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S. U. Vallerien[a]; F. Kremer[a]; G. Scherowsky[b]; A. Schliwa[b]; K. Kühnpast[c]; E. W. Fischer[a]
[a] Max-Planck-Institut für Polymerforschung, Mainz, F.R. Germany [b] Institut für Organische Chemie, Abteilung Makromolekulare Chemie, Technische Universität Berlin, Berlin 12, F.R. Germany [c] Institut für Technische Chemie, Abteilung Makromolekulare Chemie, Technische Universität Berlin, Berlin 12, F.R. Germany

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Broadband dielectric spectroscopy on ferroelectric liquid-crystalline side group polymers

by S. U. VALLERIEN, F. KREMER, G. SCHEROWSKY†, A. SCHLIWA†,
K. KÜHNPAST‡ and E. W. FISCHER

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-6500 Mainz,
F.R. Germany

† Institut für Organische Chemie, ‡ Institut für Technische Chemie,
Abteilung Makromolekulare Chemie, Technische Universität Berlin,
D-1000 Berlin 12, F.R. Germany

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Broadband dielectric spectroscopy (10^{-1} to 10^7 Hz, 100 to 450 K) has been applied, for the first time, to investigate the molecular dynamics of recently synthesized fast switching ferroelectric side group polymers. The softmode could be studied in detail in the S_C^* phase and in the S_I^* phase. At the transition a pronounced increase of the relaxational strength was found whereas its relaxational frequency remains constant. The softmode is the molecular basis for the electroclinic effect which has high application potential for ferroelectric liquid crystal polymers.

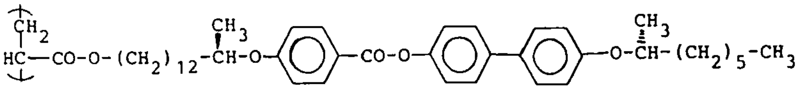
1. Introduction

Ferroelectric liquid crystals have gained considerable interest in technical applications such as optical devices [1–3]. The ferroelectric modes, Goldstone and soft mode, have been intensively studied in low molar mass systems [4–12] exhibiting fast electro-optic response times in the μs range for the S_C^* phase. These two modes have also been found in polymeric systems [13–15], which are all combined main-chain side-group liquid crystals with high rotational viscosities showing until now no measurable optical switching. Recently fast switching ferroelectric liquid crystal side group polymers have been synthesized and characterized [16]. In this paper dielectric spectroscopy on these materials is presented.

2. Experimental

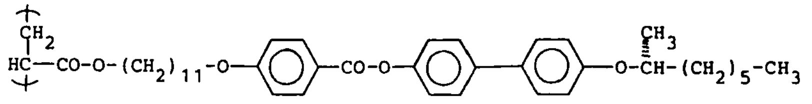
The synthesis of liquid-crystalline side group polymer PAC-1B is described in detail in [16]. PAC-7 containing an additional chiral centre in the spacer will be described [17]. The molecular weights we determined by GPC, calibrated with polystyrene standards. The phase transitions were determined by DSC and polarization microscopy. The phase characterization was done by X-ray measurements and polarization microscopy. The X-ray measurements were performed with CuK$_\alpha$ radiation using a flat-plate camera with a specimen film distance of 81 mm. Films were analysed using a Joyce–Loebl microdensitometer.

PAC-7



$M_W = 2100$; $E = M_W/M_N = 1{\cdot}8$; S_I^* 316 K S_C^* 332 K I

PAC-1B [18]



$M_W = 15{\cdot}000$; $E = M_W/M_N = 1{\cdot}5$;
g 323 K S_B 365 K S_X 389 K S_C^* 415 K S_A 424 K I

The dielectric measurements covered the frequency range from 10^{-1} to 10^7 Hz using a frequency response analyser (Solartron–Schlumberger FRA 1254, frequency range 10^{-4} to 6×10^4 Hz) with a high impedance preamplifier of variable gain [19–21] and a Hewlett–Packard impedance analyser (HP 4192 A, frequency range from 10 to 10^7 Hz) using an AC measuring field of 200 V/cm (peak-to-peak). A nitrogen gas heating system covered the temperature range from 100 to 450 K, the stability of the temperature adjustment was $\pm 0{\cdot}02$ K (resolution of the temperature measurement 0·01 K). The temperature gradient across the sample is estimated to be less than 0·04 K. The liquid-crystalline sample was kept between two glass plates coated with polyimid and separated by a spacer (10 ± 1 μm). The parallel rubbing direction and application of electric fields led to the desired uniform bookshelf geometry [1, 12, 15 (a)]. The alignment in the filled cell was checked by polarizing microscopy. The

