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Dielectric relaxation of liquid crystalline polymers used in non-linear optical materials

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Dielectric permittivity and loss have been measured over the frequency range 0.1–1000 Hz between 80 K and 300 K for side-chain and network liquid crystalline polyacrylates obtained by photopolymerization of smectic monomers. The polyacrylates were based on mixtures of chiral monofunctional monomers with a lateral nitro group attached to the outer phenyl group of the mesogen and an ester group in the mesogen and nonchiral bifunctional monomers, either with an ester group in the mesogen or with an ester group in the mesogen and a lateral nitro group, creating networks with different crosslink densities. Poled copolymers based on these monomers exhibit second-order nonlinear optical properties. Polymers based only on monomers with the chiral and nitro groups exhibited a pronounced γ process, associated with segmental motions in the methylene spacer groups and only vague signs of the high-temperature subglass process (β) associated with reorientation of the mesogen. The polymers with the bifunctional monomer without the nitro group exhibited clearly both γ and β processes. The dielectric data indicate that the ester groups in the bifunctional units undergo conventional reorientation according to the β mechanism and that the β process is suppressed in the pendant chains with the lateral nitro groups. The β process involves a coordinated torsion about two bonds in the mesogen and the swept-out volume involved in the motion becomes extensive when a lateral nitro group is present. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The dielectric relaxation of side-chain polymers, including polyacrylates, polymethacrylates, polysiloxanes and polyvinylethers, has been extensively studied in several papers[1–14]. These polymers exhibit typically five dielectric relaxation processes as schematically shown in *Figure 1*: α, the glass–rubber transition, three subglass processes referred to as β, γ and δ and a high temperature process often denoted 'δ'. The low temperature subglass process, δ, is assigned to torsion about bonds in the tail group[4,13]. The γ process was assigned to local motions in the spacer group[4,13]. The activation energy of the γ process was insensitive to the length of the spacer group, the mesogen, the terminal group and the morphology, with a value of 32 ± 5 kJ mol^{-1} [13,14]. The β process was assigned to reorientation of dipoles in the mesogen, e.g. the ester group in phenylbenzoate[4,5,13,14]. The β process showed a large variation in activation energy among the studied samples, ranging from 50 to 128 kJ mol^{-1} [13,14]. A high temperature process, denoted the 'δ' process by Williams *et al.*, causes a reorientation of the entire side-group by rotation about the backbone chain[6–8,11,12].

The realization that organic molecules may possess very high second-order hyperpolarizabilities has during the past decade led to a strong activity to make second-order non-linear materials based on side-chain liquid crystalline polymers[15]. Only materials with dipolar order exhibit second-order nonlinear optical properties[15]. The typical combination of features of a non-linear optical chromophore is an electron-donating group (e.g. –OH, –OR, $-NH_2$, $-NR_2$, –SH and –SR) connected to an electron-accepting group (e.g. –CN, $-CF_3$, –CHO, $-NO_2$ and SO_2R) via a conjugated structure[16]. The hyperpolarizability is proportional to the cube of the length of the conjugated structure[16]. Second-order non-linear optical materials, prepared by photopolymerization of poled ferro-electric liquid-crystalline monomers, were recently reported[17–19]. Smectic C* mixtures of two acrylate monomers, one being a chiral monoacrylate containing a lateral nonlinear optical chromophore and the second being a diacrylate, were aligned (polar order) in a static electric field and were subsequently photopolymerized to yield pyroelectric materials exhibiting the Pockels effect and second-harmonic generation[17–19]. The presented optical data concern

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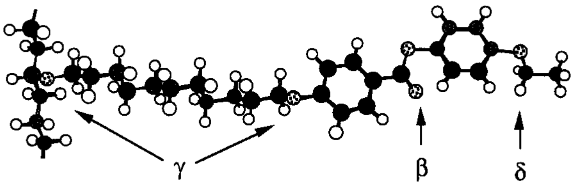

Figure 1 Schematic representation of relaxation processes in side-chain liquid crystalline polymers. Atoms: hydrogen—white; carbon—shaded; oxygen—dotted

materials fairly newly made and their long-term properties, particularly after exposure to high temperatures, is currently unknown. The polar order may decay with time by coordinated torsions about σ bonds near or in the mesogens causing reorientation of the lateral dipoles of the mesogens. The purpose of this study is to examine the dielectric relaxation of these polymers and, in particular, to establish if they exhibit a β process, i.e. the proces that would cause a reorientation of the dipoles attached to the conjugated system.

