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## Liquid Crystals

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## Thermal study of the Isotropic to Smectic C phase transition in main-chain liquid-crystalline elastomers

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High-resolution calorimetry has been used in order to investigate the nature of the Isotropic to Smectic C phase transition of main-chain liquid-crystalline elastomers. Two polydomain elastomers with a conical distribution of the layer normal with respect to the director and different compositions and crosslinking concentrations were synthesised. The heat capacity temperature profiles were measured over a broad temperature range, using ac and relaxation runs. The results reveal a first-order behaviour and a substantial amount of latent heat for the Isotropic to Smectic C transition of liquid-crystalline elastomers, with a wide phase-coexistence range.

**Keywords:** main-chain elastomers; smectic C; AC calorimetry; heat capacity

### 1. Introduction

Liquid-crystalline elastomers are materials that simultaneously possess the orientational order of liquid crystals and the rubber elasticity of polymer networks [1]. They are endowed with interesting optical, mechanical and ferroelectric properties that are potentially useful for applications as theoretically proposed in [2, 3] and experimentally found in [4–10]. The building blocks of elastomers are polymer backbones, crosslinkers and mesogens. When the mesogens are attached on the backbone as lateral monomers (with one end remaining free) a side-chain elastomer is obtained. In contrast, when mesogens are incorporated into the backbone a main-chain sample is produced. In particular, for main-chain elastomers, a coupling between the system polymer backbone and the director exists. Such monodomain (i.e. aligned) materials exhibit remarkable thermal expansion, a property which could lead to novel technological applications.

So far, an enormous amount of experimental and theoretical work exists in the literature concerning the Nematic (N) main-chain and side-chain polydomain or monodomain elastomers [11–22]. Smectic elastomers [23–26] have not been studied to the same extent, although recently they have attracted considerable interest [27–31]. In the last five years several reports on Smectic C (SmC) [32, 33] or chiral Smectic C (SmC\*) [34, 35] elastomers have appeared. In particular, novel smectic main-chain elastomers were synthesised by hydrosilylation of a new-type of mesogen. A conical orientation distribution of the layer

normal with respect to the director was deduced by X-ray scattering for these samples [32]. They do not have an N or Smectic A (SmA) phase, and thus undergo the Isotropic to Smectic C (I–SmC) transition.

The direct transition from the Isotropic to Smectic phases (I–SmA, I–SmC, I–SmC\*) is well characterised as a strongly first-order transition for chiral or non-chiral liquid crystals [36, 37]. The I–SmA (or I–SmC or I–SmC\*) phase coexistence region is wider with respect to the I–N transition, but it is still limited to the 1 K range for pure samples as demonstrated by high-resolution calorimetry. To the best of our knowledge, such thermal studies are so far absent from the literature with regard to smectic liquid-crystalline elastomers. In order to explore the nature of this transition, two types of novel SmC main-chain elastomers have been chosen in the present work. High-resolution ac calorimetry has been used to obtain the temperature dependence of the heat capacity in the vicinity of the I–SmC phase transition. This technique can efficiently distinguish between first-order and second-order transitions and quantitatively determine the latent heat when present.

### 2. Materials and methods

As mentioned above, polydomain main-chain liquid-crystalline elastomers were synthesised for this work. These samples can be considered as monodomains with respect to the orientation of the director, but they exhibit a conical distribution of the layer normal around it. The average layer angle is 30° as derived from

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previous X-ray measurements [32]. Their polymer backbones consist of tetramethyldisiloxane chain-extenders with incorporated vinyloxy-terminated mesogens. Pentamethylpentaoxapantasiloxane was used as a flexible, non-mesogenic pentafunctional crosslinker. The chemical formulas of these building blocks are shown in Figure 1. Two samples of substantially different crosslinking concentrations, the first of 2.5 mol% and second of 10.0 mol%, were investigated. The former contains, in addition, an azobenzene dye (5 mol%). Henceforth, we refer to these two samples as MCEB7Azo2-2.5 and MCEB7-10.0, respectively. The azobenzene dye was introduced as a comonomer because of additional photoisomerisation studies performed on this photoactive sample [32]. The comonomer was synthesised by alkylation of the phenolic groups, i.e. by introducing two olefine chains on both sides of the aromatic azobenzene core. Recently published X-ray data have shown a direct transition from the Isotropic to Smectic (I-SmC) phase for MCEB7Azo2-2.5 and MCEB7-10.0 [32, 33].

