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Dielectric relaxation in a mixture of a side chain liquid-crystalline polymer and a low molecular liquid crystal

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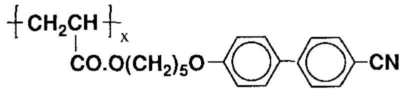
Dielectric measurements on two mixtures of a low and high molecular liquid crystal and the pure components have been carried out in the frequency range from 1 Hz to 100 kHz. In the S_A and supercooled S_A phase two absorption ranges were observed. The low frequency absorption belongs to the low molecular weight liquid crystal. The shift in the relaxation frequency of both compounds indicates complete miscibility. The strong difference of the absorption intensity of the polymer on heating and cooling can be associated with the formation of mixed crystals at smaller concentrations of the low molecular weight compound.

1. Introduction

In recent years the structural and dynamic behaviour of liquid-crystalline polymers has been studied intensively [1–15]. There are however only a few papers about mixtures of polymer liquid crystals and low molecular weight compounds [16–18]. The reason for this is that there are problems in obtaining a wide range of miscibility in such binary systems, because in many phase diagrams a gap of miscibility exist [19].

For poly {1-[5-(4′-cyano-4-biphenyloxy)pentyl-oxycarbonyl]-ethylene}

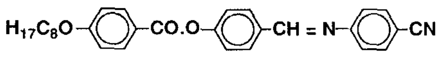


P

($\bar{x}$ = 100)

S_A 120°C N 123°C I

and 4-*n*-octyloxybenzoyloxy-benzylidene-4′-cyanoaniline



L

C 106°C N_{re} 151°C S_A 198°C N 255 I

however complete miscibility has been found by Kostromin *et al.* [20] in the N and S_A phases. The miscibility investigations have been carried out separately by the contact method, for single concentrations as well as by X-ray diffraction. At concentrations $x_L > 0.3$ crystallization could be observed using a microscope with a heating stage at temperatures below 100°C. This solid phase melts at 106°C. At

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$x_L = 0.3$ and 0.1 no crystallization was seen even at lower temperatures in this way; but such an effect has to be taken into account. Therefore, after finishing the absorption measurements for every temperature below 106°C the reproducibility of the dielectric loss at frequencies near to the first absorption maxima was tested. Phase separation of the S_A phase into two S_A ranges was not detected. One of the reasons to carry out these dielectric investigations was to try to find drastic changes in the absorption curves due to crystallization or phase separation. The high dipole moment of the CN-group in both components gives us the possibility to investigate the dynamic behaviour of the mixture with the aid of dielectric measurements.

2. Experimental

The polymer, *P*, and the low molecular weight substance, *L*, were mixed in the isotropic state. The mole fractions are related to the monomer unit of *P*. Two mixtures were prepared:

$$M30: x_L = 0{\cdot}30, \quad S_A\ 126°C\ \ N\ \ 174°C–180°C\ \ I$$

and

$$M10: x_L = 0{\cdot}10, \quad S_A\ 129{\cdot}5°C\ \ N\ \ 124°C–143°C\ \ I$$

The materials were placed in a microcapacitor consisting of two glass plates coated with ITO layers (distance 50 μm, and area 0·5 cm^2). The basic construction of the dielectric equipment and the method for the data analysis are given in [4]. The capacities C' and losses $C'' = (2\pi fR)^{-1}$ (f is the frequency and R is the resistivity) have been measured in the frequency range from 1 Hz to 100 kHz. All of the experimental data given in the figures and they contain the bridge factor F of 300 (see figures 1–3) and 100 (see figure 5). This means the measured quantities are $C' = F * C_C$ (C_C is the capacity of the cell and of the wires to the cell) and $C'' = F * (2\pi fR_C)^{-1}$ (R_C is the resistivity of the cell).

