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To cite this Article Schiewe, B. and Kresse, H.(1996) 'Dielectric relaxation in 'diluted' siloxanes with swallow-tailed side groups', Liquid Crystals, 20: 5, 635 — 640
To link to this Article: DOI: 10.1080/02678299608031153
URL: http://dx.doi.org/10.1080/02678299608031153

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LIQUID CRYSTALS, 1996, VOL. 20, NO. 5, 635–640

Dielectric relaxation in 'diluted' siloxanes with swallow-tailed side groups

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(*Received 18 September 1995; in final form 30 November 1995; accepted 21 December 1995*)

Polysiloxanes consisting of 36–$SiCH_3Z$–O– units, where Z is a swallow-tailed liquid crystal moiety S or a CH_3 group, were synthesized. Dielectric constants and relaxation frequencies were measured from 0·1 Hz to 10 MHz for four different molar ratios of CH_3 and S groups and compared with the data for the respective monomeric liquid crystal material. In all cases a δ- and an α-relaxation were detected. The relaxation frequencies f_R of the α-process increase with increasing degree of dilution and can be related to the decreasing glass temperature. The δ-process approaches the f_R-values of the monomer by dilution. Both the dielectric increments of the δ-process, as well as the static dielectric constants parallel to the director, prove that the swallow-tailed units are strongly antiparallel oriented. This correlation cannot be destroyed by dilution.

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1. Introduction

Polysiloxanes are polymers consisting of –$SiCH_3Z$–O– units and –$Si(CH_3)_3$ end groups. When the side groups Z are liquid crystal moieties coupled via a spacer with the siloxane backbone, the resulting side group polymer exhibits in most cases mesophase behaviour [1, 2]. In 'diluted' polysiloxanes, the liquid crystalline units are partially replaced by methyl groups [3]. This results in a decrease of the glass and clearing temperatures, but not in a change in the sequence of the phases as was shown by Poths and Zentel [4]. It is known that 'diluted' polysiloxanes show a strong tendency to microphase separation, which is due to the immiscibility of the siloxane backbone and the hydrocarbon side chain as reported by Diele *et al.* [5]. The spatial short range order of the liquid crystalline side chains in the 'diluted' polymer compared to the homopolymer remains unchanged as a consequence of convolution of the flexible siloxane backbone and the mobility of the spacer. Therefore, it was shown for ferroelectric 'diluted' polysiloxanes that a 'dilution' of homopolymers results in decreasing switching times for different electro-optic effects [6].

The aim of this paper is to study the influence of the degree of 'dilution' on the dynamics of polysiloxanes containing swallow-tailed liquid crystalline side groups. In addition the data are compared with the siloxane-free, low molecular weight material bearing the same mesogenic groups.

2. Substances

Synthetic routes to the alkene precursor are described in [7]. The polymers were synthesized according to well-known procedures [8]. All samples were purified by flash chromatography in order to reduce the conductivity. The polymers under discussion are presented at the top of the next page. The phase transition temperatures measured by calorimetry (Perkin-Elmer DSC 7) are listed in table 1. In addition to the expected decrease of the glass temperatures, as well as the clearing temperatures, a change in the phase sequence, namely the appearance of a broadened nematic phase range, was also observed on 'dilution'.

3. Experimental

The measurements were carried out on samples in a metallic capacitor ($d = 0{\cdot}2$ cm, $A = 2\,cm^2$) and in an ITO cell ($d = 0{\cdot}2$ mm, teflon spacer, $A = 2\,cm^2$). In both cases the measuring cells were calibrated with cyclohexane. The cells were filled with the isotropic samples. The monomer and the 'diluted' siloxanes were oriented in an external magnetic field of about 0·6 T. However, this field was not sufficient to orient sample S1. The 'undiluted' siloxane S0 was investigated using the ITO cell. To obtain an orientation, a bias voltage of 35 V was applied at the N/I transition. This resulted only in a small decrease in the conductivity and in no orientation effect. A computer controlled HP4192A impedance analyser, Hewlett Packard, was used to measure the capacitance and conductivity as a function of frequency (10 Hz–10 MHz). For the detection of the high fre-