High-resolution ac calorimetry has been employed for the study of the I-SmC phase transition of the above-described samples. This technique accurately yields the temperature profiles of the specific heat capacity  $C_p(T)$ . Our home-made computerised apparatus

operates in the ac mode and the relaxation mode. The ac mode probes only the continuous changes of the enthalpy involved in a phase transition, which are determined as  $\delta H = \int C_p(T)dT$ . The relaxation mode senses also the discontinuous part of the enthalpy (i.e. the latent heat  $L$ ), measuring the so-called effective heat capacity  $C_{p,\text{eff}}(T)$ . The total enthalpy change in this case is  $\Delta H = \delta H + L = \int C_{p,\text{eff}}(T)dT$ . The phase shift  $\phi$  of the temperature oscillations of the ac mode is inversely proportional to  $C_p$  for a second-order phase transition. In contrast, for a first-order transition it exhibits a characteristic anomalous behaviour (i.e. higher values). In such a case, one can quantitatively determine the latent heat  $L$  by simply subtracting the integrals of the two modes of operation. A detailed description of the principles of ac calorimetry and its usefulness in the study of critical phenomena has been extensively presented in [38–40].

Quantities of 17 mg of MCEB7azo2-2.5 and 15 mg of MCEB7-10.0 were used for the measurements. The samples were placed in silver cells with a very thin layer of teflon between them and the cell walls. The heat capacity data were obtained from ac heating runs and, subsequently, from relaxation runs. The heat capacity of teflon and of the empty cell were subtracted in order to obtain the net  $C_p$  of the elastomers.

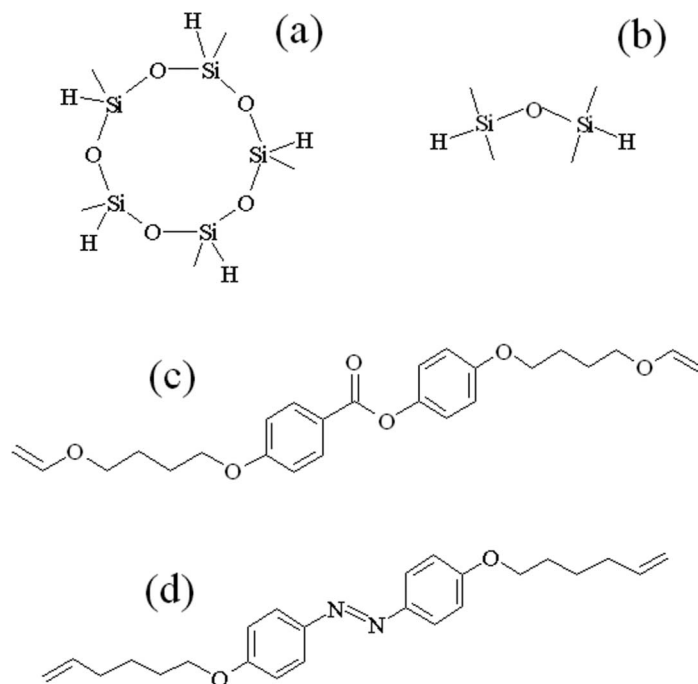


Figure 1. The building blocks of the smectic main-chain elastomers of the present study are shown in this figure. From top to bottom, the chemical formulas of the flexible pentafunctional crosslinker (a), the tetramethyldisiloxane chain-extender (b), the vinyloxy-mesogen (c) and the azo-benzene dye (d) are presented. The latter is existent only in the MCEB7Azo2-2.5 sample.