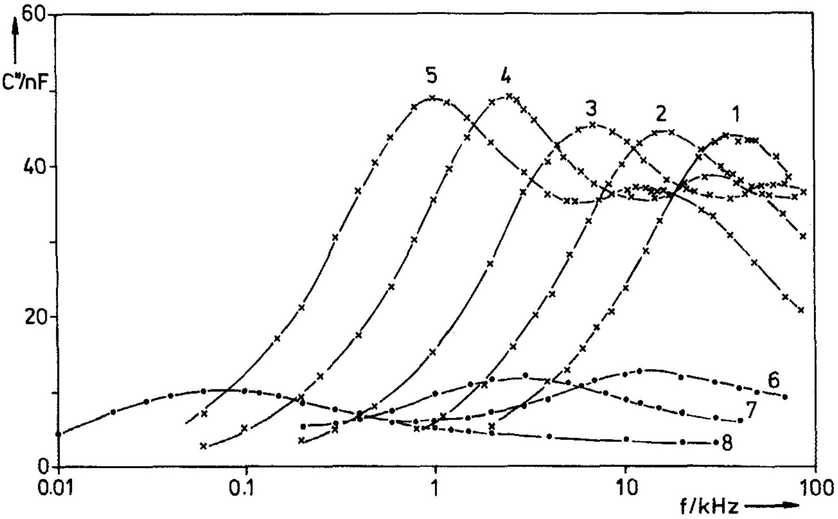

Figure 1. Dielectric absorption of *M*30 during cooling (x) and heating (●) at 1, 116·7°C; 2, 96·9°C; 3, 86·0°C; 4, 76·7°C; 5, 66·8°C (cooling); and 6, 86·4°C; 7, 76·7°C; 8, 57·6°C (heating). Bridge factor: 300.

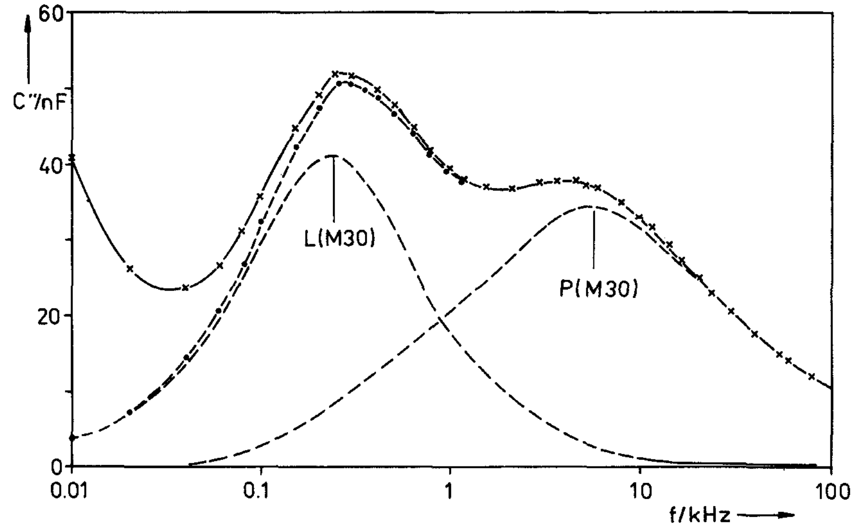

Figure 2. Separation of the absorption curves at 66·8°C into two parts. x-experimentally estimated C'' (exp) = $(2\pi fR)^{-1}$, ● only dielectric loss after subtraction of the conductivity part, $L(M30)$: absorption curve of the low molecular weight compound and $P(M30)$ of the polymer in the mixture $M30$.

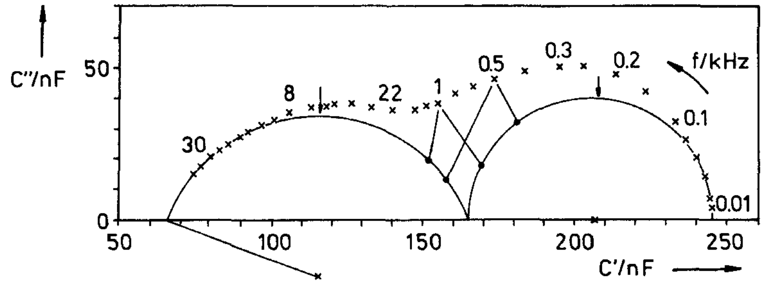

Figure 3. Cole–Cole plot of the two separated mechanisms for $M30$ at 66·8°C.

The sample was not oriented in order to avoid its decomposition during the slow cooling process from the clearing range. Dielectric absorption measurements for $M30$ for heating and cooling are presented in figure 1. At first the sample was heated to 140°C and then fast cooled to 116·7°C for the first measurement. The next two temperatures have been measured immediately. After a new heating process the dielectric loss at the last two temperatures has been investigated. At a temperature of about 57°C the absorption intensity decreases with time. After 3 days measurements with increasing temperature have been performed. Mixture $M10$ has been investigated in a similar way.

