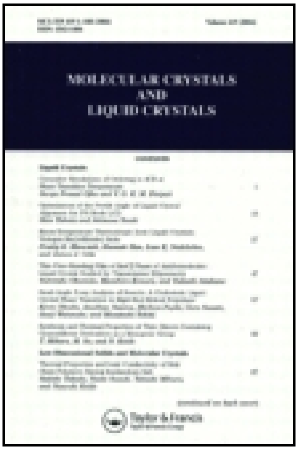

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Dielectric Spectroscopy on Two Concentrations of a Mixture of Low and High Molecular Liquid Crystalline Compounds

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Dielectric Spectroscopy on Two Concentrations of a Mixture of Low and High Molecular Liquid Crystalline Compounds

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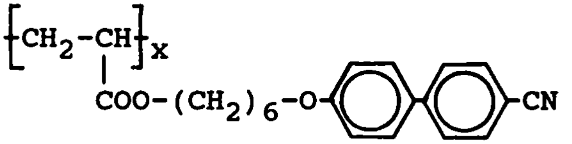
Dielectric relaxation measurements in the frequency range from 1 Hz to 100 kHz on mixtures of a substituted polyacrylate and 4-*n*-hexyloxycyanobiphenyl have been carried out. In the mixtures the dielectric absorption properties which can be related to the individual compounds has been detected. The relaxation frequency of the low molecular compound is about 50 to 100 times higher in comparison with the δ-relaxation of the polymer but it exhibits nearly the same high activation energy. From the experimental data it can be concluded that there is a molecular disperse distribution of both compounds in which the dynamics is mainly determined by the excess component, the polymer.

Keywords: dielectric relaxation, liquid crystals, polymer, low molecular compound, mixture, molecular disperse distribution

1. INTRODUCTION

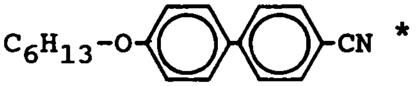
The structure and the dynamics of liquid crystals and of liquid crystalline polymers were investigated intensively in the past.[1–11] Up till now there are only few data on mixtures of low molecular and polymer liquid crystals because there is the problem of the miscibility in such a binary system.[12,13] Recently Kresse et al.[14] have reported about dielectric investigations on a substituted polyacrylate containing cyanobiphenyl in the side group and 4-*n*-octyloxybenzoyloxy-benzylidene-4′-cyanoaniline. In this binary system an unexpected result could be obtained: the dielectric relaxation frequency of the low molecular compound is lower as that of the polymer. With respect to measurements on mixtures of low molecular liquid crystals[15] the mobility of the low molecular compound in the mixture with a polymer should increase if we reduce the length-to-width ratio of the low molecular compound. Therefore, dielectric relaxation measurements on mixtures of



$\bar{X}=380$ **P**

g 313 n_{re} 357 s_A 406 ·n 409 is

and



L

Cr 331 N 350 Is

have been carried out. All temperatures are given in K. Only the phases of the pure L are indicated by capital letters. The phase diagram of both substances has been published elsewhere.[16] Here a miscibility of both compounds could be found. If $x_L > 0.25$ the smectic A and consequently the nematic reentrant phase n_{re} disappear and only a nematic phase could be observed in a wide temperature range. But contrary to the investigations of Gubina et al.[16] where the authors used a nonfractionated polymer we have taken a sample obtained after fractionated precipitation. Therefore, all phase transition temperatures are shifted to higher values in comparison to the published data.[16]

2. EXPERIMENTS AND RESULTS

The complex capacity $C^* = C' + iC''$ was measured from 1 Hz to 100 kHz using a modified Sawyer-Tower bridge. All measured data contain the bridge factor of about 300. The microcapacitor was made from two ITO coated glass plates separated by two 15 μm teflon spacers. The sample was not oriented but heated before the first measurement into the isotropic phase and then cooled down. Experimental details have been published elsewhere.[5] As one example in Figure 1 the experimentally obtained overall loss C'' of the pure polymer **P** is divided into the contribution arising from the conductivity and the dielectric contribution. The last part has been separated into two Cole-Cole mechanisms.[17] From our experimental data there is no physical reason for the separation of the dielectric results into two Cole-Cole plots. But in comparison with the results of Heinrich and Stoll[9] and our measurements[18] obtained on chemically similar substances this procedure should be justified. All these separation processes have been done by a computer without