### 3. Results and discussion

In this section the experimental results are reported for the two elastomer samples, MCEB7azo2-2.5 and MCEB7-10.0. Figure 2 shows the results of the MCEB7azo2-2.5 sample. The data were collected upon heating the sample from 305 K to 345 K, first with the ac mode and then with the relaxation mode. At the top layer (a) the specific heat capacity profiles obtained with the two modes of operation are both plotted and at the bottom layer (b) the phase shift of the ac oscillations is shown. The use of  $\Delta C_p$  instead of  $C_p$  implies that the background has been subtracted and the graphs show only the excess heat capacity related to the transition. In the vicinity of the I–SmC phase transition,  $\phi(T)$  exhibits an anomalous temperature dependence, denoted by an arrow in Figure 2. In particular, instead of showing a clear dip inversely proportional to the shape of  $C_p(T)$ , it exhibits an initial decrease followed by a bump upwards. This is indicative of a first-order transformation and it is also reflected in the significant mismatch observed between the  $\Delta C_p(T)$  and  $\Delta C_{p,\text{eff}}(T)$  profiles. This mismatch is attributed to the presence of latent heat. Thus, the I–SmC transition of the MCEB7azo2-2.5 elastomer is clearly first order, with a broad coexistence range of I and SmC phases. The

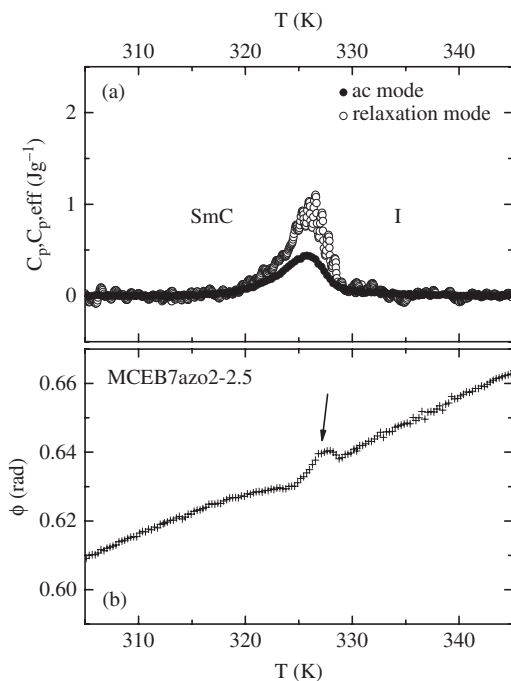


Figure 2. At the top layer (a) the  $\Delta C_p(T)$  (solid circles) and  $\Delta C_{p,\text{eff}}(T)$  (open circles) profiles are both plotted in a wide range around the I–SmC phase transition of MCEB7azo2-2.5. At the bottom layer (b) the  $\phi(T)$  profile extracted from the ac mode is shown (cross symbols), which is indicative of a first-order transition. The arrow indicates the temperature regime of the anomalous behaviour of  $\phi$ .