3. Results and discussion

The directly measured loss are given only for temperature 66·8°C in figure 2 and for $M10$ in figure 5. In order to avoid misunderstandings the part of C'' which results from the electrical conductivity has been subtracted. All experimental data measured at $T \geqslant 66{\cdot}8°C$ do not show a change with time at least within two hours. The geometrical shape of the low frequency absorption is the same at 116·7°C (stable mixture) and 96·9°C or even for 66·8°C. Therefore, we can exclude strong changes in the local environment of the molecules. The dielectric loss curves obtained have been separated into two absorption curves, a low frequency Debye absorption and a high frequency Cole–Cole absorption [21]. In the pure polymer, *P*, only one complex absorption process which shows the same shape as the absorption of *P*(*M*30) in figure 3 could be observed. The data for *M*30 at 66·8°C are given in figure 3 as a Cole–Cole representation. The separation into two different mechanisms with the increments of 80 nF (Debye) and 100 nF can only be related to the reorientation of the two CN dipoles. For component *L* we should observe the reorientation of the whole molecule around the short axis [9] whereas the dipole reorientation of *P* should be associated with the reorientation of the side chain around the main chain [4].

The interesting feature of figure 1 is the large difference of the absorption intensities on cooling and heating. In order to correlate the relaxation processes found experimentally to the respective molecular reorientations of *L* and *P*, the relaxation frequencies of the low and high frequency absorption on cooling and heating are plotted in figure 4. Additionally the relaxation frequencies of the pure polymer, *P*, and

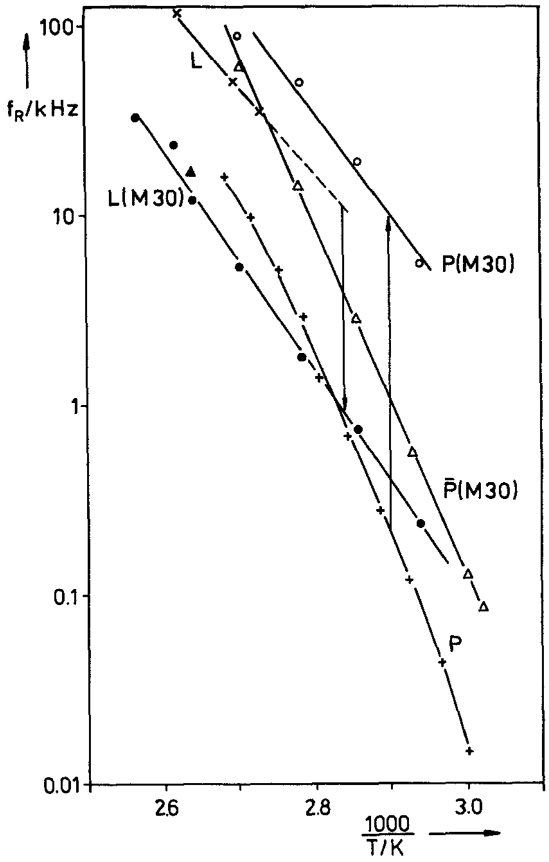

Figure 4. Arrhenius plot of the relaxation frequencies for *M*30, the pure polymer *P* and the pure low molecular weight compound *L*. For *M*30: heating: △, HF; ▲; LF maximum; cooling; ○, HF; ●, LF maximum (HF-high frequency, LF-low frequency), $\bar{P}$(*M*30)-small maximum during heating.

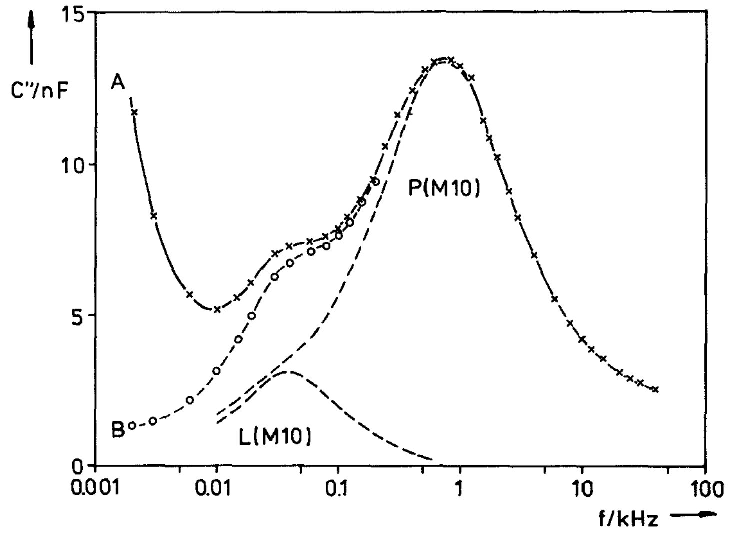

Figure 5. Separation of the absorption curves of *M*10 at 67·6°C. *AC''* including conductivity; *B* dielectric loss only.

