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Dielectric Relaxation in a Mixture of a Side Chain Liquid Crystalline Polymer and a Low Molecular Mass Azo Dye

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Dielectric measurements on a mixture of a liquid crystalline polysiloxane and a low molecular mass dye as well on the pure polymer have been carried out in the frequency range from 100 Hz to 13 MHz. Three relaxation regimes have been found for the polymer-dye mixture. The shift of relaxation frequencies in the isotropic and nematic phases of the pure polymer was used to calculate the macroscopic order parameter $\langle P_2 \rangle$.

Keywords: Dielectric relaxation spectroscopy, Azo dye, liquid crystalline polysiloxane, molecular dynamics in mixture, order parameter.

1. INTRODUCTION

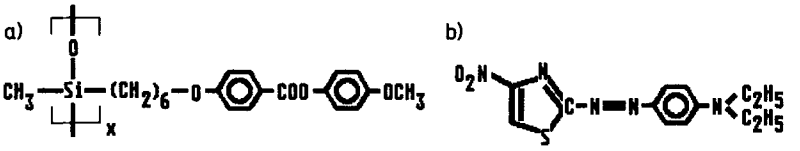
In an earlier investigation on a liquid crystalline siloxane copolymer[1] we showed that the δ-relaxation is rather caused by independent motions of the mesogenic units but can be described as collective reorientation. During the following years, a number of compounds have been synthesized,[2–5] among them cyclic polysiloxanes.[6] Recently, liquid crystalline side chain polymers with pleochroic dyes attached to the backbone (copolymers)[7–9] or dissolved in the polymeric matrix (guest host systems)[10–15] are of increasing interest because of possible applications for optical data storage[11,16] and for nonlinear optics (NLO).[17] A special interest is directed on the thermal behaviour of such systems, including disturbing influences of the guest on the transition temperatures of the host.[12,13] Also the molecular dynamics as well as orientational behaviour in dependence on thermal behaviour are of interest.[9,12–15]

In this paper we report investigations on a model system of a liquid crystalline siloxane side chain polymer doped with an azo dye and on the pure polymer by means of dielectric spectroscopy. The aim of these investigations is to obtain informations about the dynamic behaviour of the dye with a strong dipole moment dissolved in the nematogenic polymer. We decided to investigate this polymer with weak transversal and week longitudinal dipolar components in order to show clearly the dynamic

behaviour of the dissolved dye (which has a strong dipole moment) in parallel and perpendicular alignment, with respect to the measuring field.

2. EXPERIMENTAL

The samples used were a liquid crystalline polysiloxane and a low molecular weight, non mesogenic azo dye with following chemical structures:



FORMULA 1: a) Polysiloxane (PS6), x = 36; b) azo-dye under investigation.

The liquid crystalline polymer PS6 was obtained via typical hydrosilation of alkene type mesogen {4-(5-hexenyloxy)-benzoic acid 4'-methoxyphenyl ester} with commercial poly(methylhydrogensiloxane)(Merck) in the presence of a catalytic amount of hexachloroplatinic (IV) acid.[18] This polymer shows only a nematic phase between the glassy and isotropic states. The azo dye was synthesized in Institute of Dyes, Lódź Technical University, Poland. The polymer and the dye were mixed in the isotropic state. For the mixture with 8 weight% dye complete miscibility was found in the temperature range under investigation. Table 1 shows the average phase transition temperatures in °C for the pure polymer and the mixture as observed with polarizing microscopy. We found no decomposition or colour changes of the samples after prolonged periods near the clearing temperature.

For dielectric measurements in the frequency range from 10 Hz up to 13 MHz a Hewlett-Packard 4192A self balancing bridge, controlled by a modified Atari Mega STII computer was used. The temperature-dependent measurements can be done fully automated, the details of the procedure were described earlier.[19] Capillary filling of the cell was not possible due to the high viscosity of the samples under investigations. Therefore, we transferred a small amount of the substance on the electrode. Two 100 μm capton distance holders were placed on the edges of the electrode. At 50°C above T_{ni} the polymer was pressed to a film using the second electrode. The calibration constant for the microcapacitor in this case is equal to the geometrical capacitance. This is not an exact procedure, but it gives the right tendency for the relaxation parameters.

