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Dipolar association of liquid crystalline side chain homo- and copolymers

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The dipolar association of liquid crystalline side chain homo- and copolymers is analysed by dielectric relaxation spectroscopy. The side chains of the polymers possess similar shape but contain polar and/or non-polar mesogenic units. In analogy to mixtures of low molar mass liquid crystals the dielectric properties of these homo- and copolymers deviate from ideal behaviour and the deviations are clearly deduced from the dipolar associations of the polar mesogenic units. However due to the linkage of the liquid crystalline moieties to the polymer backbone the dipolar association is much more pronounced than association of low molar mass liquid crystals having a very similar chemical constitution.

1. Introduction

By applying an electric or magnetic field to liquid crystalline side chain polymers (LCSCPs) the nematic director can be macroscopically aligned, which enables us to analyse quantitatively anisotropic dielectric properties. From these measurements molecular properties can be calculated. As the static dielectric constant depends on the effective dipole moment, the effective dipole moment parallel and perpendicular to the long axis of the mesogenic group can be calculated [1] and information about intermolecular interactions between neighbouring dipoles can be obtained.

In addition to the static dielectric properties the dynamic dielectric properties are equally influenced by intermolecular interactions. The dynamic properties are determined by different relaxation processes which are related to segmental mobility within the mesogenic side groups and the polymer backbone [2, 3]. δ-relaxation is assigned to the rotation of the mesogenic group around the short molecular axis. Therefore, if the sample is homeotropically aligned between capacitor plates, δ-relaxation becomes strong [4] and reflects the dipole moment parallel to the molecular long axis. Hence, dielectric measurement of a homeotropically aligned sample allows the correlation of δ-relaxation with intermolecular interactions of the dipoles parallel to the molecular long axis. Additionally, it is possible to examine the effect of linking different mesogenic side groups, which are connected to the polymer backbone via a flexible spacer, on δ-relaxation.

If we consider nematic copolymers where the mesogenic units strongly differ with respect to the dipole moments along the long molecular axis of the mesogenic groups, strong intermolecular interactions are expected between neighbouring mesogens. The question arises, whether the static and dynamic dielectric properties will behave ideally

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with varying composition of copolymers, or whether non-linear behaviour is observed. Furthermore it is interesting to prove, whether additional effects occur in LCSCPs compared to low molar mass liquid crystals, which are caused by linking the mesogenic moieties to the polymer backbone.

Here we describe the static and dynamic properties of nematic LCSCPs, which vary in the composition of their mesogenic units. The results of the investigation of the static properties are correlated with the effective dipole moments and with the dynamic properties. The intermolecular interactions between neighbouring mesogens in the copolymers are discussed and correlated with the frequency dependent properties.

2. Experimental

The polymers were synthesized according to well-known methods [5] and the composition of the copolymers was verified by FTIR spectroscopy. The phase transitions of the polymers were determined by DSC (Perkin–Elmer DSC 7). Refractive indices were determined with an Abbé refractometer and densities were measured with an Anton Paar densimeter. The order parameter and the anisotropy of polarizability was evaluated by the method of Haller *et al* [6]. In order to obtain completely aligned samples, we used magnetic (1·8 T) or electric fields ($10\,\mathrm{V}\,\mu\mathrm{m}^{-1}$) which were stronger than the threshold field strength. The dielectric measurements were performed with an impedance analyser (Fa. Schlumberger SI 1260) within a frequency range of 10 Hz up to 1 MHZ using a voltage amplitude of 1 V. The polymers were placed between two gold coated electrodes. The sample thickness was controlled by glass spacers with varying diameters (20–90 μm). Wide angle X-ray scattering data were obtained with a Siemens D-500 diffractometer in a reflected mode using step-by-step scanning and Ni-filtered Cu–K_α radiation. All samples studied were annealed in the liquid crystalline state for 1 day prior to X-ray analysis. Additionally, one of the samples (P100) was annealed in the liquid crystalline state near the clearing temperature (50°C) for 3 days. A fit program was used to determine the positions and widths of the scattering profiles and for separating overlapping peaks [7]. From the fitted profiles d spacings were calculated according to a Bragg law and the corresponding sizes of the ordered regions L were obtained from the reflex widths β using: $L=1/\beta$ [8].

