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THERMALLY STIMULATED CURRENT IN SMECTIC LIQUID CRYSTALS

Taro TACHIBANA, Toshiaki TAKAMATSU*, and Eiichi FUKADA*
Chemical Laboratory, Ochanomizu University, Bunkyo-ku, Tokyo 112
and *The Institute of Physical and Chemical Research, Hirosawa, Wako-shi, Saitama 351

Thermally stimulated current curves were determined for two samples of smectic liquid crystals; diethyl azoxybenzene-4, 4'-dicarboxylate and ethyl p-(p-ethoxybenzylidene) aminocinnamate. The curves showed peaks or kinks at phase transition points. The form of the curves was interpreted in terms of the release of impurity ions accompanying the phase transition.

Recently Takamatsu and Fukada[1] have found that thermally stimulated current (TSC) curves for polymer electrets show peaks or kinks at temperatures, where the transition of crystalline phase or the initiation of micro Brownian motion takes place. Similar phenomena have been observed also with some triglycerides[2] and nematic and cholesteric liquid crystals[3,4]. In the present study the TSC method is applied to smectic liquid crystals. Since this type of liquid crystals is often polymesomorphic, it is interesting to investigate the transition between the mesomorphic phases by using the TSC method.

Experimental

The experimental method[1] was previously described. The apparatus is shown in the schematic diagram of Fig. 1. The principal procedure[1] is the following: The sample is allowed to melt into isotropic liquid and then polarized by a high electric field (10^3-10^4 v/cm) for 30 minutes. This polarization is subsequently frozen in by cooling the sample down to room temperature. After removal of the electric potential, the sample is heated up at a fixed rate of 1.2°C/min, and, at the same time, the liberated depolarization current is measured with an electrometer.

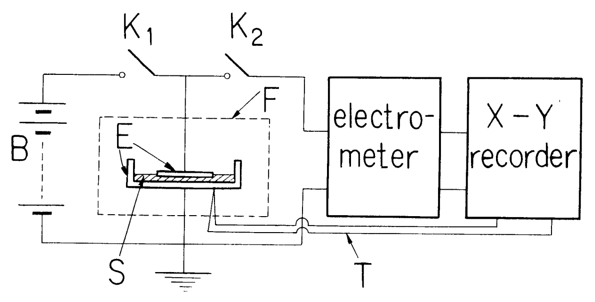


Fig. 1. A schematic diagram of the apparatus used for measuring the depolarization current.

K_1, K_2; switch T; thermojunction
E; electrode F; thermostat
S; sample
B; D.C. source

Thermally stimulated current was observed also for the samples into which no polarizations had been previously introduced.

Phase transition temperatures were determined by differential thermal analysis (DTA).

The smectic samples used were diethyl azoxybenzene-4, 4'-dicarboxylate (DADC) and ethyl p-(p-ethoxybenzylidene) aminocinnamate (EEAC) which were purified from commercial products by succesive recrystallization.