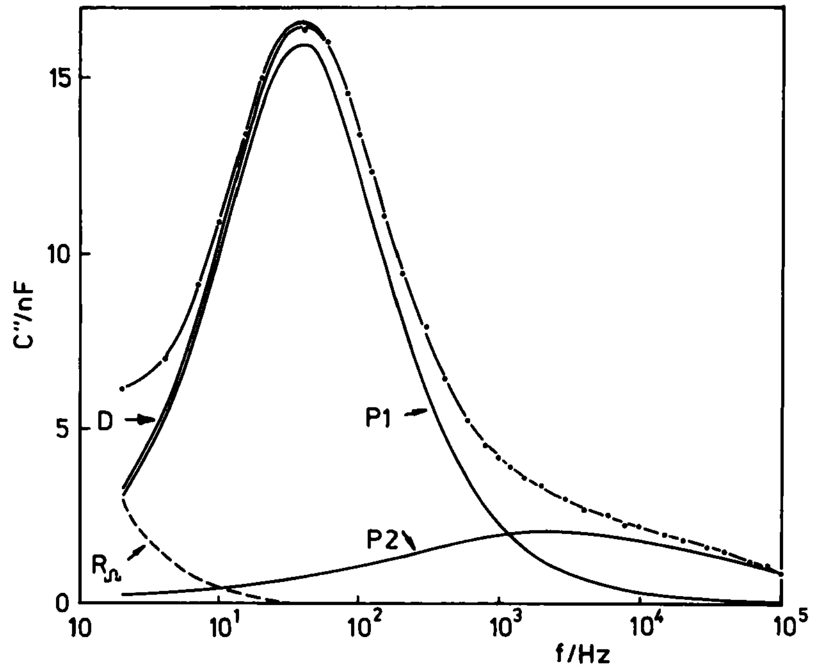


FIGURE 1 Experimentally obtained imaginary part of the capacity $C'' = (2\pi fR)^{-1}$ at $T = 337.7$ K (-●-●-●-). The whole dielectric absorption D of the pure polymer **P** was divided into two dielectric absorption ranges: the main mechanism **P1** (———) $f_1 = 37$ Hz, $h_1 = 0.15$, $\Delta_1 = 40.1$ nF and the second mechanism **P2** (———) $f_2 = 2.7$ kHz, $h_2 = 0.51$, $\Delta_2 = 10.3$ nF. The influence of the conductivity $(2\pi fR_\Omega)^{-1}$ is indicated by ---, $R_\Omega = 27.8$ MΩ. Δ and R_Ω contain the bridge factor of about 300.)

any additional information about the nature of the special relaxation process. The Cole-Cole plot in Figure 2 shows both absorptions of the pure polymer **P** at a temperature of 337.7 K. It should be mentioned here that for a second set of data we have had a more planar oriented sample. The only difference was that the intensity of the main absorption was smaller whereas the second one could be

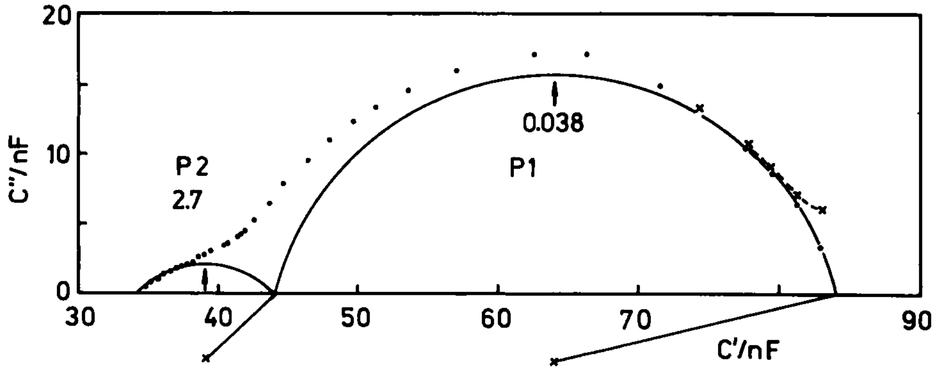


FIGURE 2 Cole-Cole representation of the data in Fig. 1.

better separated due to the higher intensity (+ in Figure 3). In Figure 3 the relaxation frequencies are plotted versus the reciprocal temperatures. There is no pronounced step in f_R at the phase transition from the s_A into the n_{re} phase. Therefore, the data for the low frequent mechanism have been fitted in both phases to the Equation[19,20]

$$\begin{aligned} f_R &= f_0 \exp[A/(T - T_0)]. \\ T_0 &= \text{Vogel-Fulcher temperature (if } T \rightarrow T_0 \text{ then } f_R \rightarrow \infty,\ A < 0) \end{aligned} \tag{1}$$

The mean deviations of the experimental points from the fitted curve are $\Delta f_R/f_R \approx 0.03$.