3. Polymer synthesis and characterization

The LCSCPs P0–P100 were synthesized by addition reaction of varying amounts of the mesogenic molecules R1 and/or R2 to a poly(hydrogen-methylsiloxane) (see figure 1). The comonomers are based on phenylbenzoate carrying a terminal methoxy or cyano group. For the comonomer R1 a methyl side group was introduced to prevent the formation of smectic layers. In table 1 the phase transition data determined by DSC, densities and polarizabilities are summarized. The phase transition of the homopolymer P0 corresponds to data given in the literature [9]. The clearing temperature of P100 is 10 degrees higher than the data obtained by Attard *et al.* [10]. This may be due to the higher degree of polymerization. Within this series of copolymers the glass transition temperatures remain almost constant, whereas the clearing temperatures decrease with increasing R1 content. The densities vary linearly with the composition of the polymers indicating ideal mixing behaviour. The polarizabilities α of the monomer units were evaluated from the refractive indices by the Lorentz–Lorentz equation [6]. The temperature dependence of α is shown in figure 2 taking into account an expansion coefficient of $4{\cdot}5\times10^{-4}\,\mathrm{cm}^3\,\mathrm{K}^{-1}$ and $5\times10^{-4}\,\mathrm{cm}^3\,\mathrm{K}^{-1}$ within the liquid crystalline and isotropic phases, respectively. At the

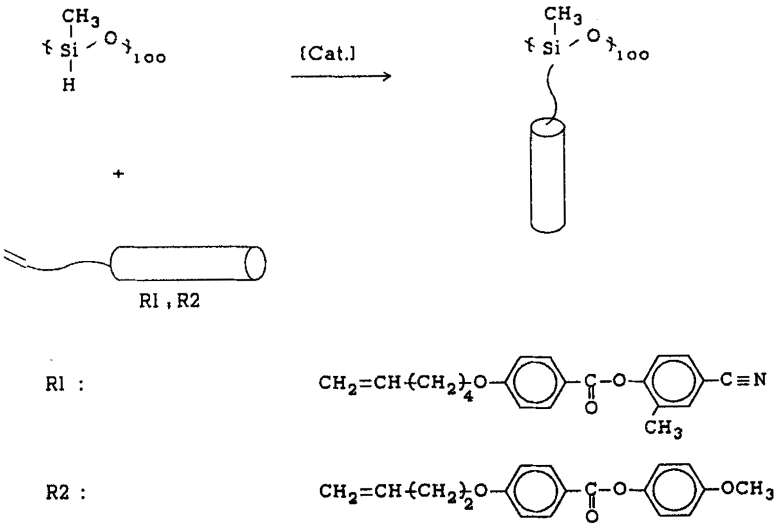

Figure 1. Synthesis and chemical structure of the mesogenic units R1, R2 and corresponding polymers.

Table 1. Composition of the polymers, DSC phase transition data, polarizability and density.

Polymer	Molar ratio R1 : R2/%	Phase transitions/°C	Polarizability $\times 10^{30}/m^3$	Density/ g/cm^{-3}
P0	0 : 100	g 11 N 99 I	38·5	1·216
P25	25 : 75	g 10 N 89 I	39·9	1·202
P50	50 : 50	g 10 N 76 I	41·1	1·193
P75	75 : 25	g 11 N 60 I	42·4	1·178
P100	100 : 0	g 6 N 53 I	43·7	1·167

