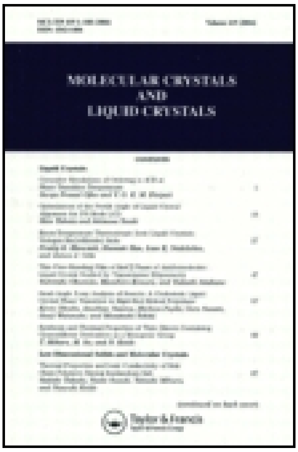

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# Calorimetric Investigation of the Isotropic to Smectic-A Phase Transition of Smectic Liquid-Crystalline Elastomers

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*A high-resolution calorimetric study has been performed in the vicinity of the isotropic to smectic-A phase transition of smectic liquid crystalline elastomers. The transition is weakly first order for both investigated samples. Nevertheless, different features have been observed when the crosslinking density is changed, such as substantial broadening of the transition and decrease of the involved latent heat. The latter is sluggishly released in a range of few K.*

**Keywords** elastomers; smectic; ac calorimetry; heat capacity; latent heat

## 1. Introduction

In smectic liquid-crystalline elastomers the rubber elasticity of crosslinked polymer chains is combined with the liquid-crystalline orientational and translational order. Such elastomers exhibit a one-dimensional layering order superimposed on the nematic rubber elasticity of the matrix [1]. For side-chain smectic elastomers, such as the ones investigated in the present study, the polymer chains are oriented perpendicular to the (smectic) layer normal. The presence of crosslinks can suppress the long-wavelength fluctuations and, at the same time, the crosslinking points act as defects. The former tends to enhance a (long-range) smectic ordering [2, 3], while the latter tends to destroy it [4, 5], i.e. they have opposite influence on the phase transition behavior.

The investigated samples exhibit a direct transition from the isotropic (I) to the smectic-A (SmA) phase. In conventional liquid crystals the I-SmA transition is well characterized as strongly first order, and high-resolution measurements have revealed a coexistence region ranging typically between 0.1 K and 1 K [6]. Increased disorder has been recently reported to severely affect the I-SmA transition of liquid crystals and change its nature to continuous

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[7]. In order to explore how the inherent disorder of liquid-crystalline elastomers influences the I-SmA phase transition, the heat capacity temperature dependence has been obtained using high-resolution ac calorimetry. The slow scanning rates and the sensitivity of the method in the presence of latent heat have been exploited.

## 2. Experimental Methods and Samples

High-resolution ac-calorimetry has been used in order to obtain the heat capacity temperature dependence $C_p(T)$ of the liquid-crystalline elastomers. In the principal *ac* mode of operation, an oscillating power of frequency $\omega$ is applied on the sample. This frequency is carefully chosen accounting for the elimination of temperature gradients within the sample as well as for the achievement of thermal equilibrium between the sample and the (surrounding) bath. Apart from the $C_p(T)$ data, the phase shift of the temperature oscillations as a function of temperature $\varphi(T)$ is monitored. The phase shift of these oscillations provides additional information concerning the order of a phase transition. Nevertheless, the *ac* mode of operation, due to the modulation of temperature, senses only the continuous changes of the enthalpy and it cannot measure directly the latent heat L, when the latter is present.

Our apparatus is modified in order to additionally operate in a *non-adiabatic* or *relaxation* mode. In this case the run is performed in small temperature steps, using a linearly-ramped change of the temperature. The *relaxation* mode senses the total change of the enthalpy (i.e. both the continuous and the discontinuous part) involved in a phase transition. By performing *ac* and *relaxation* runs and afterwards comparing the $C_p(T)$ integrals of the two modes, the latent heat is quantitatively determined as follows:

$$L = \Delta H^{relaxation} - \Delta H^{ac} = \int \Delta C_{p,eff}(T)dT - \int \Delta C_p(T)dT$$

where $\Delta H^{ac}$ and $\Delta H^{relaxation}$ stand for the total enthalpy change sensed by the two modes. The use of $\Delta C_p$ (instead of $C_p$) defines the excess heat capacity of the *ac* mode after the background heat capacity has been subtracted. Likewise, $\Delta C_{p,eff}$ stands for the excess heat capacity obtained by the *relaxation* mode. A precise description of ac calorimetry and its usefulness in the study of phase transitions and critical phenomena can be found elsewhere [8, 9].