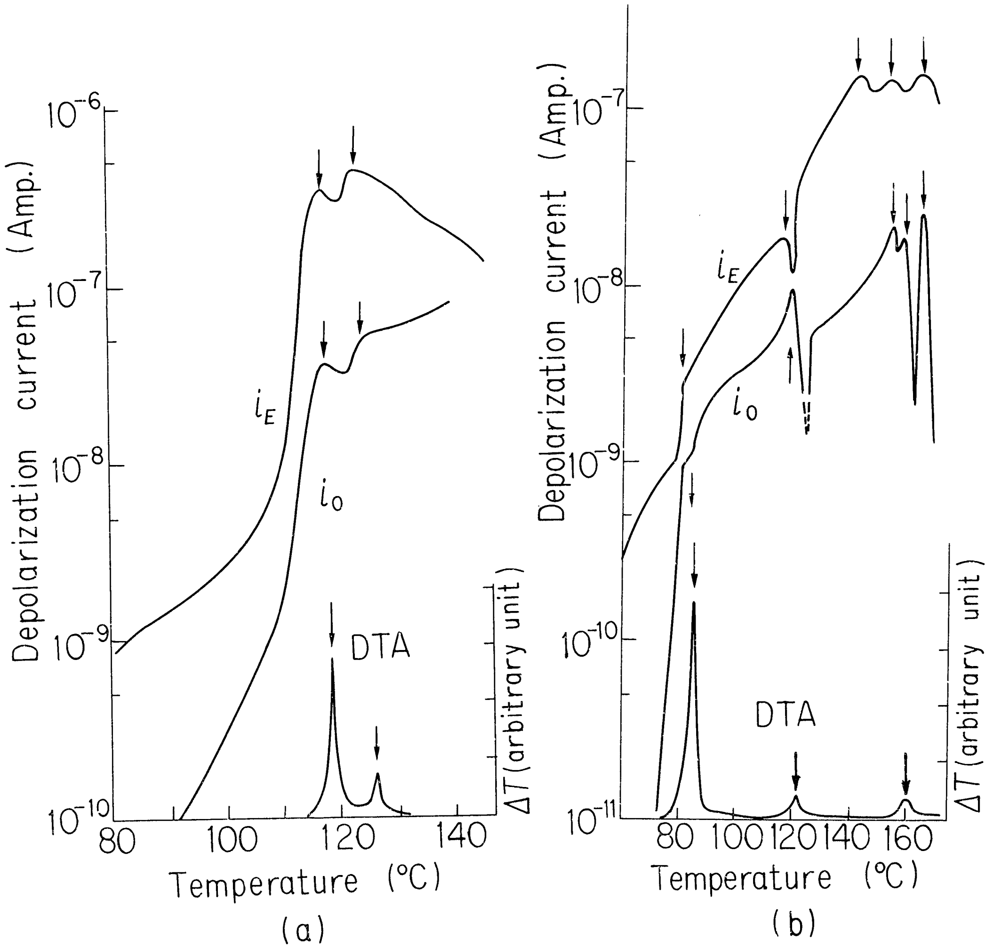


Fig. 2. TSC curves of smectic liquid crystals.
(a) DADC (b) EEAC

Results and Discussion

The TSC curves are shown for DADC and EEAC respectively in Fig. 2, where the TSC for sample polarized at fixed electric field of 1.35 kv/cm is denoted as i_E and that for nonpolarized sample, i_o. All these curves exhibited several peaks or kinks at certain temperatures. The shape of the curves changed more or less in repeated experiments, but the temperatures for the peaks and kinks were quite reproducible. These are summarized in Table 1.

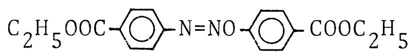
Table 1 shows that the peaks or kinks on the TSC curves correspond approximately to the phase transition temperatures derived from the DTA. Generally the TSC is due to the depolarization of space charge and of the oriented dipoles with raising temperature. If orientational polarization of dipolar molecules alone causes the TSC, the depolarized charge will be calculated by Debye's dipole theory. Rough estimation shows it to be about 10^{-10}C/cm^2 for the temperature range between 130°C and 160°C, but this value is too small in comparison with the charge calculated from the observed current, 10^{-7}C/cm^2. It is thus considered that the TSC observed was dominantly due to macroscopic space charge polarization and microscopic displacement of ions with trapping which were formed not only between sample and electrode, but also in bulk of sample. However, it is known that life time of macroscopic polarized charges is sufficiently short compared with that of microscopically polarized charges with trapping. The latter charges are due to ion impurities[5] originally present in the samples. Therefore, it is resonable to consider that the TSC is obtained by the thermal release of ions trapped in the imperfection in crystal and liquid crystal structure.

The peaks or kinks in the TSC curves are regarded to indicate several processes of the thermal release of trapped ions with an activation energy, E. Since the low temperature tail of the peaks is described as $\ln i(T) = \text{const} - (E/kT)$, the slope of the plot of ln i against 1/T gives the value of E. In this experiment the values of E were between 0.7 and 1.5 eV and were not so different from those previously observed for organic solids.[6]

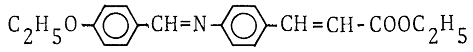
Table 1. The phase transition temperatures from the DTA and the peak temperatures in the TSC curves.

C: Crystal, Sm: Smectic phase, Nm: Nematic phase,
I: Isotropic liquid, ( ): value from the literature.[7]

1. DADC



	$C - S_m$	$S_m - I$
transition temp. (°C)	(114)	(122.9)
peak temp. (°C) for DTA	119	126.3
peak temp. (°C) for i_o	118	-
peak temp. (°C) for i_E	118	123

2. EEAC 

	C-S_mB	S_mB-S_mA	S_mA-N_m	N_m-I
transition temp. (°C)	(81.5)	(118.5)	(156.5)	(159)
peak temp. (°C) for DTA	85	120		160
peak temp. (°C) for i_o	79	119	154	164
peak temp. (°C) for i_E	79	119	154	163

It is noteworthy that peaks or kinks in the TSC curves were observed at the transition between mesophases, i.e. smectic B -smectic A and smectic A -nematic transitions. This indicates the presence of ion traps characteristic of each mesophase. Furthermore, this result suggests that, although liquid crystals have no crystal lattice, there might be any irregularities or heterogenities in liquid crystals which trap ions.

It is interesting that similar TSC curves were obtained also when the samples were not previously polarized, and that in this case also current peaks were observed at temperatures where the TSC curves for polarized samples show peaks. This seems to show that liquid crystal is liable to be spontaneously polarized by thermal stress generated during the pretreatment of samples.

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