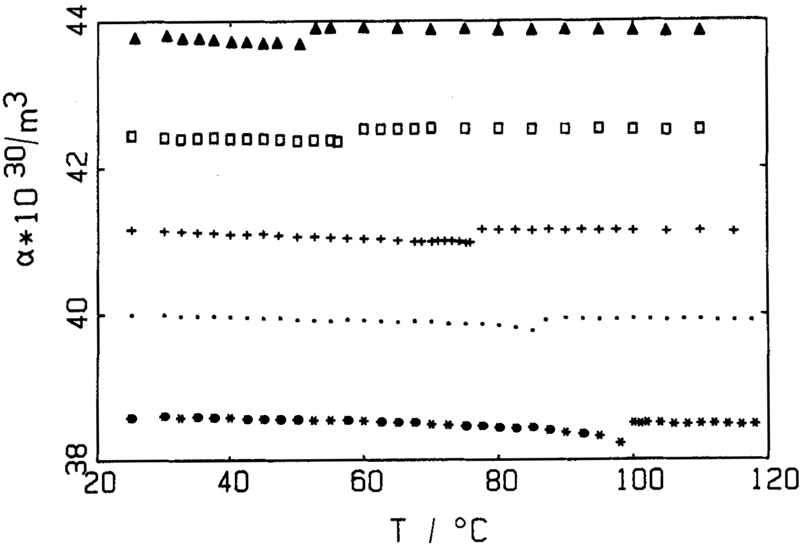

Figure 2. Mean polarizability, α, of the monomer units of polymers PO(∗), P25 (·), P50 (+), P75 (□) and P100 (▲) as a function of temperature.

clearing temperature a discontinuous jump of molar volume (4‰) was taken into account [11]. Figure 2 proves, that the polarizabilities do not depend on temperature and vary almost linearly with composition of the polymers. The non-linear behaviour of α close to the clearing temperature can be explained by the biphasic gap, where the specific volume continuously varies with temperature.

The liquid crystalline phase assignment was proved by X-ray investigations. In the X-ray diagrams for all copolymers and homopolymers only two broad, intense halos were observed (see figure 3). The positions of the halos and the relative intensities vary slightly with composition of the polymers. To separate the overlapped maxima, the curves were fitted with different scattering profiles. The best fits were obtained for a gaussian shape of maxima (residual factor R was 3–5 per cent). The corresponding parameters (d spacings and sizes of ordered regions L) were calculated from the fitted profiles and summarized in table 2. An additional halo was observed in the range of 12–13° which corresponds to the packing of the siloxane backbone fragments as known from reported data [12, 13].

In order to determine the structural parameters with varying composition of copolymers the presence of diffuse halos on the scattering curves indicates the formation of a liquid crystalline phase with short range ordering of the molecular fragments which is typical for nematics [8] and confirms the optical microscopic and calorimetric results.

As known for analogous LCSCPs the first low angle halo is attributed to weak correlations in longitudinal packing of the mesogenic side groups and the maxima of the wide angle halo around 20° reflects the ordering in lateral packing of the mesogenic units [8].

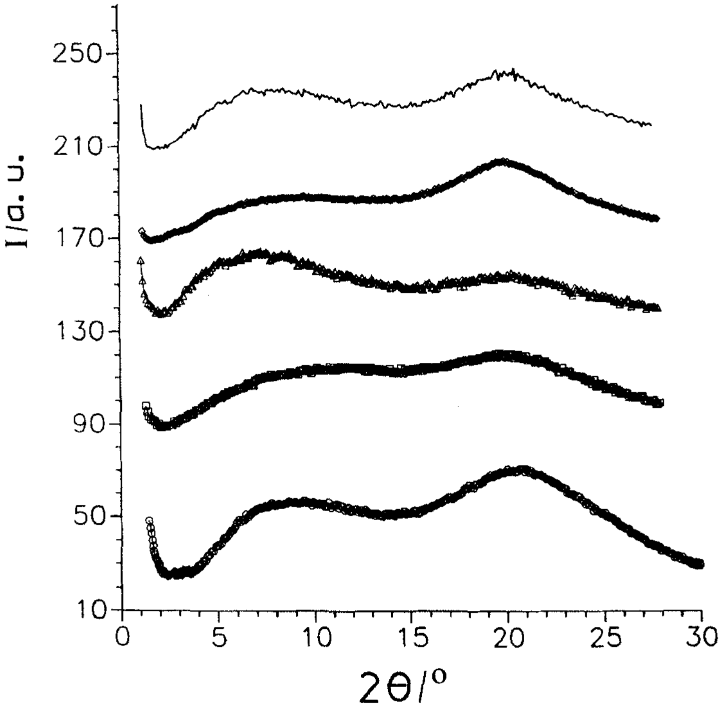

Figure 3. X-ray diagrams of polymers PO (—), P25 (◇), P50 (△), P75 (□) and P100 (○). Intensity in arbitrary units versus the angle 2Θ.