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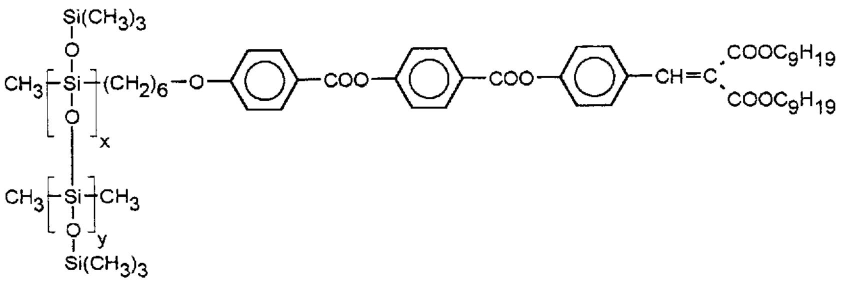

Table 1. Phase transition temperatures of the monomer (side group precursor) and the polymers.

Substance	Dilution $y:x$	Transition temperature, T/K
M	—	Cr 344 (S_C 314) S_A 352 N 359 I
S0	0:36	g 286 S_A 373 I
S1	18:18	g 265 S_A 322 N 333 I
S3	27:9	g 249 S_A 306 N 323 I
S8	32:4	g[a] S_A 266 N 277 I

[a] Could not be detected.

Table 2. Fitting parameters of S3 for the low frequency mechanism in the isotropic and nematic phases.

T/K	$f_{R1}, f_{R\parallel 1}$/kHz	$\Delta_1, \Delta_{\parallel 1}$	$h_1, h_{\parallel 1}$
323	12·2	1·27	0·21
321	11·5	1·55	0·29
318	2·32	2·68	0·27
315	1·32	3·14	0·30
312	0·84	3·00	0·21
308	0·54	2·63	0·19
307	0·35	2·1	0·21

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quency relaxation at lower temperatures, a Solartron Schlumberger impedance analyser SI1260, in combination with a Chelsea interface, was applied in the frequency range from 0·1 Hz to 10^6 Hz. This method was only useful when the electrical conductivity was low. The experimental data were fitted to the Cole–Cole equation [9],

$$\varepsilon^* = \varepsilon_\infty + \frac{\Delta}{1 + (\mathrm{i}f/f_R)^{1-h}} \qquad (1)$$

where Δ = dielectric increment, f_R = relaxation frequency, h = Cole–Cole distribution parameter, ε_∞ = high frequency dielectric constant. A term A/f^n was added to take the electrical conductivity into account.

4. Results

Two experimentally obtained absorption curves for S3 are presented in figure 1. In this case the data were fitted to two Cole–Cole mechanisms (1—low frequency mechanism) according to equation (1) and the conductivity. As shown in figure 1 (*a*), this description gives a good approximation for the low frequency absorption in the isotropic phase. Absorption data for $\varepsilon''_\parallel$ in the nematic phase and the fitted curves are given for T = 307 K in figure 1 (*b*). The measurements were carried out under the condition that the magnetic field was parallel to the electrical measuring field. Therefore, the dielectric constants in the liquid crystalline phases are designated with the index 'parallel' ($\parallel$). The dielectric increment $\Delta_{\parallel 1}$ increases after the transition from the isotropic to the nematic phase and decreases at $T < 310$ K (see table 2). A further reduction of the temperature results in a very strong decrease of $\Delta_{\parallel 1}$; hence, the dielectric absorption cannot clearly be separated from the conductivity. Therefore, no reliable data for the S_A phase were obtained. It should be pointed out that in the nematic phase, no low frequency absorption in the perpendicular direction was measured for S3. This indicates, that the sample was well oriented.