The smectic elastomers of the present work consist of a poly(methylsiloxane) backbone, two end-on attached mesogenic side-chains R2 and R7 and a bi-functional crosslinker V1 (see Fig. 1). The synthesis is carried out in a Pt-catalysed hydrosilylation reaction of a poly(hydrogenmethylsiloxane) pre-polymer, vinyl-terminated mesogens and crosslinker molecules in isotropic solution. A spin-casting technique is used in order to produce films of homogeneous thickness. After gelation the solvent is removed at elevated temperature with the sample under uniaxial load. The sample is cooled to the liquid crystalline state and the crosslinking is established for several days. In order to remove the soluble content, the networks were extracted several times in a mixture of isohexane and toluene. Afterwards, the samples were dried in the isotropic state and cooled down to room-temperature.

The chemical composition of the investigated smectic elastomers is schematically represented in Fig. 1. The two samples have the same polymer backbone and mesogen composition and they differ only with respect to the crosslinking concentration. In particular, they are composed of a mesogens ratio $x_{(R2)}/x_{(R7)} = 70/30$ and concentration $x_{(R2)} + x_{(R7)} = 1–2x_{(V1)}$, where $x_{(V1)}$ stands for the concentration of crosslinkers. The two samples contain

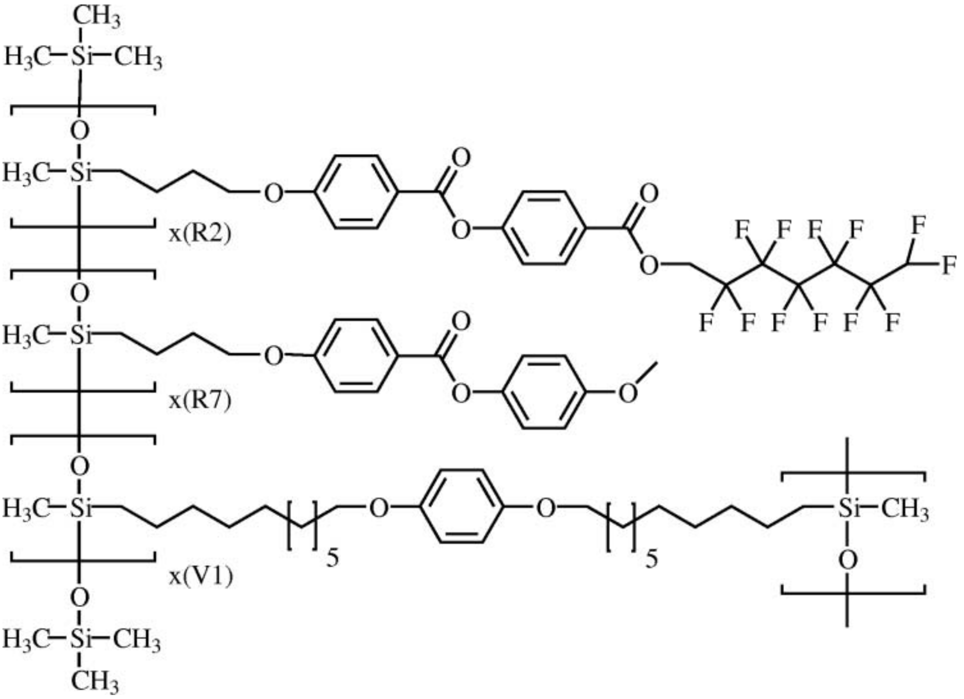

**Figure 1.** The chemical structures of the constituent units are presented here. The polymer backbone is composed of poly(methylsiloxane), the mesogenic units consist of a mixture of R2 and R7 and the crosslinker V1 is a bifunctional isotropic one.