EXPERIMENTAL

The monomers used in this study were prepared according to Trollsås *et al.*[18] {4″-[11-acryloyloxyundecyloxy]-4′-biphenyl 4-[(R)-(+)-2-octyloxy]-3-nitrobenzoate, denoted **A1**; 4″-(11-acryloyloxyundecyloxy)phenyl 4-(4′-(11-acryloyloxyundecyl-oxy)phenyl)benzoate, denoted **A2**} and Sahlén *et al.*[20] {4″-[(R)-(−)-2-octyloxy]-3″-nitro-phenyl 4-(4′-(11-acryloyloxyundecyloxy)phenyl) benzoate, denoted **A1b**; 4″-(11-acryloyloxyundecyloxy)-3″-nitro-phenyl 4-(4′-(11-acryloyloxyundecyloxy) phenyl) benzoate, denoted **A2b**) and their structures are shown in *Figure 2*.

The liquid crystalline monomers, pure or blends of two monomers mixed with 0.04% photo-initiator 1,2,6-trimethylbenzoyldiphenyl phosphone oxide (Lucirin™; BASF) and 0.1 wt% hydroquinone, were introduced into a cell consisting of two glass plates coated with conductive indium-tin-oxide in the isotropic state by capillary forces. Hydroquinone was added to inhibit early, unwanted thermal polymerization. The filling of the cell was performed in a vacuum oven to avoid thermal oxidation. The cell was inserted into a Mettler FP82 hot stage capable of controlling temperature within ±0.1 K. The mesophases could be characterized before and during polymerization, the latter being photo-initiated using an Osram Ultra-Vitalux lamp (300 W). *Table 1* shows the characteristics of samples prepared by this technique and used in this study.

The dielectric measurements were made on 50 μm or 10 μm thick samples with the lateral dimensions 10 mm × 10 mm held between two glass plates coated with conductive indium-tin-oxide and rubbed poly(imide) films of submicron thickness placed between the conductive indium-tin-oxide layers and the polymer (Y type electric cell, E.H.C. Co. Ltd, Japan). The poly(imide) film showed no measurable dielectric loss in the temperature and frequency range used in this study. 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[21]. At time $t = 0$ a step voltage of 10 V or 100 V was applied between the indium

Table 1 Studied polymers

Sample code	Monomer composition	Monomer mesophase[a]	Specimen thickness (μm)
Poly(**A1**)	A1:100%	S_A	50
Poly[**A1–A2** (30–70)]	A1:30%; A2:70%	S_A	50
Poly[**A1–A2** (50–50)]	A1:50%; A2:50%	S_C	10
Poly(**A1b**)	A1b:100%	S_C	50
Poly[**A1b–A2b** (50–50)]	A1:50%; A2:50%	S_A	50