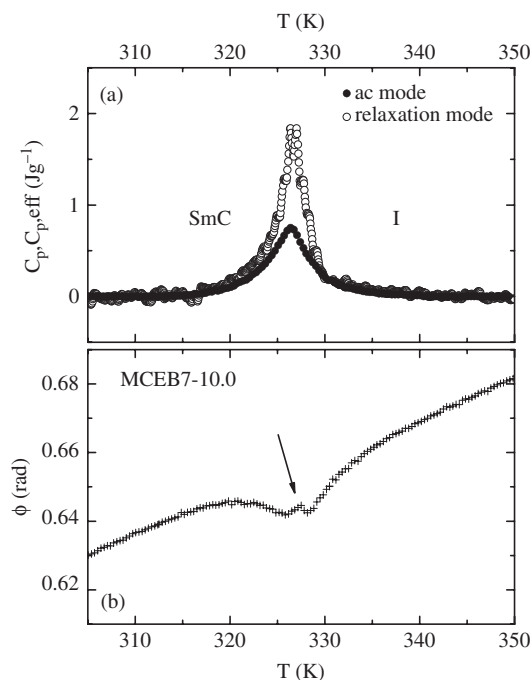


Figure 3. At the top layer the  $\Delta C_p(T)$  (solid circles) and  $\Delta C_{p,\text{eff}}(T)$  (open circles) profiles around the I–SmC phase transition of MCEB7-10.0 are both plotted. At the bottom layer the  $\phi(T)$  profile (cross symbols) indicates a first-order transition. The arrow points at the regime of anomalous  $\phi(T)$  behaviour.

transition temperature is  $T_{\text{I–SmC}} = 326.38 \pm 0.02$  K, denoted as the point of the highest value of  $C_p$  of the ac mode. This point roughly coincides with the middle of the two-phase coexistence region. The range of this region is  $\Delta T_{\text{coex}} = 9.52 \pm 0.04$  K.

The results for the heating runs of the MCEB7-10.0 sample can be seen in Figure 3. The data were collected in the range between 305 K and 350 K. The heat capacity data are shown at the top layer (a) for the ac and relaxation runs and the phase shift from the ac mode at the bottom layer (b). Even though the concentration of crosslinkers is essentially higher for this sample (10.0 mol% instead of 2.5 mol% for MCEB7azo2-2.5) the transition retains its first-order character. The temperature dependence of  $\phi$  near the transition exhibits an initial dip followed by a clear bump upwards, due to the presence of latent heat. The transition temperature is  $T_{\text{I–SmC}} = 325.76 \pm 0.02$  K and the coexistence range remains broad,  $\Delta T_{\text{coex}} = 9.02 \pm 0.05$  K. The transition temperatures of both compounds are shifted to lower temperatures compared to the pure mesogen [32]. This can be attributed to the presence of the flexible crosslinkers that lower the transition temperatures, as is known for liquid crystals that are substituted with flexible chains [32, 33]. In particular, for MCEB7azo2-2.5 the  $T_{\text{I–SmC}}$  is shifted further down and the shape of the anomaly is more smeared out due to the presence

of the additional comonomer unit in the chains. The broadness of the I–SmC phase transition in both samples can be visualised as a distribution of domains that contribute with slightly different transition temperatures. The average domain size defined by X-rays [32] is of the order of 15–20 layers. Moreover, some effects of elastic deformations are probably hidden in the conical distribution of layers. Additional experiments are needed in order to obtain a clear picture in the latter case.

All features of the ac and relaxation runs performed and the quantities determined for both samples are summarised in Table 1. The scanning rates, the transition temperatures, the two-phase coexistence range, the total amount of enthalpy as well as the latent heat involved in the I–SmC transition of both samples are given in this table. The transition temperatures were determined from the ac runs for both cases. The ac runs were performed continuously and with a slower rate than the relaxation runs and they yielded higher resolution data. The relaxation runs were performed in steps of 0.7 K and, although they are more noisy, they were of essential importance for the quantitative determination of  $L$ .

Concerning the enthalpy changes involved in the I–SmC phase transition, by integrating the  $\Delta C_p(T)$  and  $\Delta C_{p,\text{eff}}(T)$  anomalies one obtains a total enthalpy change  $\Delta H$  of  $4.93 \pm 0.04 \text{ J g}^{-1}$  for MCEB7azo2-2.5 and of  $8.53 \pm 0.04 \text{ J g}^{-1}$  for MCEB7-10.0. The amount of released latent heat corresponds to 45% of the total enthalpy for MCEB7Azo2-2.5 and to 41% for MCEB7-10.0. Although the transition of the sample with 2.5 mol% crosslinking concentration is more smeared, a larger percentage of the total enthalpy involved in the transition corresponds to latent heat  $L$ . This more smeared shape of the anomaly for a lower crosslinking concentration sample, by a factor of four, must be related to the presence of azobenzene dye molecules. In other calorimetric studies performed on samples without azobenzene dyes it has been proven that the steepness of the  $C_p$  peak is always

inversely proportional to the crosslinkers concentration for elastomers [19, 20].