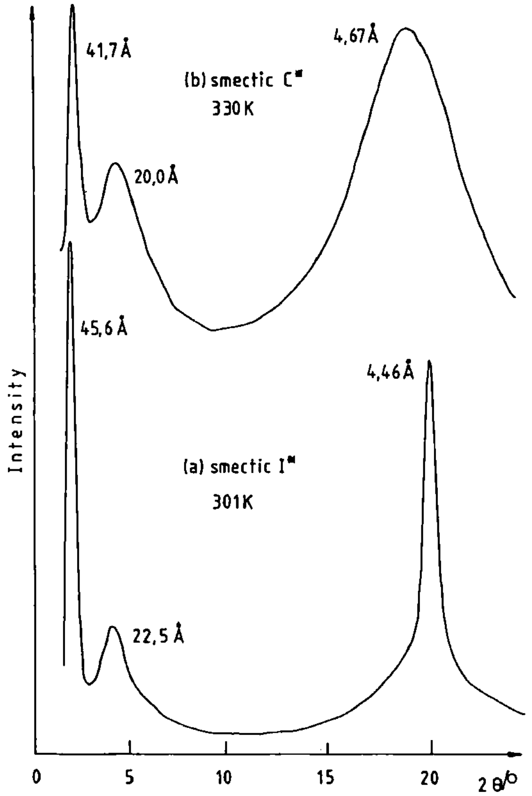


Figure 1. X-ray measurements for polymer PAC-7 at (*a*) 301 K (S_I^* phase); (*b*) 330 K (chiral smectic C phase).

voltage was applied by two evaporated indium tin oxide electrodes with an area of 4 × 4 mm^2 (LCD-cell from EHC, Japan).

3. Results and discussion

At room temperature the polymer PAC-7 is in an ordered phase (figure 1 (*a*)). The fibre patterns obtained in this phase show two small-angle reflections corresponding to 45·6 Å (first order) and 22·5 Å (second order) and a very sharp wide-angle refliction corresponding to 4·46 Å. Compared with the lattice spacing of 45·6 Å a tilted layer structure for this ordered phase can be deduced (tilt angle of 18°). The very sharp wide-angle reflection is more typical of S_I phases than S_F phases, so this phase was assigned as S_I.

The X-ray measurement at 330 K indicates a smectic C* phase (figure 1 (*b*)). The small-angle reflection corresponding to 41·7 Å indicates a tilt angle of 30°. The liquid-like packing of the mesogens leads to a broadened diffusive wide-angle reflection at 4·67 Å.

In the chiral smectic C phase two ferroelectric modes are present; A Goldstone mode which corresponds to a fluctuation of the polarization in each smectic layer with respect to the next one (resulting from a fluctuation of the director of the tilt vector at constant tilt angle), and a soft mode, which corresponds to the fluctuation of the tilt angle, θ (between the director and the normal to the smectic layers). Whereas the softmode is present in the S_A phase of chiral molecules and in tilted smectic phases in the radio frequency region [4–15], the Goldstone mode can normally be observed

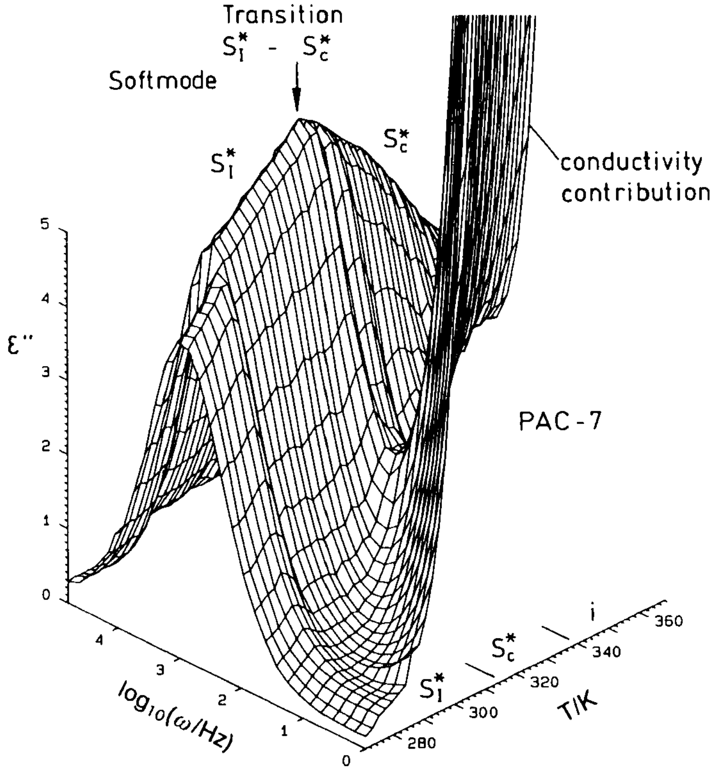


Figure 2. Dielectric loss versus frequency and temperature for polymer PAC-7.

dielectrically only at lower frequencies in the S_C^* phase [4–15]. In principle the Goldstone mode should exist in all chiral tilted smectic phases developing a helical superstructure. However, because of the shift toward lower frequencies, resulting from more dense packing of the higher ordered tilted smectic phases this process is presumably covered by a conductivity contribution, as observed in polymeric systems [13, 15].