[a] During polymerization

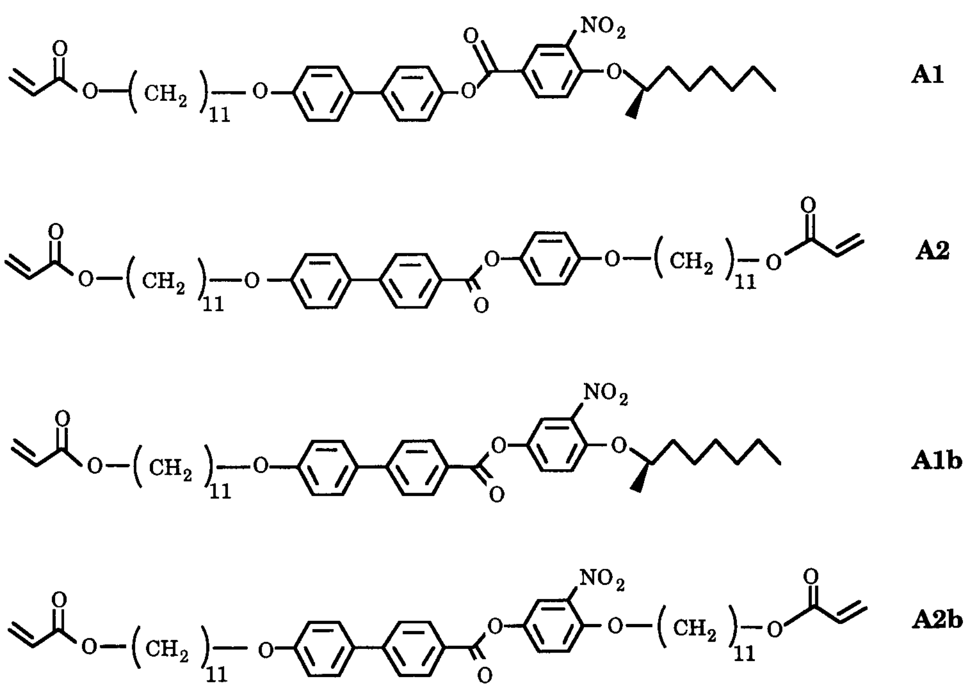

Figure 2 Structure and abbreviated names of used monomers

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 90 K and then heating it while making measurements at progressively higher temperatures. Temperature equilibrium was established prior to each measurement.

RESULTS AND DISCUSSION

Figures 3 and *4* shows the three isochronal sets of data for the dielectric loss and the dielectric permittivity as a function of temperature for poly(**A1**). The low temperature process (γ) appeared clearly at 120 K (10 Hz) which is within 10 K from earlier reported dielectric data of the γ process in polyvinylethers[13,14]. A weak shoulder appears on the loss curve at 190 K which is 10–20 K below the temperature at which the loss peak of the β process in polyvinylethers with phenylbenzoate mesogens[13]. The intensity of the β process in poly(**A1**) is thus very low, at least an order of magnitude lower than in polyvinylethers with phenylbenzoate mesogens[13].

Figure 5 shows the dielectric loss data for poly(**A1b**), which shows great structural resemblance with poly(**A1**) as can be seen in *Figure 2*. The γ loss peak appears exactly at the same temperature as for poly(**A1**) and the

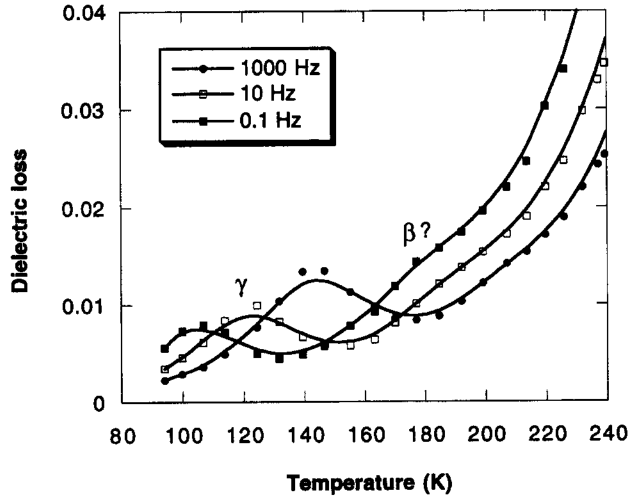

Figure 3 Dielectric loss as a function of temperature for poly(**A1**). Isochronous curves taken at the frequencies shown in the graph

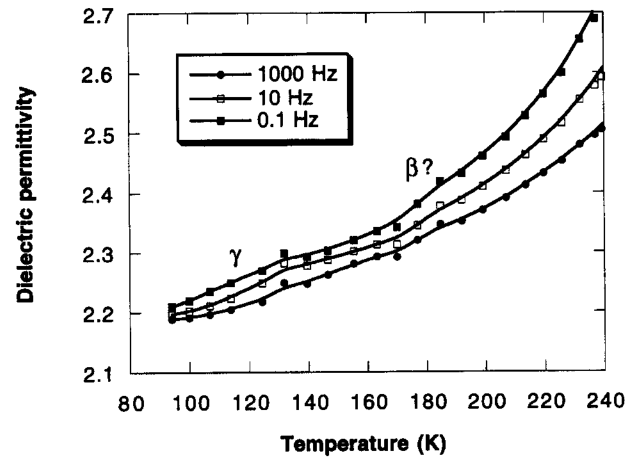

Figure 4 Dielectric permittivity as a function of temperature for poly(**A1**). Isochronous curves taken at the frequencies shown in the graph