of the low molecular weight component, *L*, measured under the same conditions are given. There are three straight lines:

(i) the connection of the highest absorption maxima (low frequency absorption) during cooling and the maximum at 105·6°C for heating, (not given in figure 1; the absorption is between the curves 1 and 2 with the same intensity). This Debye absorption could not be detected after crystallisation of the substance and heating up to 86·4°C. It should be the absorption of the low molecular component in the mixture indicated by *L*(*M*30).

(ii) the connection of the Cole–Cole absorption processes at high frequencies *P*(*M*30) is the Arrhenius plot of the reorientation of the side chain around the main chain in the mixture.

(iii) the low intensity absorption during heating ($\bar{P}(M30)$) which is split at higher temperature into the mechanisms discussed.

The conclusions will be clear if we take into account the absorption curves of *M*10. Here we could not find any recrystallization during three days; the curves for heating and cooling are similar. The high frequency Cole–Cole absorption, in figure 5 shows now a much larger intensity than that at low frequencies indicating that it is the absorption of the polymer. The relaxation frequencies obtained are compared in figure 6 with data of *P*(*M*30) from figure 4 and of the pure polymer. By comparison of figures 4 and 6 the following conclusions can be made:

(1) The addition of the low molecular weight liquid crystal produces an increase of the molecular mobility of the polymer. The relaxation frequencies increase by a factor of 50 for $x_L = 0{\cdot}3$ and of 6·5 for $x_L = 0{\cdot}1$ with respect to the pure polymer at 72°C.

(2) The molecular mobility of the low molecular weight liquid crystal decreases in the mixture. By addition of 30 mole per cent we can observe at 79°C a decrease by a factor of 1/11 and of 1/70 for $x_L = 0{\cdot}1$.

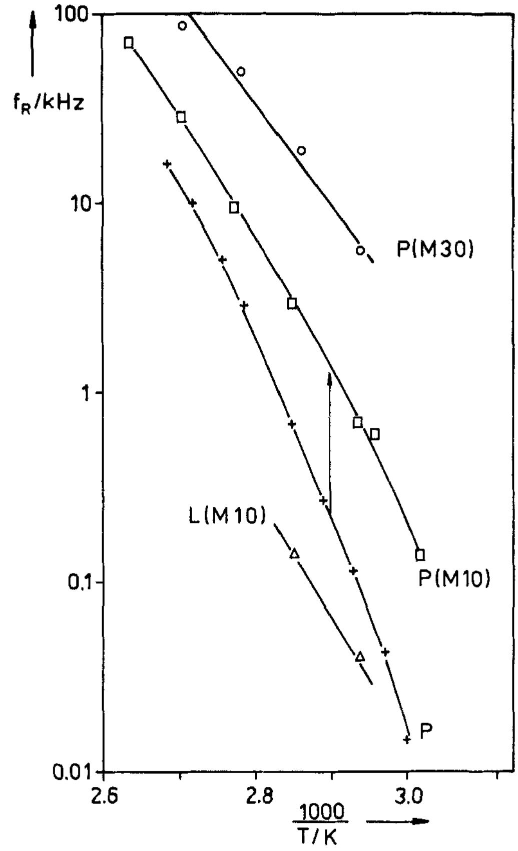

Figure 6. Arrhenius plot of the relaxation frequencies of *M*10 in comparison with the relaxation frequencies of *P* and *P*(*M*30).

(3) The small absorption intensity found on heating *M*30 differs in relation to the intensity and frequency from the absorption of the polymer, *P*, in figure 2. It seems to be that the relaxation frequency of $\bar{P}(M30)$ changes continuously between the relaxation frequency of *P* and *P*(*M*30). The change of the relaxation frequency and of the absorption intensity with increasing temperature seems to indicate the formation of mixed crystals of *P* and *L*, if we compare the data with that of a eutectic system [22]. The observed absorption of $\bar{P}(M30)$ should be the absorption of the pure polymer in which a small concentration of *L* (or of impurities of *L*) causes a plasticizer effect [23].

Generally the observed shift in the relaxation frequencies, especially the f_R shift of the low molecular weight compound to lower frequencies can only be interpreted as a complete molecular distribution of both compounds in each other.

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