Table 2 confirms the decrease of the dielectric increment with falling temperature in the parallel direction. For the relaxation frequencies, a step at the I/N transition was detected (see also figure 2). Due to all of these experimental findings, we designate this relaxation as a δ-process, which is related to the reorientation of the longitudinal dipole of the side groups. The low frequency absorption was found in all samples. An experimental problem occurred concerning the separation of this diminishing absorption from the background conductivity. Furthermore, the full absorption intensity in the liquid crystalline phase can only be obtained by a sufficiently good orientation. This is the reason why we could not obtain f_R-values for the mesomorphic states in most of the measurements. All the f_R-data are summarized in the Arrhenius plot of figure 2. In the temperature range investigated by us, the relaxation frequencies can be fitted within experimental error to a straight line with respect to the coordinates of figure 2 with the given activation energies E_A (table 3). This experimental result cannot be interpreted in terms of the low frequency mechanism not being influenced by the glass transi-

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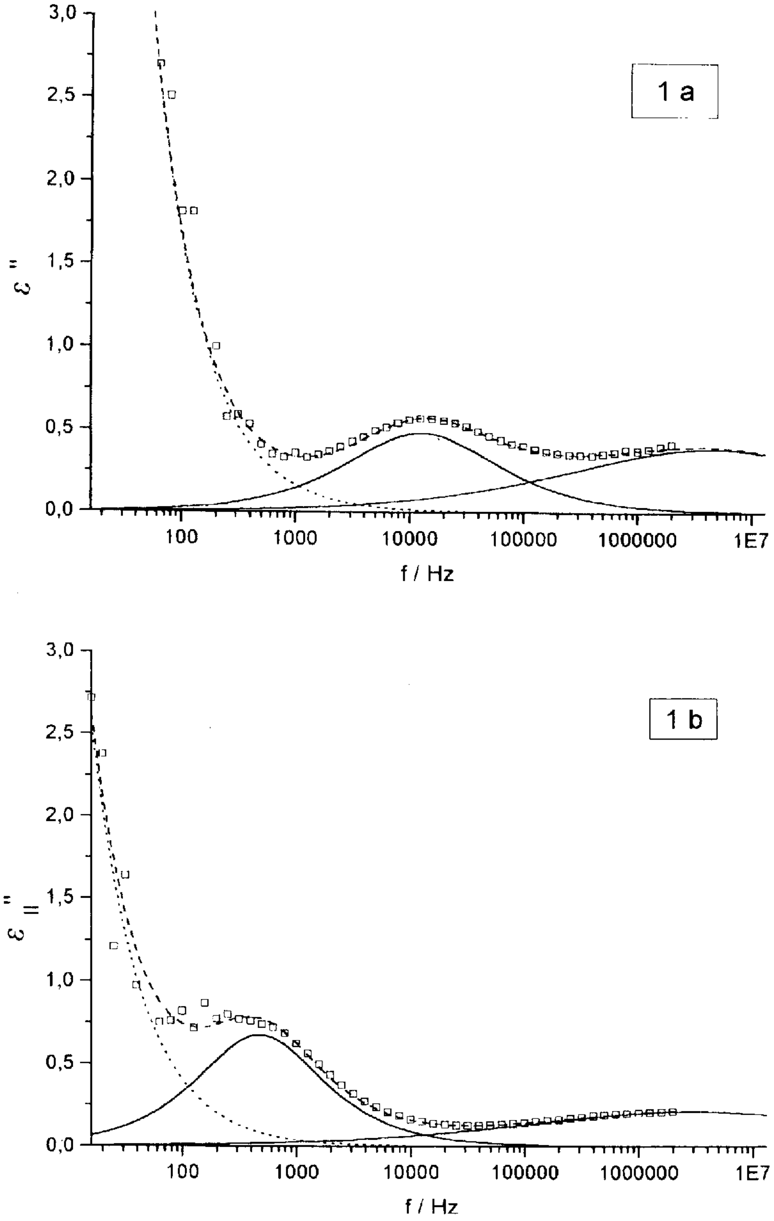

Figure 1. Absorption curves of S3. The conductivity and the overall loss are indicated by different broken lines; separate curves are given for the dielectric absorptions at low and high frequencies: (*a*) $T = 323\,\mathrm{K}$ (isotropic phase); (*b*) $T = 307\,\mathrm{K}$ (nematic phase).