For the pure polymer we obtained $f_o = 2.5\ 10^{10}$ Hz, $A = 1736$ K, and $T_0 = 251$ K.

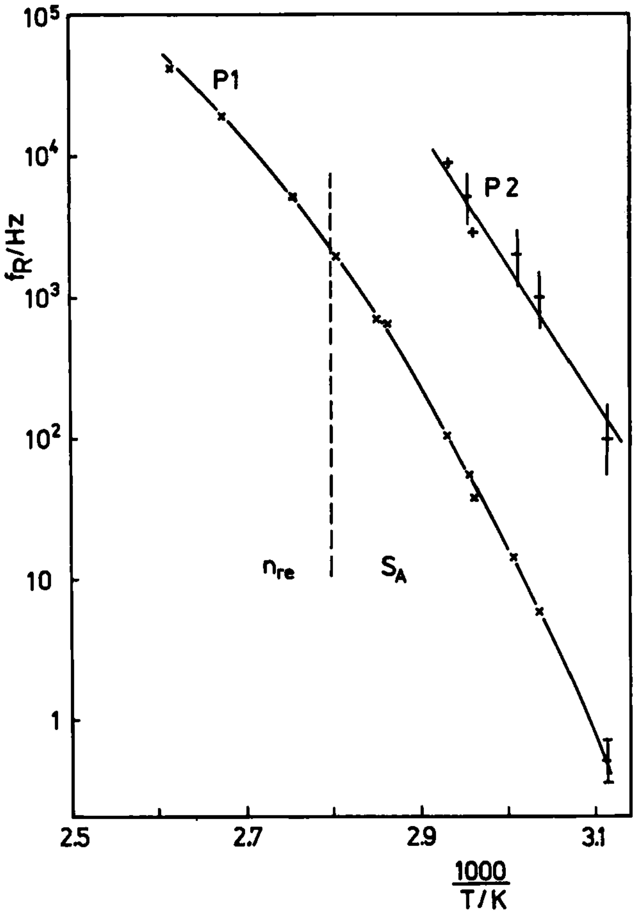


FIGURE 3 Arrhenius plot of the two relaxation mechanisms for all measured temperatures. The fitted curve according to (1) is given only for **P1**. The mechanism **P2** was estimated from the Cole-Cole plots (+) and the maxima of the absorption intensity of a more planar oriented sample (+).

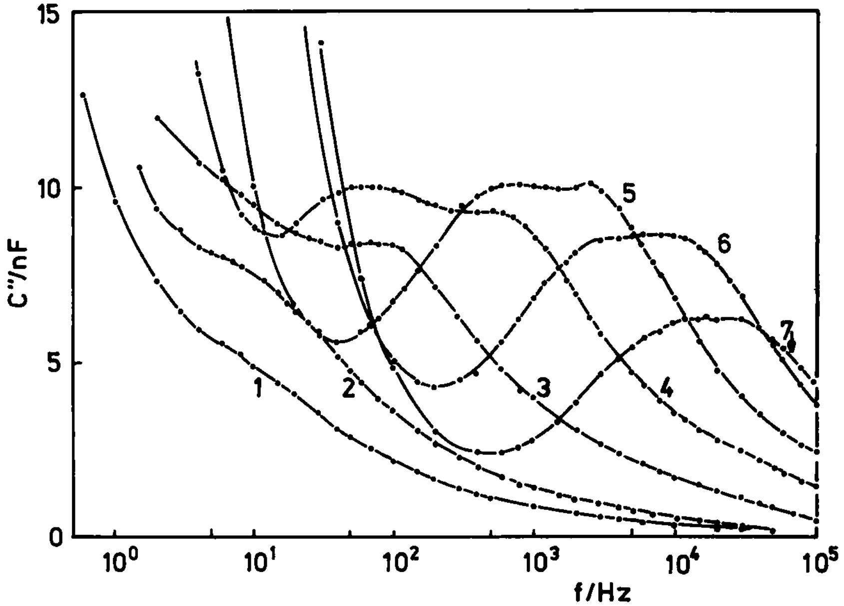


FIGURE 4 The complex capacity of the mixture of 80 mole% **P** and 20 mole% **L**. Temperatures T_1 = 299.6 K, T_2 = 300.8 K, T_3 = 310.2 K, T_4 = 320.3 K, T_5 = 329.8 K, T_6 = 339.7 K, T_7 = 346.5 K.