Table 2. Structural parameters of the polymers from X-ray analysis. *d* refers to corresponding molecular distances and *L* to the correlation length of the low (longitudinal) and wide (lateral) angle reflexes.

	Low angle		Wide angle	
Polymer	*d*/nm	*L*/nm	*d*/nm	*L*/nm
P0	1·17	1·25	0·442	1·25
P25	1·06	1·10	0·443	1·17
P50	1·25	1·35	0·448	1·00
P75	1·02	1·25	0·449	0·97
P100	1·20	1·35	0·45	0·95

The calculated *d* spacings of the first halo are in the range of 1–1·3 nm which corresponds to the distances between the centres of mass of partially overlapped mesogenic units along the side chains for a local antiparallel packing. As is known, such types of interdigitated longitudinal packing of the side groups occurs frequently in cyano containing liquid crystals [14]. The *d* spacings for the diffuse wide angle halo vary from 0·44 to 0·45 nm which are typical intermolecular distances for the lateral packing of phenylbenzoate in nematic phases [8]. The calculated sizes of the ordered regions *L* vary from 0·9–1·2 nm for lateral packing of mesogenic groups (see table 2) and also correspond to a common short range ordering. Hence both halos reflect the existence of liquid-like ordering in systems with expansions of the short range correlations in the lateral and longitudinal packing of the mesogenic groups only up to 2–3 nearest macromolecular fragment as known from conventional nematic phases [8].

The X-ray diagrams for the polymers P100 and P75 were recorded at different temperature intervals of the liquid crystalline and isotropic state (see figure 4). In the case of P75, no change in the X-ray diagram appears at different temperatures and the pure nematic ordering is confirmed. In the case of P100 a sharp peak with a maximum at about 2·9° is observed after prolonged annealing near the clearing temperature. The sharp reflex corresponds to a periodicity of 3·14 nm which corresponds to a double layered packing of the mesogenic side groups of length l with partial overlapping ($d = 1{\cdot}3 \times l$) [8, 14, 15]. During heating (cooling) of the sample the intensity of this peak disappears (increases) continuously at temperatures near the transition to the isotropic state (see figure 4). From these results for P100 we conclude a nematic phase containing local smectic ordering. This phase assignment is consistent with miscibility experiments and the induction of a cholesteric phase by chiral dopants.

Taking into account the results from X-ray analysis of the homo- and copolymers, changes of longitudinal and lateral packings of the mesogenic groups can be discussed.

Comparing the results of temperature dependent X-ray measurements, it is obvious, that copolymerization fully destroys the local smectic ordering which appears in the annealed sample P100. Considering changes of structural parameters as a function of polymer composition, all parameters are virtually similar for all polymers and only minor changes of the ordering in the nematic phases occur. Two additional conclusions follow from the analysis of the data described. Firstly, the ordering in the lateral packing of the mesogenic groups decreases monotonically on increasing the molar ratio of R1 which can be attributed to the bulky methyl side group in the phenyl

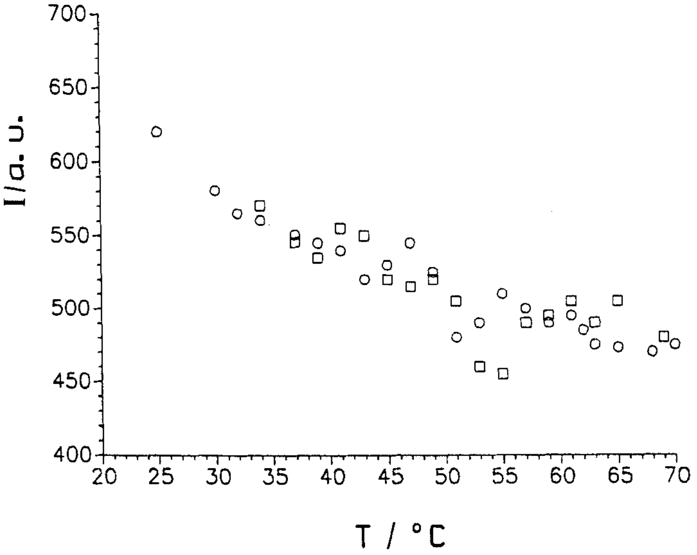

Figure 4. Intensity of the small angle peak (arbitrary units) versus temperature for polymer P100 annealed near to the clearing temperature, heating cycle (○), cooling cycle (□).