In figure 2 the dielectric loss ε'' is shown as a function of temperature and frequency for polymer PAC-7. In the S_C^* phase the soft mode can be found. Its relaxation strength increases with decreasing temperature and reaches its maximum at the transition to the S_I phase. Since both phases are ferroelectric, the frequency position of the soft mode in PAC-7 is unaffected, whereas close to the phase transition ferroelectric/non-ferroelectric in smectic phases the frequency of the soft mode obeys

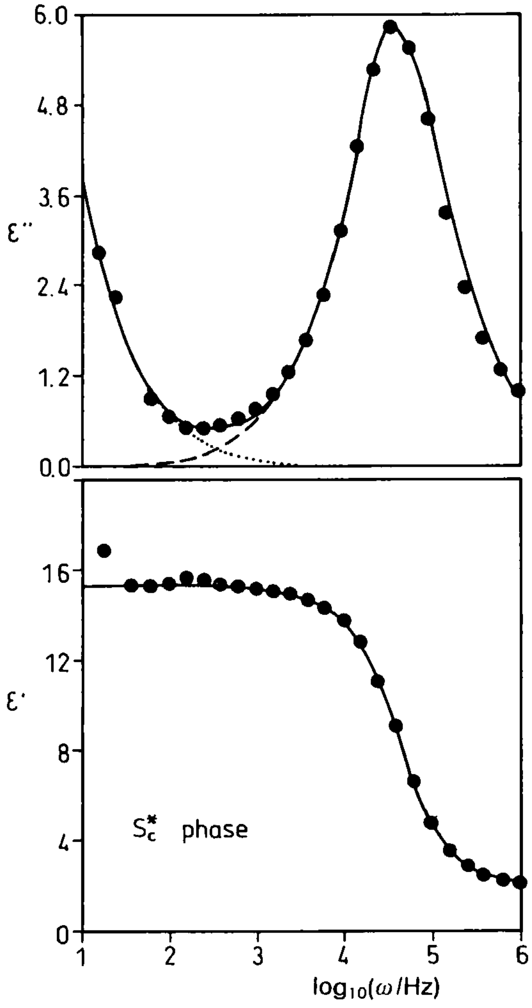


Figure 3. Dots correspond to the experimental values at 321·0 K. The dotted line shows the conductivity contribution (according to equation (1), using the fit parameters $\delta_0 = 1·5 \times 10^{-7}$ 1/Ωcm and $s = 0·8$). The dashed line shows the Cole–Cole function (according to equation (2), using the fit parameters $\varepsilon_\infty = 2$, $\Delta\varepsilon = 14,0$, $\alpha = 0·86$ and $\tau = 3·8 \times 10^{-6}$ s).

the Curie–Weiss law in both phases [7, 8, 9(b), 12, 15(b)]. The soft mode in this polymer occurs at lower frequencies compared to the soft mode in other polymeric system [13–15], which is not surprising because all of these systems have mesogenic units composed of two phenyl rings, whereas in PAC-7 this mesogenic unit is a biphenylbenzoatester group. The experimental data of the soft mode are well describable by the Cole–Cole equation (see figure 3)

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (i\omega\tau)^\alpha)}, \tag{1}$$

where ε_∞ and ε_s are the values of the complex dielectric function on the high frequency and low frequency side of the relaxation process, respectively, τ is the mean relaxation time and the parameter α describes the symmetric broadening of the relaxation time distribution. The values for τ and α are only slightly temperature dependent and comparable to the fit parameters found for combined side-group main-chain ferroelectric liquid-crystalline polymers [13, 14, 15(a), (b)], whereas $\Delta\varepsilon$ is for these side group polymers larger due to the higher concentration of mesogenic groups carrying a chiral terminal group. At lower frequencies the contribution of the conduction occurs. Its frequency dependence obeys the equation [21, 22]

$$\varepsilon''(\omega) = \frac{\delta_0}{\varepsilon_0 \omega^{(1-s)}}, \tag{2}$$

and can thereby be subtracted (see figure 3); δ_0 and s are fit parameters. For s, values of about 0·8 are found, which indicates a hopping conductivity. The Goldstone mode is, in the S_C^* phase, presumably covered by the conductivity contribution. In the S_I phase it has to be expected at lower frequencies, because (i) the S_I phase has a hexagonal packing, and (ii) the S_I orientational viscosity is higher.