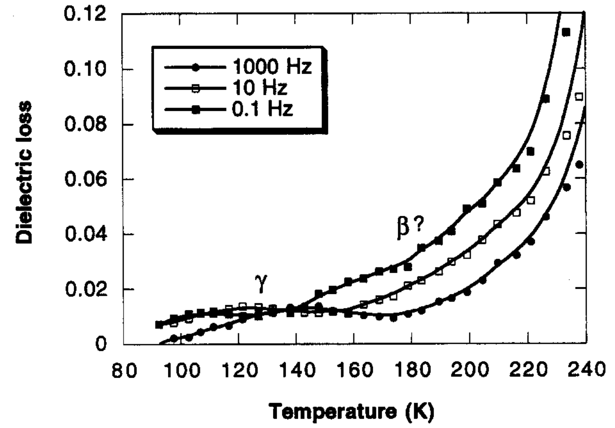

Figure 5 Dielectric loss as a function of temperature for poly(**A1b**). Isochronous curves taken at the frequencies shown in the graph

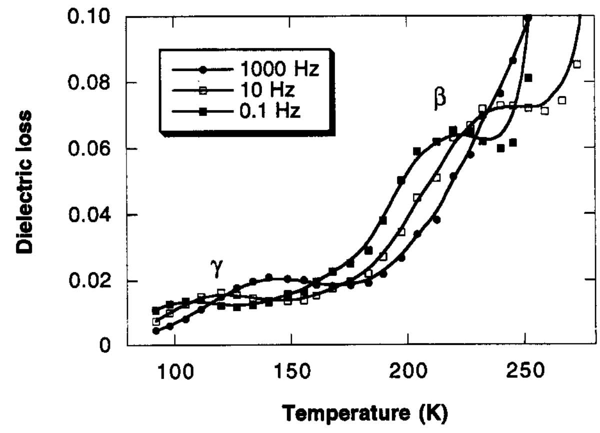

Figure 6 Dielectric loss as a function of temperature for poly[**A1**–**A2**(30–70)]. Isochronous curves taken at the frequencies shown in the graph

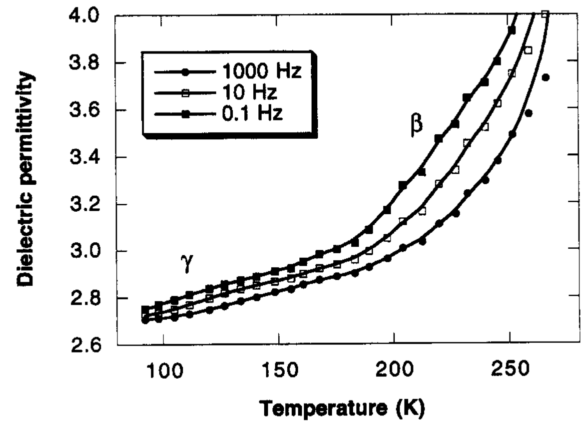

Figure 7 Dielectric permittivity as a function of temperature for poly[**A1**–**A2**(30–70)]. Isochronous curves taken at the frequencies shown in the graph

existence of a weak β process is less obvious in poly(**A1b**).

The polymers containing the bifunctional monomer **A2** showed strong γ and β processes [*Figures 6* and *7*; only shown for poly[**A1**–**A2**(30–70)]. The other polymers based on bifunctional monomers, poly[**A1**–**A2**(50–50)] showed similar dielectric loss curves with pronounced γ and β peaks. The temperature positions of the loss peaks for poly[**A1**–**A2**(30–70)] at 10 Hz, 120 K (γ) and 230 K (β), were very similar indeed to those reported for polyvinylethers with phenylbenzoate mesogens[13]. The copolymer poly[**A1b**–**A2b**(50–50)] exhibited a pronounced γ process and only a weak β process.