ring and secondly, for the copolymer P50 containing equimolar amounts of the mesogens R1 and R2 a slightly higher level of ordering in the longitudinal packing is detected (see table 2).

4. Dielectric properties of the polymers

Analysis of the phase behaviour shows the homo- and copolymers to possess nematic phases. The density and polarizability (see table 1 and figure 2) of the systems depend linearly on the composition which indicates ideal behaviour. On the other hand, it is well known, that for mixtures of low molar mass liquid crystals, having a chemical constitution very similar to the monomer units of the polymers under investigation, dipolar coupling has to be expected [16]. By changing the composition of a copolymer, starting with the non-polar homopolymer P0, by adding increasing amounts of polar, cyano-substituted side groups to the polymer backbone, should lead to strong dipolar coupling which causes deviation from the ideal behaviour of the dielectric constant as a function of composition. The question arises as to whether this behaviour is similar to that of mixtures of low molar mass liquid crystals or whether the linkage of the monomer units to the polymer backbone has additional effects on the dipolar coupling.

To investigate this effect the dielectric permittivity $\varepsilon_{(\omega)}$ was measured as a function of frequency ω.

$$\varepsilon_{(\omega)j} = \varepsilon'_{(\omega)j} - i\varepsilon''_{(\omega)j}, \quad j = \parallel, \perp \tag{1}$$

where ε' and ε'' reflect the real and imaginary parts of the dielectric permittivity and the indices $\parallel$ and $\perp$ correspond to sample orientation, where the nematic director is aligned parallel and perpendicular to the electric field, respectively.

To evaluate the static dielectric constant ε and dynamic parameters of the relaxation processes a Cole–Cole fit has been applied [9]. Accordingly, the relaxation processes are described in terms of relaxation frequencies, relaxation strength and

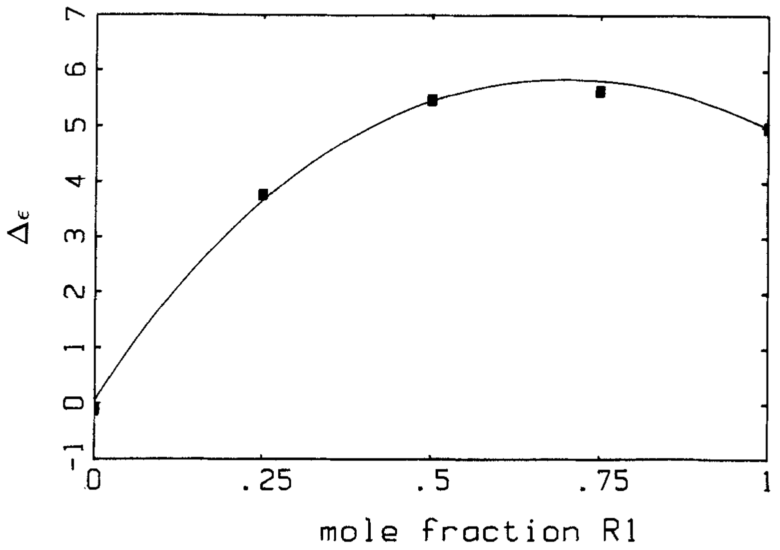

Figure 5. Dielectric anistropy, $\Delta\varepsilon$, as a function of polymer composition at a constant reduced temperature, T_{red}, of 0·95.