TABLE 1

Transition temperatures for polymer and mixture as determined by polarizing microscopy

Polymer:	n 84°C-i
Mixture:	n 77.5°C-i

For data analysis, the Fuoss–Kirkwood relaxation function[20] was used in one-, two- and three-line fits. Additionally, a conductivity term C/f^n (C, n: fitparameters; f: frequency) was used to separate low frequency conductivity from dipolar relaxation processes in order to obtain accurate parameters.

The polymer and the mixture were oriented by slowly cooling (3 K/h) from the isotropic state into the liquid crystalline state under action of a 1.2 T magnetic field.

A pronounced difference in the relaxation behaviour for the parallel and perpendicular aligned samples can be seen from the three-dimensional plots (Figures 1 and 2),

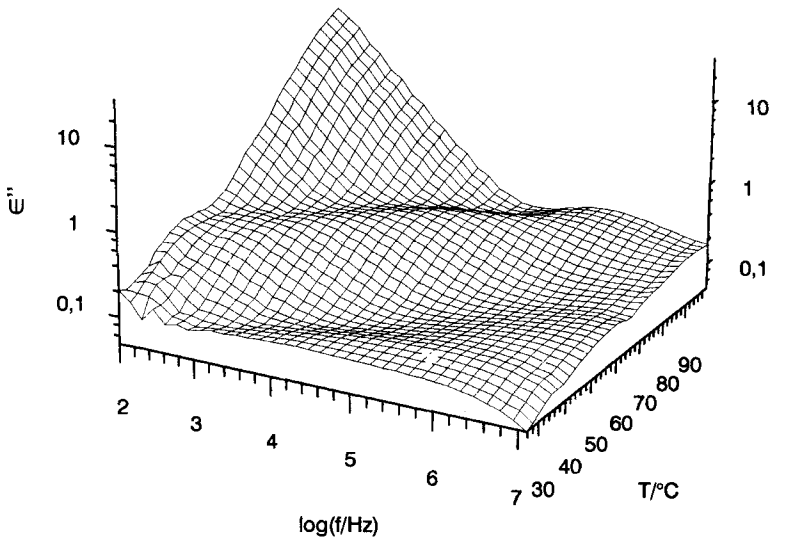


FIGURE 1 Three dimensional plot of ε'' versus frequency and temperature for parallel alignment of pure polymer.

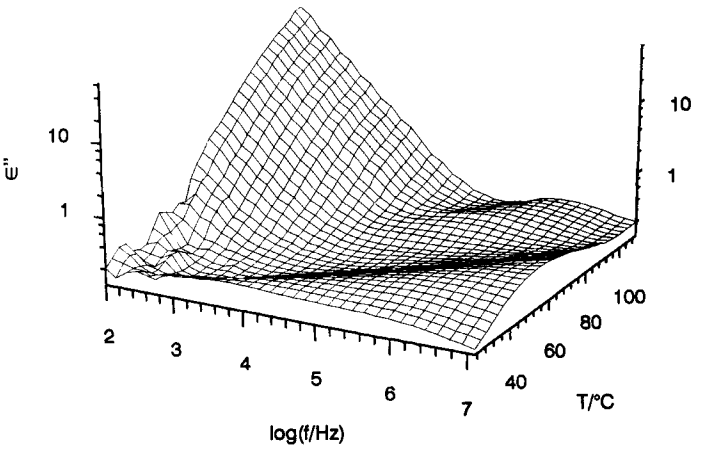


FIGURE 2 Three dimensional plot of ε'' versus frequency and temperature for perpendicular alignment of pure polymer.

which show ε'' as function of the frequency and the temperature for the pure polymer.

3. RESULTS AND DISCUSSION

3.1 Dielectric Data for Pure Polymer

For the pure polymer three absorptions were observed, δ-, α- and β-relaxations. Fitting a superposition of three Fuoss–Kirkwood functions and an additional term for low frequency conductivity to the experimental points of ε'' (f, T), we obtained relaxation frequencies for the isotropic phase and the low frequency relaxation in the nematic state. For the high frequency relaxations we determined relaxation parameters only for the low temperatures because of numerical instabilities in the fits at higher temperatures.