One important question is whether the β loss peak is masked by the pronounced upturn in dielectric loss with increasing temperature. The magnitude of this upturn showed variation among the samples studied but it did not show any systematic trend with respect to the monomeric structure. It is believed that the upturn is related to the presence of small concentrations of impurities in the samples. Poly(**A1**) and poly(**A1b**) showed only weak β peaks whereas different poly(**A1**–**A2**) showed pronounced β peaks. It is important to compare the 'background' dielectric loss level in the β region for the different samples (*Figures 3*, *5* and *6*) which is low for poly(**A1**) and higher for poly(**A1b**) and poly[**A1**–**A2**(30–70)]. It may thus be concluded that the β process is not masked by the upturn in dielectric loss for poly(**A1**) and poly(**A1b**).

The Havriliak–Negami equation[22] which can be expressed as

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

where ϵ^* is the complex dielectric permittivity, ϵ_u is the unrelaxed dielectric permittivity, ϵ_r is the relaxed dielectric permittivity, $\bar{\alpha}$ is the symmetric broadening factor and $\bar{\beta}$ is the asymmetric broadening factor, was fitted to the dielectric data. The processes are very broad in the frequency domain and it is difficult to judge their shapes precisely. However, from the complex plane plots there was no apparent evidence for skewing. Thus, the assumption was made that they are symmetrical and the fits of equation (1) were carried out with $\bar{\beta}$ constrained to unity (Cole–Cole process). *Figure 8* shows a few selected and typical complex plane plots with experimental and fitted data.

The temperature dependences of the γ process for the different polymers were always almost the same (*Figure 9*) and the activation energies ranged between 27 and $34\,\mathrm{kJ\,mol^{-1}}$ (*Table 2*) which are similar to earlier reported data, $30–35\,\mathrm{kJ\,mol^{-1}}$, for the γ process in polyvinylethers with 11-carbon-methylene spacers. The symmetric broadening factor was near 0.3 at 120 K which is greater than the 0.1–0.2 that was reported[13] for the polyvinylethers as the same temperature. The relaxation strength was 0.070 [for poly(**A1**)] to 0.22 {for poly[**A1**–**A2**(50–50)]} which is less than half that reported[13] for the polyvinylethers with 11-carbon-spacer and phenylbenzoate mesogen. The very low value of the relaxation strength for poly(**A1**) should be viewed in light of its relatively high value of the symmetric broadening factor (*Table 2*). A lowering of