Dielectric data obtained on a mixture of 80 mole% **P** and 20 mole% **L** (n_{re} 352 s_A 385 n 395 is) are presented in Figure 4. For the calculation of the molar fraction of **P** we have taken the monomer units of **P**. Contrary to the measurements on the pure polymer **P** in which the electrical conductivity does not play an important role here the measurements are limited down to about 10 Hz due to the increasing conductivity. The main absorption peak obviously is splitted into two dielectric absorptions. One of them should be connected with the low molecular compound. All parameters of the three Cole-Cole plots and the electrical conductivity could be freely chosen. The results are plotted in Figure 5 for T = 329.8 K. The respective fitting parameters as the dielectric increments Δ, the relaxation frequencies f_R, and the Cole-Cole distribution parameters h^{17} are listed in Table I.

The Cole-Cole plot of the data in Figure 6 shows the differences in the geometry with respect to Figure 2. From the experiments results that

—the Cole-Cole distribution parameter of the first mechanism of Figure 6 and of the main mechanism of **P** in Figure 2 is about 0.15,

—the difference in f_R of the first and the third mechanism is about two decades and $h(3) > 0.5$ and

—the second mechanism is in the limits of the experimental accuracy a Debye mechanism ($h \approx 0$).

From this one can conclude that the second mechanism belongs to the substance **L** (indicated by **L(20)**) whereas the first and the third one belongs to the polymer.

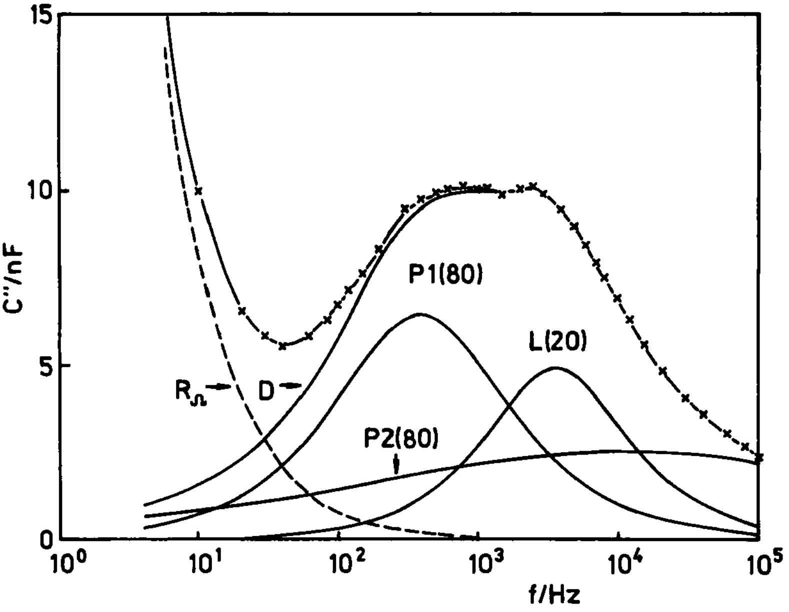


FIGURE 5 The imaginary part of the capacity at T = 329.8 K from Figure 4. The whole dielectric absorption D has been divided into **P1(80)** and **P2(80)** from Figure 1 and **L(20)** of the low molecular liquid crystal.