Table 3. Activation energies of the δ-process in $\mathrm{kJ\,mol^{-1}}$.

Substance	I	N	S_A
S0	102	–	64
S1	106	160	–
S3	88	127	–
S8	70	83	–
M	96	184	87

tion. This is a statement which is valid only for a limited temperature interval.

In contrast, the high frequency absorption presented in figure 3 clearly shows a glass behaviour. Therefore, we have designated this mechanism to be an α-relaxation. In this case measurements could be carried out at lower temperatures, especially in the S_A phase, where the δ-process exhibits a very small increment. Furthermore, $\varepsilon''_{\perp}$-data were used for the fit, because the absorption intensity in the perpendicular direction is about double. The relaxation frequencies of S0, S1, and S3 were fitted to the Vogel–Fulcher–Tamman (VFT)

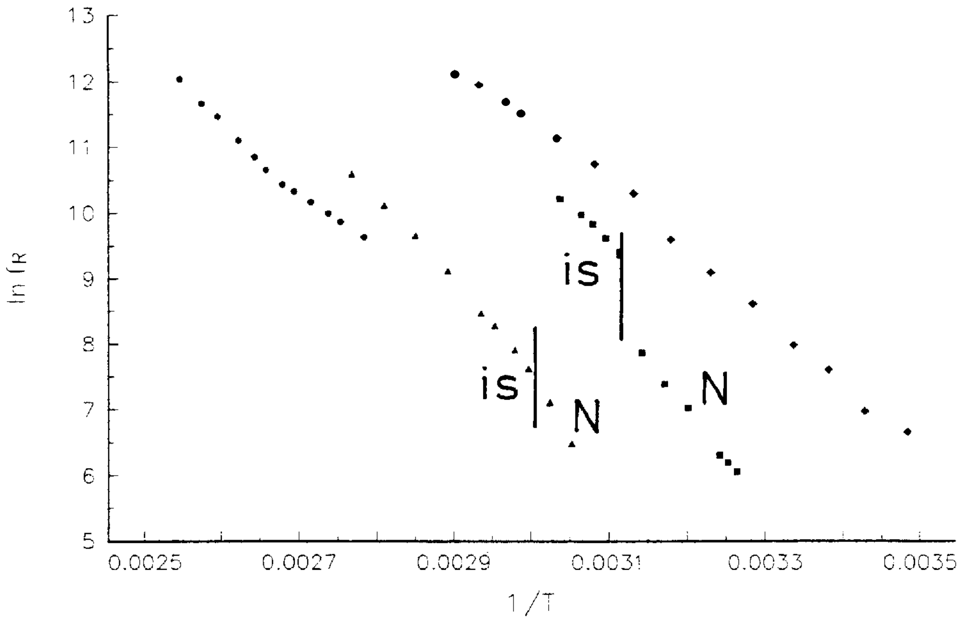

Figure 2. Arrhenius plot of the low frequency mechanism of the polymers: S0 (●), S1 (▲), S3 (■), S8 (◆).