distribution of relaxation frequencies. The static dielectric constants were obtained from planar and homeotropically aligned samples and the dielectric anisotropy $\Delta\varepsilon$ is evaluated as a function of polymer composition (see figure 5). The values of $\Delta\varepsilon$ refer to the same reduced temperature $T_{\mathrm{red}} = T/T_{N,I}$ in order to be able to compare on corresponding state. As expected increasing the mole fraction of R1, increases the dielectric anisotropy strongly and it goes through a maximum at a R1 mole fraction of 0·75, whereas for the pure homopolymer P100 the value of the dielectric anisotropy is about 5. The quadratic relation of $\Delta\varepsilon$ as a function of mole fraction clearly indicates non-ideal behaviour. The dielectric anisotropy of the pure homopolymer P100 was measured, which confirms earlier results [17]. This value considerably deviates from $\Delta\varepsilon$ for low molar mass liquid crystals ($\Delta\varepsilon \approx 16$) having a very similar structure to the monomer units of P100 [18]. Obviously for the pure polar polymer P100 the linkage of the mesogenic units to the backbone causes stronger dipolar coupling between the mesogens due to their antiparallel association.

The assumption of an antiparallel orientation of the dipoles might be confirmed by the following arguments, which refer to the calculation of the effective dipole moments of the examined systems on the basis of the experimental results and from theoretical values of the dipole moments calculated from increments [18]. To calculate the effective dipole moments from the experimental results, the theory of Maier and Meier was used [1],

$$\bar{\varepsilon} = \frac{\varepsilon_\parallel + 2\varepsilon_\perp}{3} = \frac{NhF}{\varepsilon_0}\left(\alpha + F\frac{\mu^2}{3k_B T}\right) + 1, \qquad (2)$$

$$\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp = \frac{NhF}{\varepsilon_0}\left(\Delta\alpha - F\frac{\mu^2(1 - 3\cos^2\beta)}{2k_B T}\right)S, \qquad (3)$$

where $\bar{\varepsilon}$ and $\Delta\varepsilon$ are calculated from the static dielectric constant obtained for homeotropically, $\varepsilon_\parallel$, and planar, $\varepsilon_\perp$, aligned samples. The determination of the number density N, polarizability α, anisotropy $\Delta\alpha$ and order parameter S is described in the

Experimental section. ε_0, h and F refer to the vacuum dielectric constant, cavity field and reaction field as described by Maier and Meier [1], k_β is the Boltzmann constant and T the temperature. β represents the angle between the effective dipole moment and the molecular long axis, which is assumed as the axis connecting the centres of the two phenyl rings. The results of these calculations are summarized in table 3. The dipole moments parallel μ_l and perpendicular μ_t to the molecular long axis can be compared with the dipole moments calculated theoretically. For P0 and P25 we find reasonable agreement between the effective dipole moments obtained from experiment and theory. For these systems we can assume that essentially no dipolar interactions occur between the polar components. For R1 mole fractions higher than 0·25 the experimental dipole moments deviate increasingly from theory, which does not take into account intermolecular interactions. It is interesting to note that if we roughly estimate the value of P100 from the initial slope of $\Delta\varepsilon$ as a function of mole fraction, we obtain a value of $\Delta\varepsilon \approx 16$. With this value the dipole moments, summarized in table 3, coincide for both calculation methods.

The question arises as to whether the association can be related to the dynamic properties of the polymers. This will be disucssed for δ relaxation, which is described as a rotation of the mesogenic side group around the molecular short axis and reflects the effective dipole moment parallel to the molecular long axis. In analogy to the behaviour of the dielectric anisotropy as a function of mole fraction, the relaxation strength of the δ relaxation varies non-linearly with polymer composition (see figure 6). Figure 6 clearly demonstrates, that the increase of relaxation strength becomes smaller on increasing the mole fraction of R1. This result is consistent with the behaviour of the dielectric anisotropy and confirms the model of antiparallel packing of the polar mesogenic groups. So far we have only discussed the dielectric behaviour at a constant reduced temperature, where association of the polar monomer units occurs at a mole fraction of R1 $\gg$ 0·25. For this association a temperature dependence has to be expected. This dependence is clearly found, if we analyse the temperature dependence of the mean dipole moments. In analogy to the procedure described above the dipole moment is calculated from the dielectric constant ε in the isotropic state and $\varepsilon_\parallel$ and $\varepsilon_\perp$ in the nematic state according to equation (2). The results of these calculations are given for P100 and P75 in figure 7. If no dipolar interaction exists, the dipole moment μ should remain constant. However, for the polar polymers μ is a function of temperature and increases with temperature as expected. Furthermore, at the nematic to isotropic phase transformation a discontinuous jump of μ towards higher values is obtained.

