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Preliminary communication

Broadband dielectric investigations on a compound consisting of bent-shaped molecules

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Dielectric measurements on the antiferroelectric smectic C (SmCP_A) and isotropic (I) phases of a substance formed by bent-shaped molecules were performed in the frequency range from 0.1 Hz to 0.1 GHz. Three absorption ranges, corresponding to a slow collective process, the reorientation of the molecular core around the long axes and the fast dynamics of the terminal groups, were detected in the SmCP_A phase, whereas only two ranges, related to the two last processes, appear in the isotropic state. At the I–SmCP_A phase transition the process of molecular reorientation around the long axes changes stepwise with respect to the absorption band intensity and the relaxation time, while the activation energy remains practically unchanged. The activation energy for the dynamics of the terminal groups increases at the I–SmCP_A transition.

Bent-shaped molecules are able to form different phases with short-range ferroelectric order [1, 2]. In such cases, the ferroelectricity is based on the hindered rotation of the central core of the molecules around their long axis [3]. Thus, in a given layer of the smectic C (SmC) phase, the tilted molecules are ordered in such a way that the dipole moments show preferably in the direction perpendicular to the layer normal and to the tilt plane resulting in a spontaneous polarization. To distinguish them from bulk polarization, the local polarization of neighbouring layers shows in opposite directions, resulting in the antiferroelectric behaviour (denoted by subscript A) of the compound. Recently, dielectric measurements have revealed that at the transition from the isotropic liquid (I) to the SmCP_A phase the following features can be observed: (i) a new low-frequency absorption band appears in the SmCP_A phase and it can be related to collective dynamics of ferroelectric units, and (ii) at the transition, the relaxation time and the dielectric increment corresponding to the reorientation of the molecules around their long axis increases stepwise [4]. Besides, dielectric studies show that in the isotropic phase of some bent-core mesogenic compounds ferroelectric-like clusters can exist [5].

The aim of this paper is to report the dynamic behaviour of a compound composed of the bent-shaped molecules with the chemical formula shown in scheme 1. Compound **1** exhibits the phase transitions Cr 90°C (SmCP_A 86°C) I, whereby the SmCP_A phase appears as monotropic. Methods for the synthesis and purification of the compound are described elsewhere [6].

Dielectric measurements were carried out in the frequency (f) range from 0.1 Hz to 100 MHz. In the region of low frequencies (0.1 Hz–1 MHz), a Solartron-Schlumberger Impedance Analyzer Si 1260 was used, and for higher frequencies (300 kHz–100 MHz), a HP 4194A impedance/gain phase analyser was used. Experimental details are given elsewhere [3, 7].