In the second polymer PAC-1B, the phase transitions are shifted towards higher temperatures. The conductivity contribution covers all processes; however by taking a superposition of the ferroelectric modes and the conductivity into account, a qualitative approach is possible. In figure 4 the isochronal representations of the dielectric loss (ε'') and the real part (ε') of the complex dielectric function versus temperature are shown. Entering the S_A phase from the isotropic phase leads to a strong increase in ε' and ε'' arising from the occurrence of the soft mode. This increase continues in the S_C^* phase arising there from the additional Goldstone mode. At the transition temperature $S_A \rightarrow S_C^*$ the modulations in ε' and ε'' arise probably from the soft mode feature [8, 9(b), 12, 15(b)]. At the transition from S_C^* to the tilted highly ordered S_X phase ε'' decreases because of the stronger hindrance of the Goldstone mode in the S_X phase. The transitions S_X–S_B can again be seen in ε', ε'' where both increases result from the rearrangements of the molecules from the tilted hexagonal packing to the crystal-like S_B phase with an orthogonal layering structure. A quantitative analysis is not possible so far with polymer PAC-1B. A purification procedure for this polymer from the ionic contamination should be one way to achieve this.

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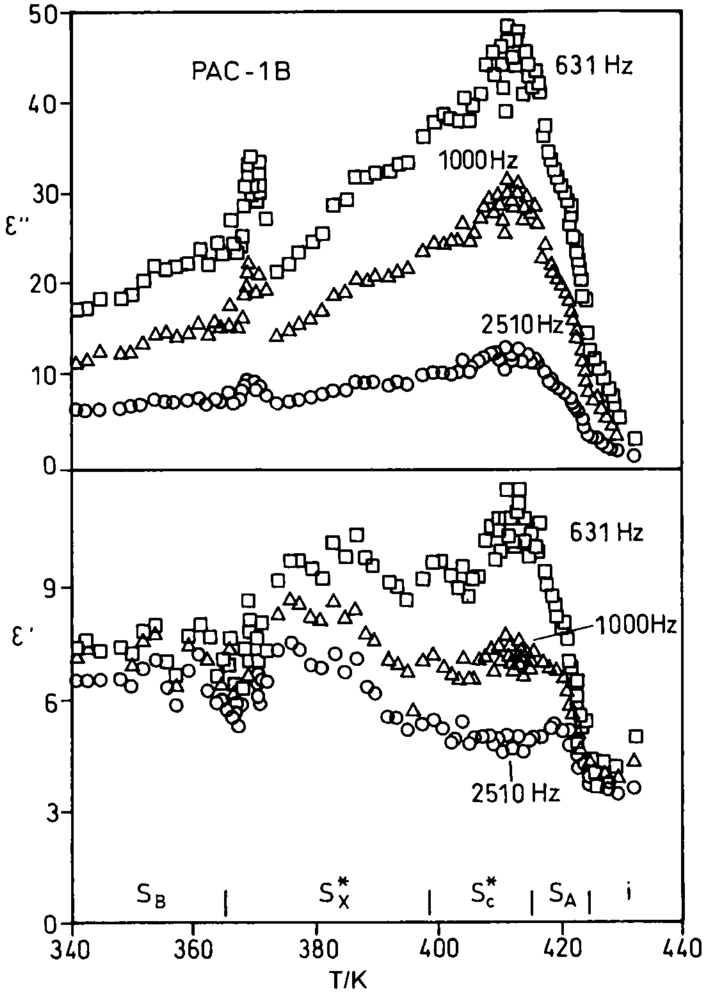

Figure 4. Isochronal representation of the real part (ε′) and the imaginary part (ε″) of the complex dielectric function versus temperature for PAC-1B for the frequencies indicated.

References

[1] (a) Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36**, 879. (b) Lagerwall, S. T., Otterholm, B., Sharp, K., 1987, *Molec. Crystals liq. Crystals*, **152**, 503.

[2] Beresnev, L. A., Blinov, L. M., Osipov, M. A., and Pikin, S. A., 1988, *Molec. Crystals. liq. Crystals* A, **158**, 1.

[3] Blinc, R., Filipič, C. Levstik, A., and Žekš, B., 1987, *Molec. Crystals liq. Crystals*, **151**, 1.