Table 3. The different polymers and their corresponding experimental and calculated values of the dipole moment, μ. μ_l and μ_t denote the dipole moment longitudinal and transverse to the molecular long axis, respectively.

	Experimental		Calculated	
Polymer	μ_l	μ_t	μ_l	μ_t
P0	1·32	2·27	1·54	2·29
P25	2·58	2·16	2·58	2·26
P50	3·05	2·21	3·62	2·22
P75	3·19	2·64	4·67	2·19
P100	3·15	2·92	5·71	2·15

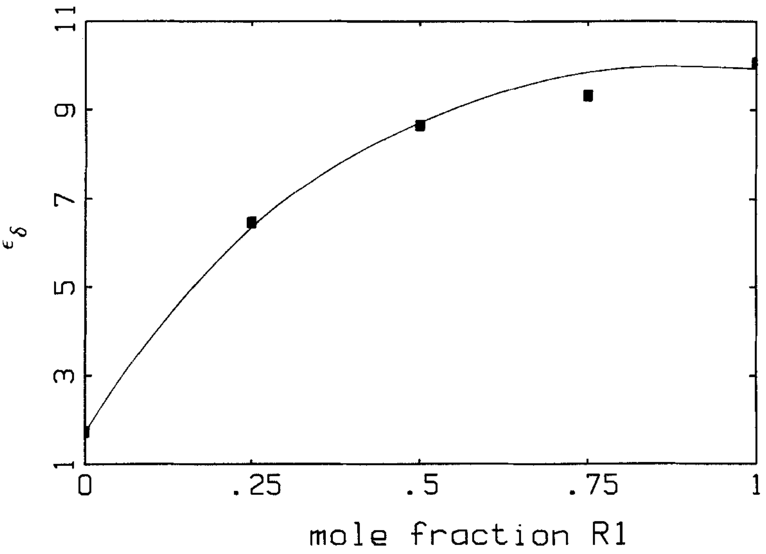

Figure 6. Relaxation strength ε_δ of the δ process as a function of polymer composition at a constant reduced temperature, T_{red}, of 0·97.

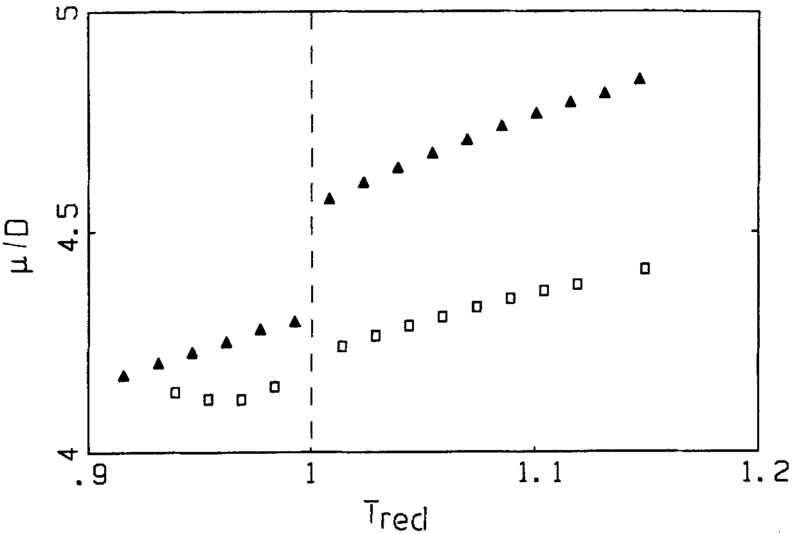

Figure 7. Temperature dependence of the mean dipole moment, μ, of polymers P75 (□) and P100 (▲) on reduced temperature.