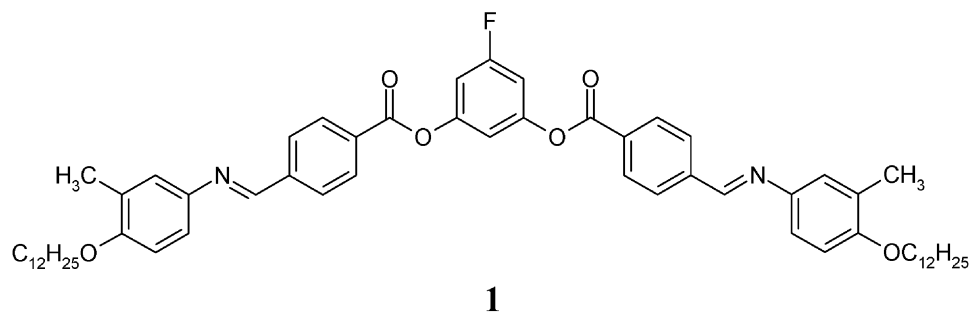
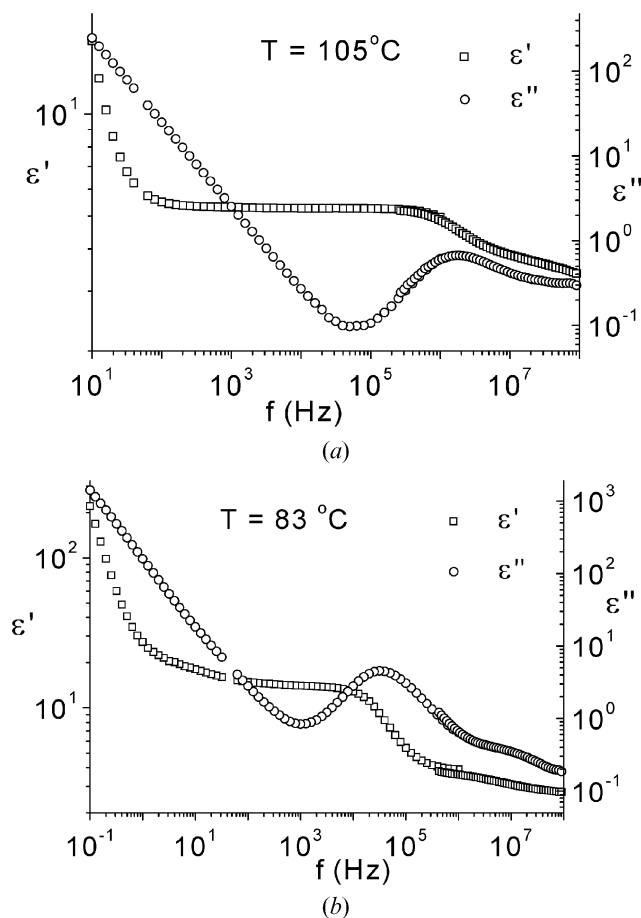
Figure 1 presents, as an example, the dielectric relaxation spectra, dispersion $\varepsilon'(f)$ and absorption $\varepsilon''(f)$, recorded in the isotropic and SmCP_A phases of compound **1** on cooling.

The spectra were resolved into elementary absorption bands of the Cole–Cole type [8]:

$$\varepsilon^* \equiv \varepsilon' - j\varepsilon'' = \varepsilon_3 + \frac{\varepsilon_0 - \varepsilon_1}{1 + (j\omega\tau_1)^{1-\alpha_1}} + \frac{\varepsilon_1 - \varepsilon_2}{1 + (j\omega\tau_2)^{1-\alpha_2}} + \frac{\varepsilon_2 - \varepsilon_3}{1 + (j\omega\tau_3)^{1-\alpha_3}} - j\frac{A}{f^M} + \frac{B}{f^N}$$

and the contributions from the double layers (to the real part of the permittivity, ε') and of the conductivity (to

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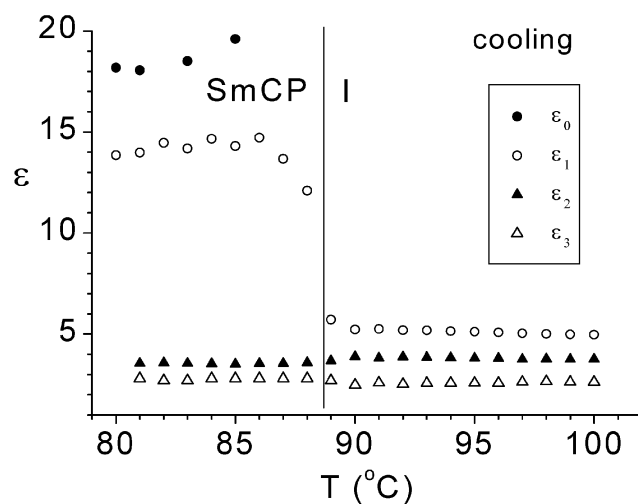
Scheme 1. Chemical structure of compound **1**.Figure 1. Dielectric relaxation spectra recorded in the (a) isotropic and (b) SmCP_A phases of the compound **1**.

the imaginary part, ε''), were taken into account. In equation (1) $\omega (=2\pi f)$ denotes the angular frequency, τ_i and α_i are the relaxation time and the Cole-Cole distribution parameter, respectively, of a given relaxation process, $\varepsilon_0-\varepsilon_1$, $\varepsilon_1-\varepsilon_2$ and $\varepsilon_2-\varepsilon_3$ are the strengths of the processes, M , A and N , B are adjustable parameters describing the conductivity and double-layers effects, respectively, and $j=\sqrt{-1}$. Equation (1) was taken as sufficient for the analysis of the raw data in the

mesophase because the absorption curves are symmetric and the splitting into two mechanisms at high frequencies can be clearly seen in figure 1 b. For the isotropic phase the same model was used because the stepwise increase of the relaxation frequency for the low-frequency process at the phase transition causes a superposition of both molecular processes.