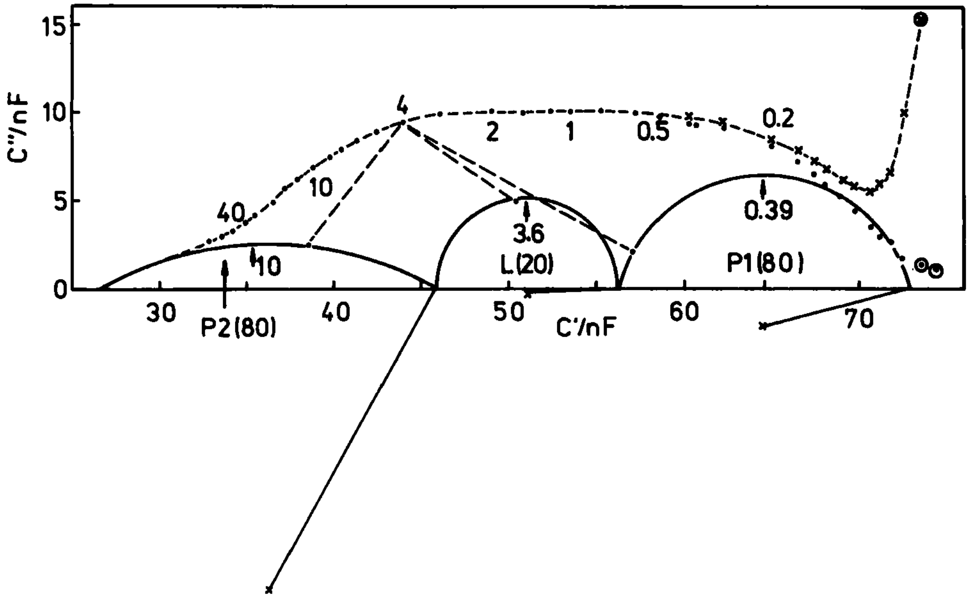


FIGURE 6 Cole-Cole plot of the data in Figure 5. O: Data have not been taken into consideration.

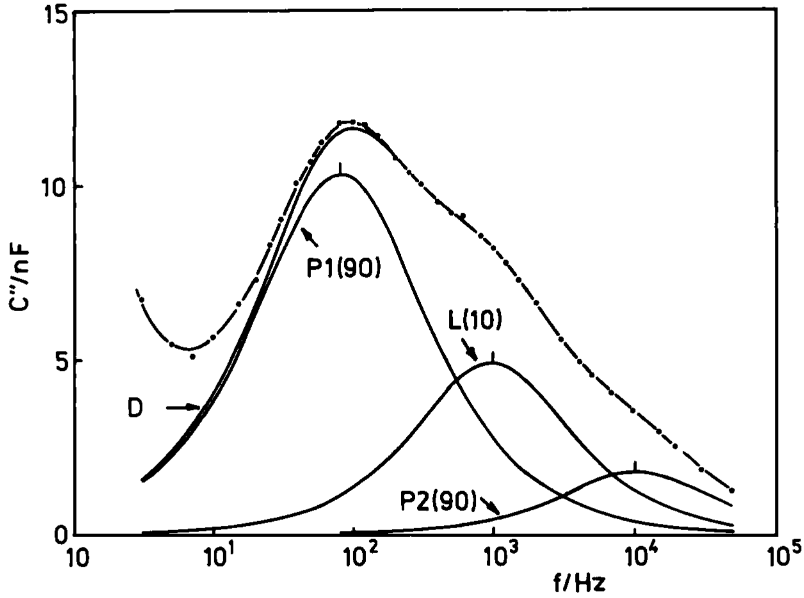


FIGURE 7 The imaginary part of the capacity of the mixture of 90 mole% **P** and 10 mole% **L** at T = 331.6 K. The designation is analogous to Figure 5.

The last two mechanisms are indicated by **P1(80)** and **P2(80)** respectively where the numbers are the concentrations of **P** in mole%. A further proof of the relative positions of the relaxation maxima of **P** and **L** in the mixture has been done by changing the concentrations to 90 mole% **P** and 10 mole% **L** (n_{re} 354 s_A 395 n 402 is). The dielectric absorption curve in Figure 7 shows a relative decrease of the second absorption maximum with respect to Figure 5. The fitted data analogous to Table I are summarized in Table II. There are only few experimental points at high frequencies. Therefore, the characteristic data of the third mechanism have a big error. From these measurements the classification of the absorption maxima to the respective mechanisms of the polymer **P1** and **P2** and the concentrations 100, 90, and 80 as well as of the low molecular compound in the mixtures **L(10)**

TABLE I

The fitted parameters of the three Cole-Cole mechanisms for the dielectric absorption curve of 80 mole% **P** and 20 mole% **L** at 329.8 K. Only for $\Delta f_R/f_R$ the error which arises from the experiment has been estimated.

	1. mechanism	2. mechanism	3. mechanism
Δ/nF	16.6	10.3	19.5
f_R/kHz	0.39	3.6	10.7
$\Delta f_R/f_R$	0.07	0.15	0.50
h	0.16	0.033	0.67

Resistivity R_Ω = 10.4 MΩ

TABLE II

The fitted parameters of the three Cole-Cole mechanisms for the absorption curve of 90 mole% P and 10 mole% L at 331.6 K.