The frequency shift to lower values and the increase in the activation energy (Arrhenius-Plot, see Figure 7) by going from the isotropic to the nematic state show that the low frequency process is connected with the movement of the mesogene groups around their short axis, the δ-relaxation. It is observed in parallel alignment. The separation between conductivity part and dipolar relaxation for the parallel and perpendicular aligned pure polymer is shown in Figure 3. The absorption is described as the superposition of two Fuoss–Kirkwood functions. The activation energies are 89 kJ/mol in the isotropic phase and 154 kJ/mol in the nematic phase for the parallel alignment.

α- and β-processes can be observed well resolved only at the low temperatures in the perpendicular aligned pure polymer (Figure 4). The corresponding frequencies for the α-relaxation are shown as open squares in the Arrhenius-plot (Figure 7). Numerical values for the high frequency β-relaxation are not shown in the plot.

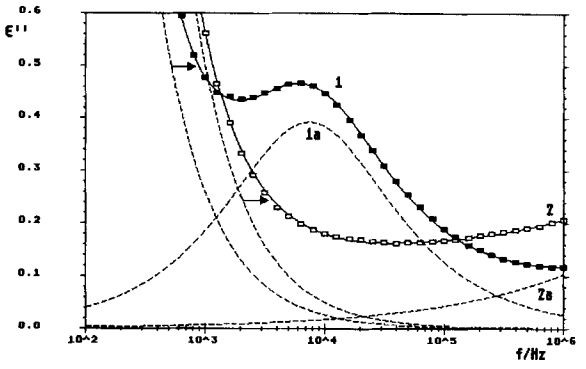


FIGURE 3 Examples for absorption curves at 70°C for parallel (filled squares) and perpendicular (open squares) aligned polymer. The solid lines show the overall-absorptions, described with the superposition of two Fuoss–Kirkwood relaxation functions and an additional term considering low frequency conductivity. The dashed lines show the separation between conductivity and dielectric absorption, δ-process (1a) for parallel alignment and α-process (2a) for perpendicular alignment.

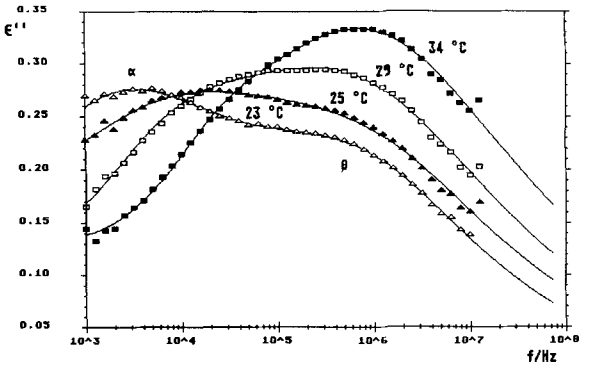


FIGURE 4 Dielectric spectra for perpendicular aligned polymer between 23°C and 34°C. Resolved α- and β-relaxations can be observed.

3.2 Dielectric Data for Mixture

For the mixture in the parallel alignment we observed in the nematic phase an additional strong relaxation process which should be connected with the dye relaxation. The activation energies are 100 kJ/mol in the isotropic phase and 129 kJ/mol in the liquid crystalline phase. Between 84°C and 50°C, a weaker process can be resolved (see Figures 5, 6) which is the polymers δ-relaxation. The activation is the same as for the pure polymer within the error range.