[4] Martinot-Lagarde, Ph., and Durand, G., 1981, *J. Phys., Paris*, **42**, 269.

[5] (a) Levstik, A., Carlsson, T., Filipič, C., and Žekš, B., 1988, *Molec. Crystals liq. Crystals*, **154**, 259. (b) Levstik, A., Carlsson, T., Filipič, C., Levstik, I., and Žekš, B., 1987, *Phys. Rev.* A, **35**, 3527. (c) Filipič, C., Carlsson, T., Levstik, A., Žekš, B., Blinc, R., Gouda, F., and Skarp, K., 1988, *Phys. Rev.* A, **38**, 5833.

[6] (a) Cava, R. J., Patel, J. S., Collen, K. R., Goodby, J. W., and E. A. Rietman, 1987, *Phys. Rev.* A, **35**, 4378. (b) Cava, R. J., Patel, J. S., and Rietman, E. A., 1986, *J. appl. Phys.*, **60**, 3093.

[7] Muševič, O., Blinc, R., Žekš, B., Filipič, C., Copič, M., Seppen, A., Wyder, P., and Levanyuk, A., 1988, *Phys. Rev. Lett.*, **60**, 1530.

[8] Gouda, F., Andersson, G., Carlsson, T., Lagerwall, S. T., Skarp, K., Stebler, B., Filipič, C., Žekš, B., and Levstik, A., (a) 1989, *Liq. Crystals*, **6**, 219. (b) 1989, *Molec. Crystals liq. Crystals Lett.*, **6**, 151. (c) Gouda, F., Skarp, K., Andersson, G., Kresse, H., and Lagerwall, S. T., 1989, *Jap. J. appl. Phys.*, **28**, 1887.

[9] Biradar, A. M., Wrobel, S., and Haase, W., (a) 1989, *Phys. Rev.* A, **39**, 2693; (b) 1989, *Ferroelectrics*, **100**, 271.

[10] (a) Parneix, J. P., and Legrand, C., 1988, *Ferroelectrics*, **84**, 199. (b) Legrand, C., Parneix, J. P., M'Kadmi, A., Tinh, N. H., Destrade, C., Salleneuve, C., and Isaert, N., 1988, *Ferroelectrics*, **84**, 249.

[11] (a) Kresse, H., Tschierske, C., Vallerien, S. U., and Kremer, F., *Physica Stat. Sol.* (in the press). (b) Vallerien, S. U., Kremer, F., Geelhaar, T., and Wächtler, A. E., *Phys. Rev.* A (in the press).

[12] Vallerien, S. U., Kremer, F., Kapitza, H., Zentel, R., and Frank, W., 1989, *Physics Lett.* A, **138**, 219.

[13] Vallerien, S. U., Zentel, R., Kremer, F., Kapitza, H., and Fischer, E. W., 1989, *Makromolek. Chem. rap. Commun.*, **10**, 333.

[14] (a) Kremer, F., Vallerien, S. U., and Zentel, R., 1990, *Adv. Mater.*, **2**, 145. (b) Kremer, F., Vallerien, S. U., Zentel, R., and Kapitza, H., 1989, *Macromolecules*, **22**, 4040.

[15] (a) Vallerien, S. U., Zentel, R., Kremer, F., Kapitza, H., and Fischer, E. W., 1990, *Ferroelectrics* (in the press). (b) Vallerien, S. U., Kremer, F., Kapitza, H., Zentel, R., and Fischer, E. W., 1990, *Ferroelectrics* (in the press).

[16] Scherowsky, G., Schliwa, A., Springer, J., Kühnpast, K., and Trapp, W., 1989, *Liq. Crystals*, **5**, 128.

[17] Scherowsky, G., Rhode, E., Schliwa, A., Springer, J., and Trapp, W., 1989, *Second International Conference on Ferroelectric Liquid Crystals*, Göteborg, 30 June 1989 (024).

[18] The phase idenitification for PAC-1B was done by Dr. P. Davidson, Laboratoire de Physique des Solides, Associé au CNRS, Université Paris XI, and will be published elsewhere.

[19] Pugh, J., and Ryan, J. T., 1977, *Measurements and Applications, No. 177.* pp. 404–407.

[20] Vallerien, S. U., Kremer, F., and Boeffel, C., 1989, *Liq. Crystals*, **4**, 79.

[21] Vallerien, S. U., Kremer, F., Hueser, B., Spieß, H. W., 1989, *Colloid Polymer Sci.*, **267**, 583.

[22] Mott, N. F., and Davis, E. A., 1979, *Electron Processes in Non-Crystalline Materials*, second edition (Clarendon Press).