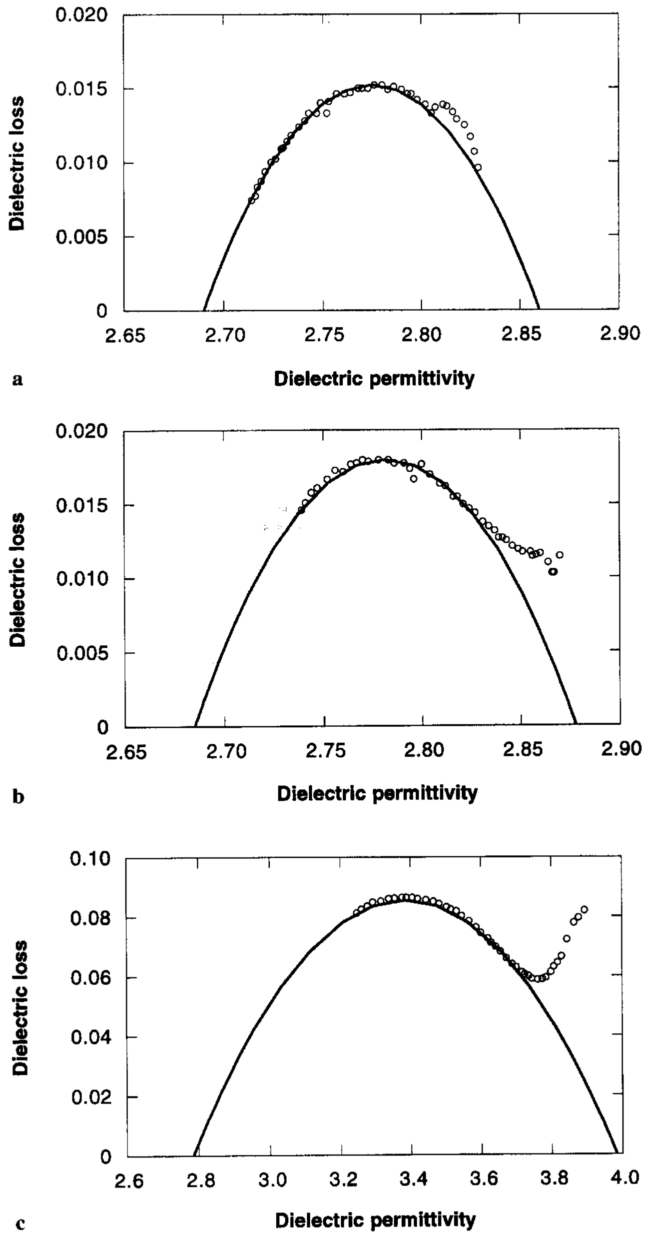

Figure 8 Complex plane plots. The solid lines are best fits of equation (1) to the experimental data. (a) γ process of poly[**A1**–**A2**(30–70)] at 111.4 K; (b) γ process of poly[**A1**–**A2**(30–70)] at 126.6 K; (c) β process of poly[**A1**–**A2**(30–70)] at 245.5 K

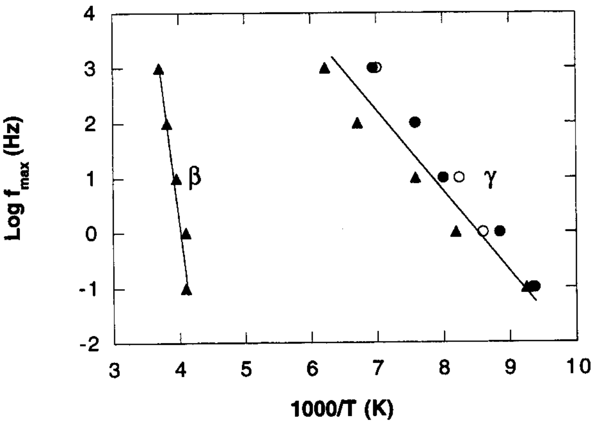

Figure 9 Temperature dependence of the relaxation processes as obtained from plots of isochronal dielectric loss vs temperature: poly(**A1**) (●), poly(**A1b**) (○) and poly[**A1**–**A2**(30–70)] (△)

Table 2 Characteristics of the relaxation processes

Polymer	Process	ΔE (kJ mol^{-1})	$\Delta\epsilon$	$\bar{\alpha}$
Poly(**A1**)	γ	31	0.070 (124 K)	0.39 (124 K)
	β (weak)			
Poly[**A1**–**A2**(30–70)]	γ	27	0.193 (127 K)	0.24 (127 K)
	β	79	1.20 (246 K)	0.18 (246 K)
Poly[**A1**–**A2**(50–50)]	γ	33	0.22 (127 K)	0.31 (127 K)
	β	97	0.6–0.9 (200–240 K)	0.1–0.25 (200–240K)
Poly(**A1b**)	γ	33	0.105 (127 K)	0.34 (127 K)
	β (weak)			
Poly[**A1b**–**A2b**(50–50)]	γ	34; 44	0.20 (122 K)	0.27 (122 K)
	β	weak; 168	–; 0.18 (224 K)	–; 0.69 (224 K)

the fitted $\bar{\alpha}$ value causes an increase in the optimum relaxation strength value. The fitted Havriliak–Negami equation-plots for the other samples are in agreement with the experimental data (*Figures 8a* and *b*). The mass fraction of spacer groups is lower in **A1** and **A1b** than in the aforementioned polyvinylethers. Both **A2** and **A2b** contain however a larger mass fraction of spacer groups than the polyvinylethers. The reported data thus indicate that the ester and ether dipoles attached to the spacer groups are more constrained in the polymers reported here than in the earlier reported polyvinylethers.