Comparing the spectra in the parallel alignment of the mixture and those of the pure polymer one can see, that the frequency of polymers δ-relaxation is only slightly affected by the dye. An example at T = 54°C is given in Figure 6. It should be noted, that the separation between δ-process and dye relaxation process is about one decade, the low molecular mass dye exhibits the higher frequency relaxation. Moreover, it is seen from Figure 6, that the halfband-width of the dielectric absorption connected with the dye relaxation is smaller than that of the pure polymer. Such a result was also

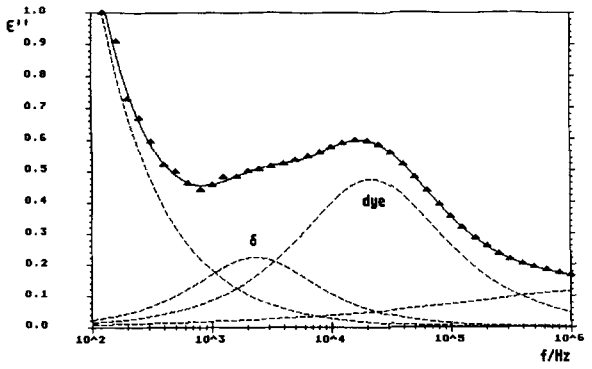


FIGURE 5 Absorption curve for mixture at 60°C in parallel alignment. Dashed lines show the separated relaxation processes.

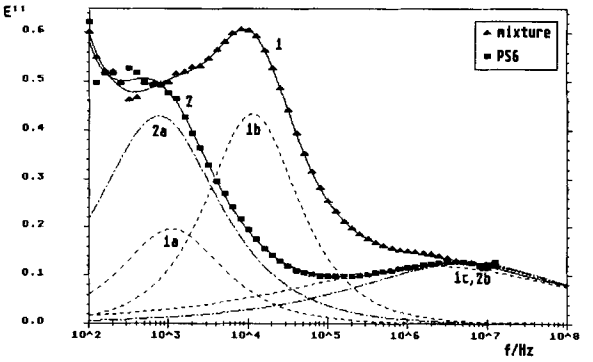


FIGURE 6 Absorption curves for mixture and pure polymer at 54°C in parallel alignment. Dashed lines show the separated relaxation processes for the mixture (1a, 1b, 1c) and for the pure polymer (2a, 2b).

observed previously.[21] This means that the nonmesogenic dye molecules move independently of the surrounding mesogenic groups of the polymer. The azo dye being only with 8 weight % in the mixture has a pronounced relaxation strength, due to the strong contribution of the NO_2-group to the longitudinal dipole moment $\mu_\parallel$. However, the contribution of the COO- and CH_3O- groups to the longitudinal dipole moment of the polymer side chain is small and therefore the dye relaxation dominates the spectrum. We have estimated $\mu_\parallel$, dye $\cong 10\mu_\parallel$, polymer. These results are in good agreement with the observations reported in[21] for a mixture of an acrylate polymer with a low molecular mass liquid crystal having very similar structure to the polymer mesogenic groups. In our case, however, no plasticizer effect[21,22] was found.

In the perpendicular alignment, we found a broad process in the liquid crystalline phase which should be connected with the dyes transversal dipole moment component and the polymers α-relaxation.

The relaxation frequencies for both, the pure polymer and the mixture are summarized in the Arrhenius-plots, presented in Figure 7.

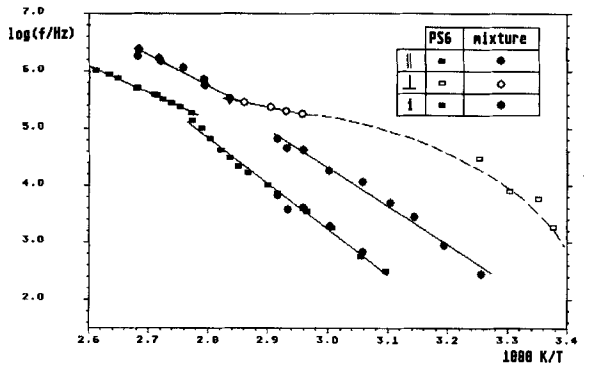


FIGURE 7 Arrhenius-plot for the pure polymer and the mixture in parallel and perpendicular alignment in the nematic and in the isotropic phases.