$x = 0.05$ mol % and $x = 0.10$ mol % of the bifunctional crosslinker V1, values that correspond to 10 mol % and 20 mol % of reactive vinyl-groups. We henceforth refer to these samples as E4 and E11, respectively.

Sample quantities of 30 mg were placed in home-made cells made of high-purity silver. A very thin layer of Teflon (~0.1 mm) was placed between the sample and the cell walls in order to prevent any unwanted stress that could affect the phase transition behavior. Sufficient free space was accounted for an unhampered change of the sample's dimensions that are expected to change in the vicinity of the phase transition. The heat capacity of the empty cell and all other components (i.e. heater, copper wires, Indium paste) was subtracted in order to obtain the net $C_p$ of the elastomer.

## 3. Results and Discussion

After placed in the cells and prior to measurements, the samples were annealed twice by heating them highly above the I-SmA phase transition temperature. Afterwards, they were cooled deep in the SmA phase and slow heating runs have been performed using both *ac* and *relaxation* modes. The runs were performed over a wide temperature range of 60 K. For the ac runs the scanning rate was 0.9 $Kh^{-1}$, while for relaxation runs steps of 0.7 K were chosen.

The excess heat capacity temperature profiles $\Delta C_p$ and $\Delta C_{p,eff}$ are shown in Fig. 2 for the E4 sample with $x = 5$ mol% crosslinkers. The data of the two modes are commonly plotted for comparison. The anomaly is steep, especially on the side of I phase. Nevertheless,

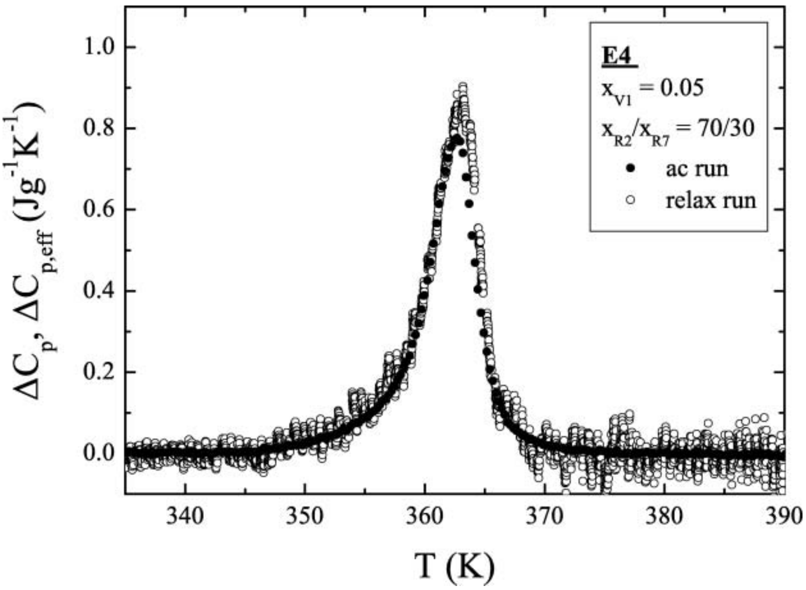

**Figure 2.** The excess heat capacity temperature profiles obtained with the *ac* and *relaxation* mode (solid and open circles, respectively), are depicted here for E4 sample.

its pretransitional wings cover a temperature range of ~25 K. The mismatch between the ac and relaxation mode evidences the presence of latent heat, which is released sluggishly in few K range. The total enthalpy change involved to the I-SmA transition of E4 is $\Delta H_{(E4)} = 5.05 \pm 0.06$ $Jg^{-1}$ and the latent heat is estimated to be $L_{(E4)} = 0.42 \pm 0.05$ $Jg^{-1}$.