	1. mechanism	2. mechanism	3. mechanism
Δ/nF	26.2	11.5	4.2
f_R/kHz	0.08	0.98	10.1
$\Delta f_R/f_R$	0.05	0.20	0.40
h	0.15	0.10	0.07

Resistivity R_Ω = 10.4 MΩ

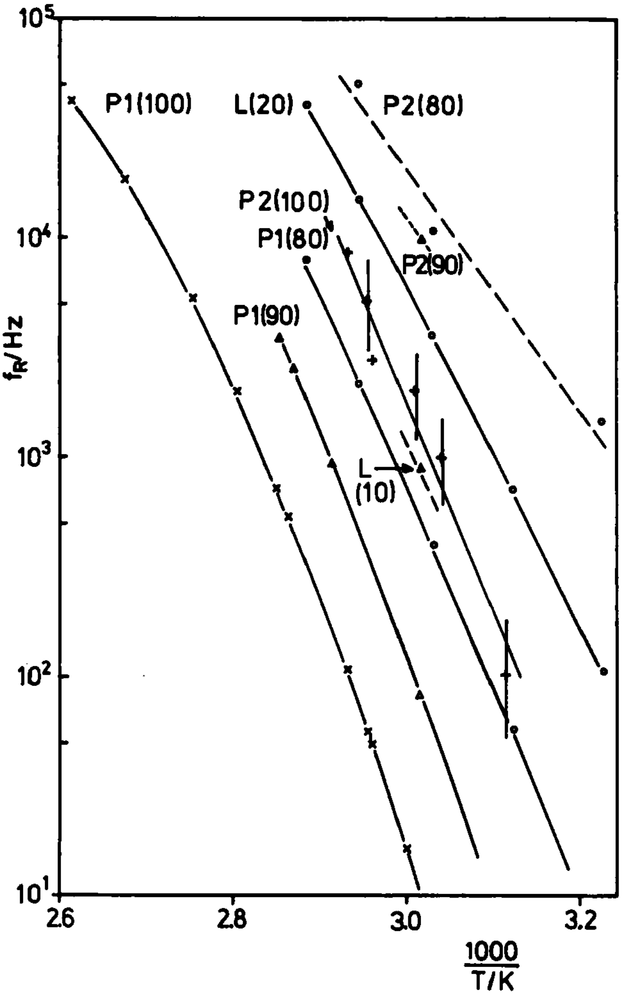


FIGURE 8 Arrhenius plot of the results of the two mixtures containing 20 mole% and 10 mole% of L. There are given the relaxation frequencies of the main mechanism of the polymer (**P1(100)**, **P1(90)**, **P1(80)**), the mechanism of the low molecular compound **L(10)** and **L(20)** as well as the second mechanism of the polymer **P2(90)** and **P2(80)**. The data of **L(10)** indicated by Δ and **P2(90)** resp. are only given for T = 331.6 K.

and **L(20)** is fixed. A survey about all measurements is presented in Figure 8. The relaxation frequency of the main absorption mechanism of **P1** increases with decreasing concentration. At $T = 333$ K the relaxation frequency of **P1** increases from 16 Hz (**P1(100)**) to 140 Hz for **P1(90)** and 750 Hz of **P1(80)**. This plasticizer effect has been detected already before.[14] The second relaxation mechanism of **P2** is shifted in the same way.

The relaxation frequency of 4-*n*-hexyloxycyanobiphenyl depends on the concentration. At 333 K f_R increases from 1.2 kHz (**L(10)**) to 5 kHz for **L(20)**. The activation energy of **L(20)** is about 150 kJ/mol. A pure 4-*n*-alkyloxycyanobiphenyl for example 4-*n*-heptyloxycyanobiphenyl (Cr 327 N 348 Is) has f_R (333 K) = 6 MHz and E_A = 65.9 kJ/mol.[21] This difference can be explained in the following way: the low molecular compound is strongly influenced by the nematic potential of the surrounding which is determined at these concentrations mainly by the side chain polymer. Low and high molecular compounds form a molecular disperse mixture without a phase separation. In the opposite case the relaxation frequency of the low molecular compound should be nearly constant because it is surrounded by the same molecules as the pure low molecular substance.

Acknowledgment

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