3.3. Order Parameter Calculations from Dielectric Data

According to the Maier–Saupe mean field theory of the nematic phase[23] the nematic potential U is given by $U = -q\cos^2\beta$, where q is the height of the potential barrier and β is the angle between the long molecular axis and the nematic director. The order parameter $\langle P_2\rangle$ describes the long range orientational order in the nematic state and is defined by[24]

$$\langle P_2\rangle = \tfrac{1}{2}(3\langle\cos^2\beta\rangle - 1), \tag{1}$$

where

$$\langle\cos^2\beta\rangle = \frac{\int_0^{\Pi/2}\cos^2\beta\, f(\beta)\sin\beta\, d\beta}{\int_0^{\Pi/2} f(\beta)\sin\beta\, d\beta} \tag{2}$$

$f(\beta)$ is the undisturbed distribution function of the molecules and its simplest form according to[23] is $f(\beta) = \mathrm{C}\exp\{-q/\mathrm{kT}\sin^2\beta\}$, where k is Boltzmann's constant and T the absolute temperature.

Meier and Saupe[25] showed that the potential barrier q is connected with the retardation factor g, which is given by the ratio of $f(q=0)/f(q\neq 0)$. $f(q=0)$ can be identified with the relaxation frequency f_{iso} in the isotropic state for compounds having a Debye-type relaxation spectrum in this phase. We found that the polymer used in our study satisfies this requirement in first approximation. The measurements of f_{iso} were done at various temperatures in the isotropic phase and $f(q=0)$ was obtained through the extrapolation to the temperature of interest. $f(q\neq 0)$ is the experimental frequency observed in the nematic phase. Hence the retardation factor g was calculated. Knowing g one can estimate the barrier height of the nematic potential q and the order parameter $\langle P_2\rangle$. The dependence of $\langle P_2\rangle$ on the reduced temperature for pure polymer is given in Figure 8.

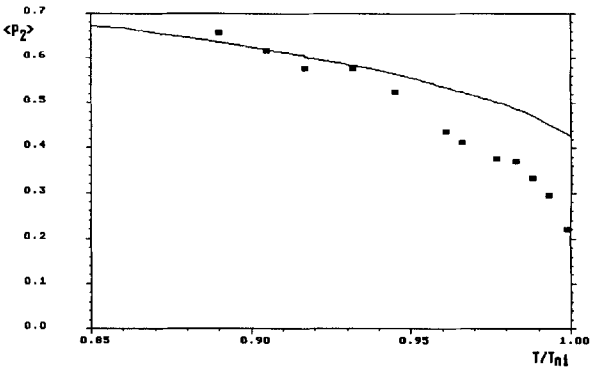


FIGURE 8 Order parameter $\langle P_2\rangle$ for the pure polymer versus reduced temperature T/T_{ni} (T and T_{ni} in K).

The solid line in Figure 8 is the theoretical prediction obtained from the Maier–Saupe theory.[23] It is seen that the agreement between theory and experiment is satisfactory for low temperatures, what means that the polymer is very efficiently oriented in the 1.2 T magnetic field. The differences close to T_{ni} between $\langle P_2 \rangle$ values obtained experimentally and from the theory arise from the fact, that the Maier–Saupe theory was derived for low molecular weight nematics and can thus illustrate the influence of the backbone on the side chain dynamics.

4. SUMMARY AND CONCLUSIONS

We investigated a siloxane polymer with weak longitudinal and transversal dipole moment component and the mixture of this polymer with 8 wt% azo dye having very strong dipole moment connected with the NO_2-group. The orientation by the magnetic field was possible for both, the pure polymer and the mixture. For the pure polymer we observed three relaxations, δ-, α- and β-processes. For the mixture in parallel orientation we observed an additional relaxation process which has been absent in the relaxation spectrum of the pure polymer. From this we conclude, that the non-mesogenic azo dye movement in the polymer matrix is different from the neighbouring mesogenic groups of the polymer, the frequency separation in the ε'' spectra is about one decade. The activation energy and frequency of the δ-relaxation process occuring in the mesophase (mixture) is almost unaffected by the dye.

For the mixture in the perpendicular alignment we observed a strong relaxation which is obviously connected with the dye transversal dipole component and the polymer α-relaxation.

By means of dielectric spectroscopy we can observe a different behaviour of the dye molecule in the parallel and perpendicular alignment. These observations lead to the final conclusion, that the nonmesogenic dye molecules are oriented in the polymeric matrix to some extent, but rather due to their geometry (elongated shape) than the nematic potential of mesogenic side chains.

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