The β process showed a similar temperature dependence (activation energy) as was reported earlier for the polyvinylethers[13,14] (*Table 2*). The β process was weak in poly[**A1b**–**A2b**(50–50)] and the presented value (168 kJ mol^{-1}) is associated with a considerable uncertainty. The relaxation strength values of the β process presented in *Table 2* should be compared with values reported for polyvinylethers between 0.6 and 1.0 which is thus similar to the data reported in *Table 2*. The uncertainty in the obtained fitted values is considerable, which is illustrated in *Figure 8c*. The absence or the very low intensity of the β process in poly(**A1**) and poly(**A1b**) indicates that the β process is either 'locked-in' (not occurring) in pendant chains with lateral nitro groups and a chiral centre or that the β process involves coordinated torsions that cause 'cancelling' reorientations of the ester and nitro groups. The presence of an extra, strong dipole (nitro group) in the mesogen of poly(**A1**) and poly(**A1b**) should favour an increase in the intensity of the β process. This together with the fact that these materials also show second-order nonlinear susceptibility after a month of storage at room temperature indicate that the β process is locked-in in these polymers. The ester groups in the bifunctional unit **A2**, however, undergo conventional reorientation according to the β mechanism. The weak β process in poly[**A1b**–**A2b**(50–50)] is basically consonant with this view. The relaxation strength of the β process was only 20% of that of poly[**A1**–**A2**(50–50)] (*Table 2*). In conclusion, the lateral nitro group attached to the outer aromatic ring of the mesogen inhibits the β mechanism to a large extent.

The β mechanism involves the reorientation by 180° of the ester dipole of the phenylbenzoate unit of the mesogen[4,13,14]. This can be accomplished by a 180° torsion about either of bonds **A** and **B** (*Figure 10a*). The torsion about bond **B** involves a greater *intra*molecular energy barrier than the torsion about bond **A**. The *intra*molecular energy barrier for torsion about bond **B** is of the order of 20 kJ mol^{-1} [23]. *Figure 10a* shows a structure which is part of monomer **A2**. Two stable states thus exist, both being characterized by the carbonyl group being in the same plane as the adjacent aromatic ring due to resonance stabilization (*Figure 10a*). Any torsion about bond **C** causes a pronounced change in the orientation of the outer aromatic ring and is not likely to occur in a smectic mesophase. The torsion about bond **A** (or **B**) causes a moderate shift in position of the outer phenylene group and there is a sizeable swept-out volume involved in the motion that can be reduced by a co-ordinated torsion about bond **D**. *Figure 10b* shows the same structure with an added lateral nitro group. This structure is a part of **A1b** and **A2b**. The torsion about bond **A** (or **B**) involves a substantially larger swept-out volume than for the previous presented case (*Figure 10a*). It is thus not surprising that the lateral nitro group substantially inhibits the β mechanisms in poly[**A1b**–**A2b**(50–50)]. It is also very likely that the presence of the nitro group causes a considerable energy difference between the two conformers due to intermolecular interactions (biased states) which should decrease the strength of the β process.

The important part of the structure of **A1** with the nitro group removed is shown in *Figure 10c*. The reorientation of the ester dipole occurs by torsion about bond **A** (or **B**). The swept-out volume seems larger than for the case with the reversed ester group (cf. *Figures 10a* and *c*). *Figure 10d* shows the very same structure with the lateral nitro group included. The swept-out volume for the motion becomes very substantial and it is not surprising that the lateral nitro group nearly completely locks the mesogen reorientation in poly(**A1**). The above reasoning about the biased states also holds in this case.

Carr *et al.*[24] reported a suppression of the β process in a side-chain LC-polymethacrylate with a terminal nitro group. They proposed that *inter*molecular interaction played the major role in the suppression of the β process. This is in essence what is proposed for the polymers with the lateral nitro groups dealt with in this study.