This indicates that a stronger dipole association occurs in the nematic state which can be reasonably explained by the denser packing of the mesogens.

Finally it should be noted, that for all polymers only one δ relaxation is observed. Fitting the dynamic dielectric permittivity yields relaxation frequencies and distribution parameters for the δ relaxation. The values of the distribution parameters were adjusted by values between 0·89 and 0·93, typical for LCSCPs, and indicate a small deviation of a single relaxation process which is described by a distribution parameter of 1 [9]. The fact that only one δ relaxation appears in the copolymers demonstrates, that the δ process is affected by the local environment [9] and the molecular shape of

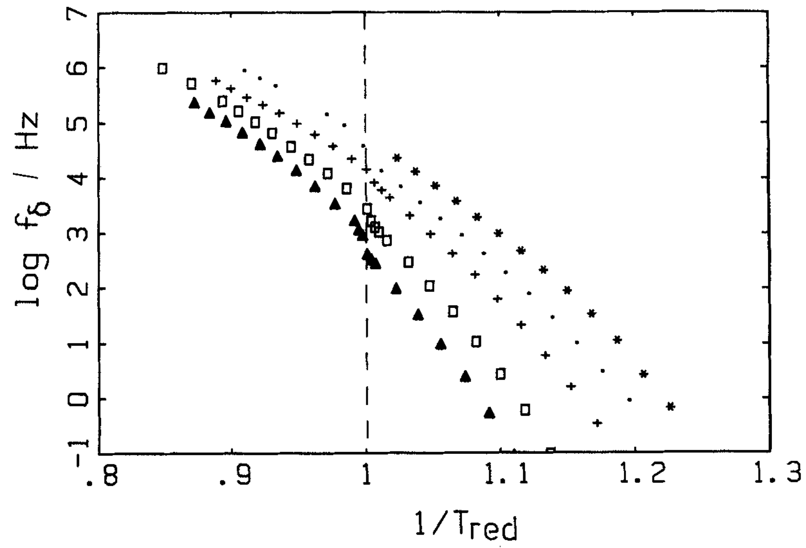

Figure 8. Relaxation frequencies f_δ of the δ process versus the reciprocal reduced temperature $1/T_{red}$, PO (*), P25 (·), P50 (+), P75(□), P100 (▲).

Table 4. Activation energy of δ relaxation in the isotropic and liquid crystalline (lc) phase.

	Activation energy/kJ mol^{-1}	
Polymer	isotropic	LC
PO	—	136
P25	93	148
P50	95	157
P75	106	181
P100	112	196

the mesogenic side groups [19]. The dependence of relaxation frequencies on temperature is shown in figure 8, where the logarithmic relaxation frequencies are plotted against the reciprocal reduced temperature. The slope at temperatures far from the glass transition is nearly linear with the reciprocal temperature showing Arrhenius-like behaviour. The slope found for the liquid crystalline state displays a higher value than for the isotropic state (see table 4). The result that the activation energy is enhanced in the liquid crystalline phase is attributed to the nematic potential, which renders δ relaxation more difficult. Within the series of polymers the slope increases reflecting an increase of activation energy. Again the increase of activation energy when increasing the content of R1 reflects the association of the mesogenic groups having the polar cyanoend-groups.

5. Conclusion

The investigation of the dielectric properties of liquid crystalline side chain polymers proves that these properties strongly depend on the molecular structure of the mesogenic side groups.

The results show, that the dielectric properties of LCSCPs are influenced by formation of antiparallel associations of the polar mesogenic side groups. Therefore copolymers can exhibit larger values of dielectric anisotropy than homopolymers. These antiparallel dipolar interactions are stronger than for low molar mass liquid crystals of similar chemical structure and hence lower values of dielectric anisotropy result. In further experiments it would be interesting to examine whether this effect arises from the linkage of the mesogenic groups to the polymer backbone via the flexible spacer of whether simply the lower specific volume of the polymer causes this effect. This point could be clarified by investigation of the dielectric properties of mixtures of LCSCPs with low molar mass liquid crystals containing polar and non-polar groups.

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