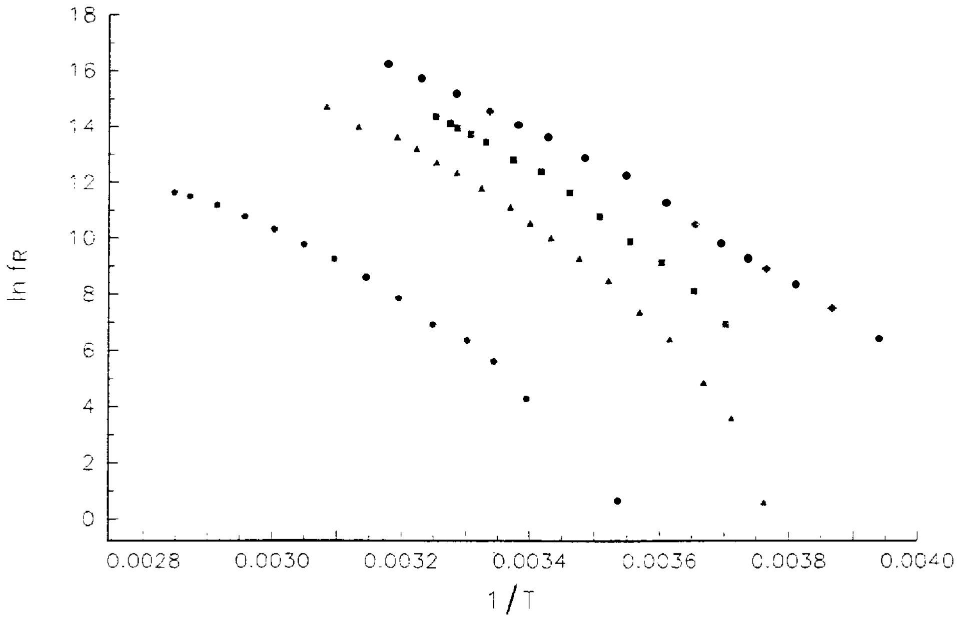

Figure 3. Arrhenius plot of the α-relaxation of the polymers: S0 (●), S1 (▲), S3 (■), S8 (◆).

equation [10]

$$\ln f_R = A + B/(T - T_\infty). \qquad (2)$$

The respective constants A, B, and T_∞ are given in table 4. For S8 we found no VFT behaviour and therefore no fitted data can be presented. The glass transition occurs at lower temperatures where no experimental data could be obtained. As shown in table 4, the difference between the Vogel temperature T_∞ and the glass

Table 4. Fit parameters according to the Vogel–Fulcher–Tamman equation and measured glass temperatures T_g obtained by DSC.

Polymer	A	B/K	T_∞/K	T_g/K
S0	19·31	878·9	236	286
S1	24·54	1022·0	221	265
S3	26·17	1135·3	211	249

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Table 5. Static dielectric constants of the isotropic phase extrapolated at $T = 353$ K.

Substance	M	S0	S1	S3	S8
$\varepsilon_{0,\mathrm{is}}$	4·67	6·3[a]	7·50	6·35	5·05

[a] Measured in an ITO cell, maximal error 10%.

temperature T_g, estimated from DSC measurements, is about -45 K. A β-process could not be separated at low temperatures and high frequencies. From Cole–Cole plots the static dielectric constants ε_0 were calculated. The experimental data for the isotropic phase are listed in table 5. The smaller value of the dielectric constant of S0 indicates a stronger dipole–dipole correlation in this sample. 'Dilution' results initially in an increase of the static dielectric constant due to the higher mobility of the dipoles of the liquid crystalline side group. The static dielectric constants of S3 presented in figure 4 show a strong decrease of $\varepsilon_{\parallel 0}$ in the nematic phase and a cross-over point with $\varepsilon_{\perp 0}$. This cross-over effect indicates that we are not dealing with a change in the orientation during the measurement. Therefore, the strong decrease of the absorption intensity can only be the result of the reduction of the effective dipole moment parallel to the director.

5. Discussion

The data shown in figure 4 demonstrates that a 'dilution' of 27 : 9 results in a strong antiparallel order of the

