltzmann constant, T is the absolute temperature and g is the dipolar correlation factor. In the calculation of the correlation factor, the experimental unrelaxed and relaxed dielectric permittivity values shown in *Table 3* were used. It was assumed that the two ether dipoles, each with a dipole moment[36] of 1.1 D, could potentially participate in the γ process. The correlation factor was also calculated for the β processes, in that case assuming that the carboxylic group with the dipole moment[36] of 1.7 D could potentially participate in the β process. The density of the polymer was assumed to be 1300 kg m^{-3}.

The low values of the g factor for the γ process shown in *Figure 9* indicate that the dipoles are spatially restricted and that the reorientation of dipoles is hindered. For the P-EtO, the ratio between the g values of PLAN and ISO samples is always >1, i.e. 1.5 ± 0.1 for γ and 1.26 ± 0.1 for β. The sample with planar orientation of the mesogens has the participating dipoles essentially lying in the plane perpendicular to the film plane. The dielectric activity should thus in this case be higher than in the case of a globally isotropic polymer, which is in accordance with the data presented in *Figure 9*. The behaviour of P-CN is anomalous with ratios of the g values of PLAN and ISO samples smaller than 1 and we have presently no explanation. It cannot be excluded that in these samples orientation is biaxial, i.e. that the relaxing dipoles in the plane are oriented.

CONCLUSIONS

Dielectric permittivity and loss measurements on two mesomorphic side-chain poly(vinyl ether)s, P-EtO and P-CN, showed the presence of four relaxation processes: a glass–rubber transition (α) and three subglass processes denoted β, γ and δ in order of descending temperature. The low temperature process δ was assigned to torsion about the outer phenyl group carbon and the end group. This was not present in P-CN due to symmetry of the cyano dipole. The γ process showed morphological insensitivity and was assigned to local motions within the spacer whereas the β process showed a strong variation in activation energy among the different samples reflecting variations in local order. It is suggested that the β process leads to reorientation of the carboxylic group in the phenyl benzoate moiety.

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