Three relaxation processes were found in the SmCP_A phase (see also Diez *et al.* [9]) and two processes in the isotropic state of compound **1**. The fitted limits of the dielectric permittivity and the corresponding relaxation times are shown in figures 2 and 3 as a function of temperature.

The first relaxation process, seen only in the SmCP_A phase, reduces the dielectric permittivity from ε_0 to ε_1 and is related to the already mentioned collective dynamics of the ferroelectric units. Due to considerable difficulties in separation of this relaxation band from the contribution of the double layer and the conductivity, the error of the ε_0 values obtained can reach about 30% and even more for values of the relaxation time. For this process an activation energy, estimated from

Figure 2. Limits of the dielectric permittivity resulting from the best fit of equation (1) to the experimental spectra of **1**.

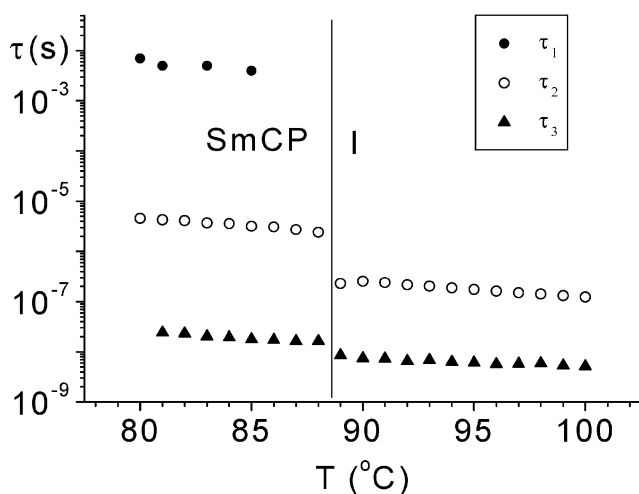


Figure 3. Temperature dependence of the relaxation times corresponding to different processes in **1**.

the temperature dependence of the relaxation time τ_1 , is equal to $E_A(1)=97 \pm 50 \text{ kJ mol}^{-1}$. The second relaxation process is caused by the reorientation of the molecules around their long axis. This process appears both in the SmCP_A and the isotropic phases. As can be seen in figures 2 and 3, a big step of the dielectric increment $\epsilon_1-\epsilon_2$ and the relaxation time τ_2 appears at the I-SmCP_A transition. This effect is related to the strong positive dipole correlation resulting from the tendency of a lateral packing with the same direction of the bent molecules. This packing hinders the reorientation of the molecules about the long axes [4]. The decrease of the dielectric increment $\epsilon_1-\epsilon_2$ with decreasing temperature within the SmCP_A phase may be related to the decreasing number of rotating dipoles reduced by the additional hindrance potential [3]. Surprisingly, the

activation energies for the reorientation of the central core of the molecules about the long axis in the isotropic phase $E_A(2, I)=82 \pm 2 \text{ kJ mol}^{-1}$ and the SmCP_A phase $E_A(2, \text{SmCP}_A)=82 \pm 6 \text{ kJ mol}^{-1}$ are, within the experimental errors, quite similar. The unexpected high value of E_A in the isotropic state may be result from the destruction of the ferroelectric clusters in the phase transition range [5].

The high-frequency relaxation process observed reduces the dielectric permittivity ϵ_3 to about 2.8. The related activation energy in the SmCP_A phase, $E_A(3, \text{SmCP}_A)=71 \pm 9 \text{ kJ mol}^{-1}$, is much higher than that in the isotropic liquid: $E_A(3, I)=39 \pm 7 \text{ kJ mol}^{-1}$. This indicates that the dynamics of the polar alkyloxy groups is also strongly influenced by the molecular packing in the SmCP_A phase.

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