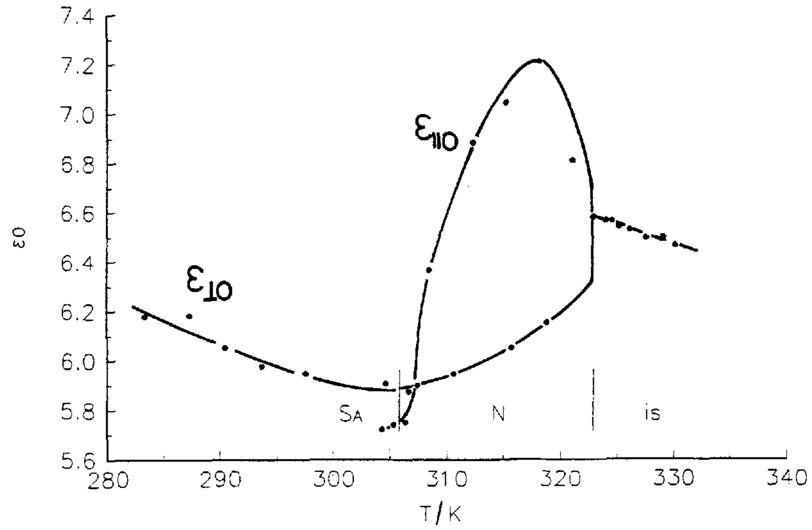

Figure 4. The static dielectric constants of S3.

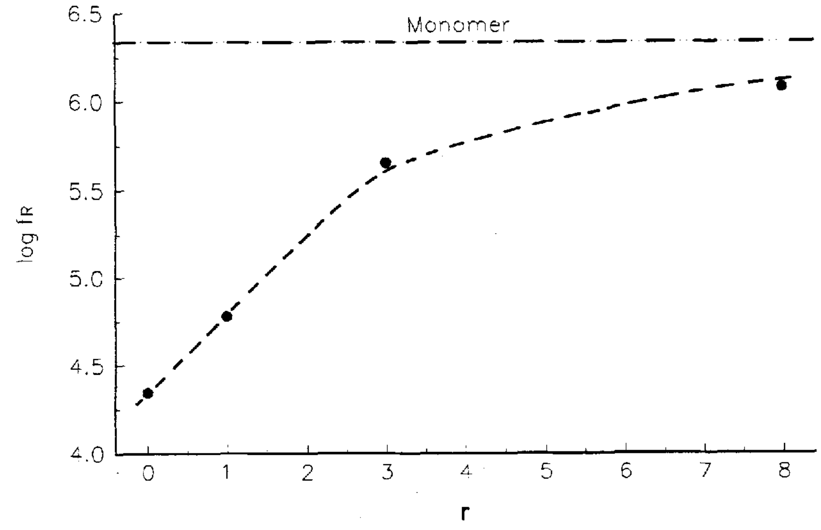

Figure 5. The relaxation frequencies at different degrees of 'dilution' $r = y/x$.

side groups in the nematic phase. As in the oligosiloxane, $\varepsilon_{\|0}$ decreases in the nematic phase with falling temperature [11]. The dramatic change in the antiparallel order around 310 K can also be detected in the dielectric absorption as demonstrated in table 2. Due to this antiparallel orientation of the side groups, we have described this effect in terms of 'molecular zip-fasteners' [12]. The strong efficiency of such molecular zips cannot be destroyed by elimination of some 'links'. This experimental result confirms that the side groups are closely neighbouring or, in other words, the polymer backbone is convoluted and shows a tendency to phase separation.

Elongation of the mean distance between the side groups changes their molecular mobility. For comparison, the relaxation frequencies f_R at $T = 363$ K (isotropic phase) were calculated from the fitted linear function and plotted against the degree of 'dilution' (see figure 2). The result is presented in figure 5. It is evident from this picture that f_R increases with increasing 'dilution' and seems to be limited by the relaxation frequency of the monomer.

Summarizing, it can be concluded that 'dilution' results in a higher mobility of the polymer backbone and the side groups. The tendency to form antiparallel oriented side groups is only slightly influenced. Up to 'dilution' degrees of 27:9 we found that the antiparallel correlation in the oligosiloxanes, which contain the same side groups, was maintained unchanged.

The authors are indebted to the Consortium für Elektrochemische Industrie and A. Hohmuth (Max-Planck-Arbeitsgruppe 'Flüssigkristalline Systeme' Halle) for the help provided, and to the DFG for financial support.

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