The heat capacity data for the E11 sample are shown in Figure 3. The anomaly has been shifted to lower temperatures, with the maximum heat capacity values observed at 350.21 K, while being 362.19 K for E4. The phase transition signature in this case is wider, reaching a range larger than 35 K, and more suppressed. The pretransitional effects are greatly extended with respect to E4 sample, especially on the isotropic side. The increasingly pronounced broadening of the transition may be attributed to the increased random-fields originating from the doubled crosslinking density with respect to the E4 sample. A slight mismatch is still observed between the two $\Delta C_p(T)$ integrals obtained in the *ac* and *relaxation* mode, demonstrating that the I-SmA phase transition retains its (weakly) first order character with a small but non-zero latent heat for the x = 10 mol% crosslinking concentration. For E11 a total enthalpy $\Delta H_{(E11)} = 4.78 \pm 0.08$ $Jg^{-1}$ and a latent heat $L_{(E11)} = 0.25 \pm 0.06$ $Jg^{-1}$ are measured.

The I-SmA phase transition exhibits a first order character for both samples measured here. Nevertheless, by changing the crosslinking density the anomaly is widened, suppressed and shifted to lower temperatures. Contrary to liquid crystals, where the latent heat related to the I-SmA transition is released in a short temperature range, in case of smectic elastomers it is sluggishly released in a range of several K. Similar effect concerning the latent heat has been observed in the isotropic to nematic and isotropic to smectic-C phase transition of side-chain and main-chain liquid-crystalline elastomers [10–13]. It has been also proven that for side-chain and main-chain nematic elastomers the increased crosslinking concentrations drive the system towards the critical point at which the latent heat vanishes and, finally, in the supercritical regime [10, 11]. In case of smectic elastomers the

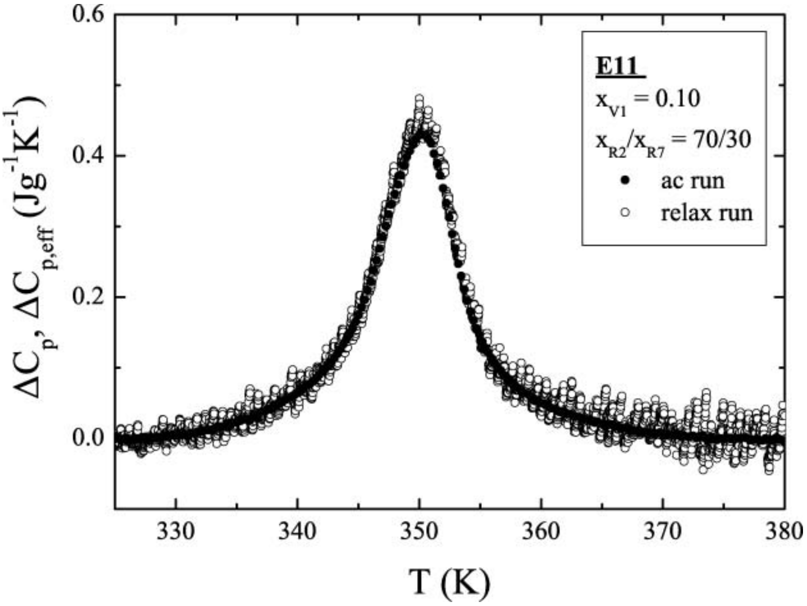

**Figure 3.** The excess heat capacity temperature profiles obtained with the *ac* and *relaxation* mode (solid and open circles, respectively), are presented here for E11 sample.

orientational (nematic) and the translational (smectic) ordering are coupled. Hence, it is possible that this coupling shifts the I-SmA phase transition towards a critical point and this can be the reason behind the weakly first order character and the subsequent decrease of latent heat with increasing crosslinking concentrations observed in the present work. Further studies are needed in order to resolve this issue and arrive at a solid conclusion.

## 3. Conclusions and Perspectives

A high-resolution calorimetric study has been performed for two smectic liquid-crystalline elastomers, differing only with respect to the crosslinking density. Both samples exhibit first order I-SmA phase transitions, with the higher crosslinking density one (i.e. E11) having a more suppressed, smeared but still weakly first order heat capacity anomaly. The present results, as well as other recent high-resolution calorimetric measurements [13], suggest that elastomers entering the smectic phases directly from the isotropic phase exhibit first order transitions even for high crosslinking concentrations.

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