Nematic main-chain elastomers of crosslinker concentrations of 10.0 mol% exhibit reduced or absent latent heat (within ac calorimetry resolution) for the Paranematic to Nematic (PN–N) transition [20]. In contrast, as shown in this work the I–SmC transition remains clearly first order with a substantial amount of latent heat for the concentrations of crosslinkers up to 10.0 mol%. The anomaly for the sample without azobenzene dye also remains very steep for such high crosslinking concentrations. In nematic elastomers a critical point of water-vapour type was found for main-chain and side-chain samples when changing the crosslinking concentration [19, 20]. In contrast, here a similar critical point either does not exist (i.e. the transition remains always first order) or it can be reached only in very high concentrations. Nevertheless, the synthesis of such samples might meet unrivalled practical difficulties (e.g. related to the increase of the glass transition temperature  $T_g$  where the liquid crystalline structure becomes frozen-in). The observed phase transition behaviour suggests a rather *on-off* thermomechanical response for these systems. In order to create a more continuous response, instead of increasing the crosslinking concentration one may turn to alternative strategies, e.g. changing of the type of mesogen. This has recently been proven to strongly affect the phase transition features for nematic elastomers [41] and it could also be explored for smectic elastomers. The presence of azobenzene dye at 5 mol% smears the phase transition as shown for the MCEB7azo2-2.5 sample; nevertheless, it does not really affect its order.

For the liquid-crystalline elastomers of the present work the two-phase coexistence region is very wide in the order of several degrees kelvin. In liquid crystals the compounds that undergo a direct transition to smectic phases exhibit a typical phase coexistence range from 100 mK to 1 K [36, 37]. In smectic

Table 1. The features of all runs performed for the MCEB7azo2-2.5 and MCEB7-10.0 samples. From left to right, the kind of sample, the scanning rates and  $T$ -steps, the transition temperature  $T_{I-SmC}$ , the coexistence range  $\Delta T_{\text{coex}}$ , the total enthalpy change  $\Delta H$  and the latent heat  $L$  are shown.

Sample	Scanning rate <sup>a</sup> (K h <sup>-1</sup> ) [ $T$ -step <sup>b</sup> (K)]	$T_{I-SmC}$ (K) [ $\Delta T_{\text{coex}}$ (K)]	$\Delta H$ (J g <sup>-1</sup> ) [ $L$ (J g <sup>-1</sup> )]
MCEB7azo2-2.5	1.0 [0.7]	326.38±0.02 [9.52±0.04]	4.93±0.04 [2.22±0.05]
MCEB7-10.0	1.2 [0.7]	325.76±0.02 [9.02±0.05]	8.53±0.04 [3.51±0.05]

<sup>a</sup>Scanning rate refers to the ac runs.

<sup>b</sup> $T$ -step refers to the relaxation runs.

elastomers, the transition retains its first-order character even for high crosslinking densities, although the coexistence range increases remarkably. A similarly broad coexistence range was recently observed for PN and N phases of nematic side-chain and main-chain elastomers [19, 20].

#### 4. Conclusions

A high-resolution calorimetric study of the I–SmC phase transition of conically distributed polydomain liquid-crystalline elastomers has been performed. The obtained heat capacity anomalies of this work unambiguously reveal the first-order nature of this transition even for high crosslinking concentrations. The phase coexistence range is considerably increased with respect to the I–SmC phase transition of conventional liquid crystals [36], similar to what has been recently observed in nematic main-chain [20] as well as side-chain elastomers [19]. The transition exhibits a steep peak for the pure sample without the azobenzene dye in spite of its high crosslinking concentration of 10.0 mol%. The I–SmC transition is expected to either always retain a first-order character or reach a critical point of water-vapour type only in exceptionally high crosslinking concentrations.

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