CONCLUSIONS

Dielectric relaxation measurements on polyacrylates based on mixtures of chiral monofunctional and bifunctional monomers indicate that the mesogenic ester groups in the bifunctional units containing no lateral nitro groups undergo conventional reorientation according to the β mechanism and that the β process is almost completely

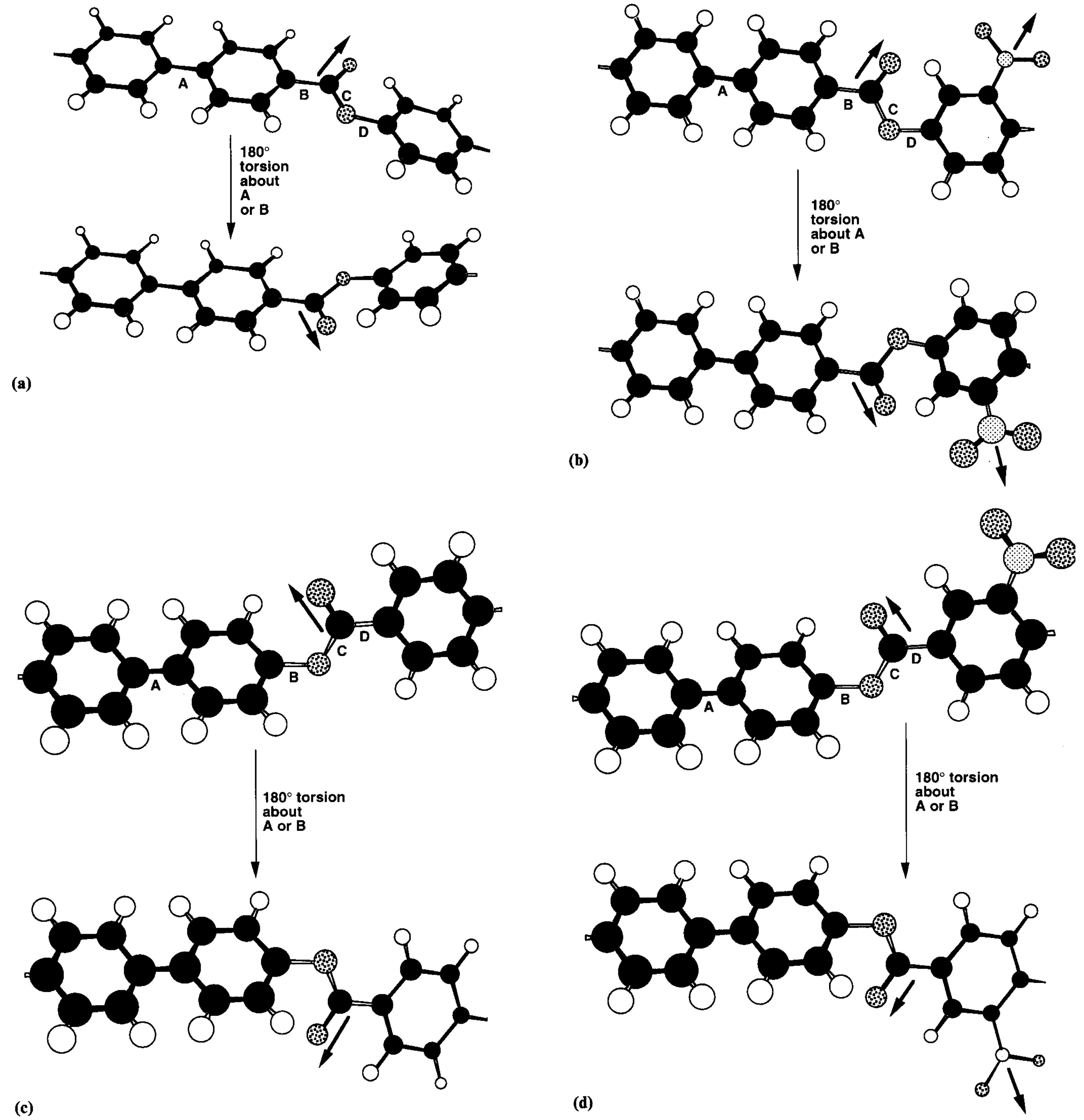

Figure 10 Simple models of the β mechanism in different groups: (a) part of **A2**; (b) part of **A1b** or **A2b**; (c) part of **A1** without nitro group; (d) part of **A1**. Atoms: hydrogen—white; carbon—shaded; oxygen—large dots; nitrogen—small dots. The arrows indicate major dipole moments

suppressed in the pendant chains with lateral nitro groups. This finding is important because it suggests that the polar order that is a prerequisite for the second-order nonlinear optical properties should remain over long time periods in polymers with chiral centres incorporating mesogens with lateral nitro groups.

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