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Differences between smectic homo- and co-polysiloxanes as a consequence of microphase separation

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This paper compares smectic phases formed from LC-homo- and LC-co-polysiloxanes. In the homopolysiloxane, each repeating unit of the polymer chain is substituted with a mesogen, whereas in the copolysiloxanes mesogenic repeating units are separated by dimethylsiloxane units. Despite a rather similiar phase sequence of the homo- and co-polysiloxanes—higher ordered smectic, smectic C* (SmC*), smectic A (SmA) and isotropic—the nature of their phases differs strongly. For the copolymers the phase transition SmC* to SmA is second order and of the 'de Vries' type with a very small thickness change of the smectic layers. Inside the SmA phase, however, the smectic thickness decreases strongly on approaching the isotropic phase. For the homopolymer the phase transition SmC* to SmA is first order with a significant thickness change, indicating that this phase is not of the 'de Vries' type. This difference in the nature of the smectic phases is probably a consequence of microphase separation in the copolymer, which facilitates a loss of the tilt angle correlation between different smectic layers. This has consequences for the mechanical properties of LC-elastomers formed from homo- and co-polymers. For the elastomers from homopolymers the smectic layer compression seems to be rather high, while it seems to be rather small for the copolymers.

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1. Introduction

Classical calamitic smectic phases such as smectic A (SmA) or smectic C (SmC) are well investigated [1]. However, little is yet known about the smectic order parameter or how well the mesogens are located within the smectic layer plane and how strong the out-of-plane fluctuation and interdigitation of the mesogens are. Most SmA or SmC phases show only the (1 0 0) reflection and no higher orders during X-ray reflection measurements. This is interpreted with the assumption of a sinusoidal density correlation, which allows much out-of-layer fluctuation.

The question of the correlation between individual smectic layers has gained more interest recently, because it has strong implications on phenomena such as antiferroelectric ordering [2–4] or the occurrence of SmA–SmC phase transitions of the 'de Vries' type [5–8]. In this case, it is assumed that the SmA phase originates from a low temperature SmC phase, not by an up-rise of the long axis of the mesogens to a perpendicular orientation, but by a loss of correlation of the tilt direction (in the systems considered here, the correlation of tilt between adjacent smectic layers); i.e. SmA phases with the 'de Vries' transition are, within a single layer, still locally SmC-like. Such phases are usually found in systems in which the mesogens are strongly bound to the smectic layer planes (higher orders of layer reflections by X-ray), and thus interdigitation of the mesogens can be expected to be weak. The occurrence of these phases is often linked to the occurrence of a smectic sublayer formation due to partial segregation of molecular fragments.†

We have recently observed SmA–SmC* phase transitions of the 'de Vries' type for smectic polysiloxanes [9], i.e. polymers in which only a few of the repeating units of the polymer chain are substituted with mesogens. As a result a microphase separation occurs into sublayers of the mesogens, which are separated by sublayers of

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†We are aware that just the observation of a phase transition (SmC–SmA) without a change of the layer spacing is insufficient for a clear assignment, because it can be interpreted by different models.

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unsubstituted dimethylsiloxane units (figure 1) [10, 11]. Again, a correlation between a strong localization of the mesogens within the smectic layer structure (identical to a minimization of interdigitation) and the occurrence of de Vries phases is evident. If this is true, then polysiloxane homopolymers in which each repeating unit is substituted should behave differently, because the above-described microphase separation between substituted and unsubstituted repeating units cannot occur. We have therefore made a systematic comparative study of both types of polymer, which indeed show a different behaviour with regard to the smectic phase transitions.

2. Experimental

The smectic layer thickness was determined by temperature-dependent small angle X-ray scattering (SAXS), using Cu-K_α radiation, a Kratky-compact X-ray camera (Paar, Graz) and a position-sensitive electronic detector (Braun, Munich). The preparation of the polymer was carried out in a Mark capillary (diameter 0.7 mm). The LC-polymer was filled into the tube either as isotropic melt (copolysiloxane backbone) or as solid state (homopolysiloxane backbone). The samples were then held at different temperatures for 10 min.

The LC-elastomers were prepared by photopolymerization from the polysiloxanes **3a**,**b**, which contain a crosslinkable acrylate group. For that, the Mark capillary containing the crosslinkable polysiloxane and 2 wt % of a photoinitiator (Lucirin TPO) was exposed to UV light for 20 min in the SmC* phase.

The properties of free-standing films of homo- and co-polysiloxane elastomers during stretching were investigated between two moveable edges. The smectic film thickness was determined from the interference colours of the submicrometer films. The preparation of the films and their analyses are described in more detail in [12].

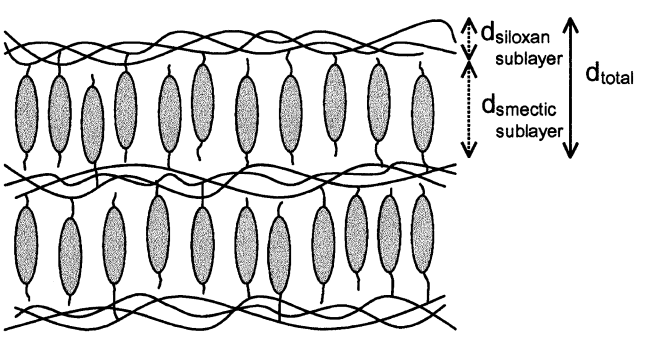

Figure 1. Schematic representation of the microphase separation.

3. Results and discussion

As polymers for this comparison we selected a polysiloxane system (homopolymer **1**, copolymer **2**) with three-ring mesogens investigated previously [9, 11, 13–15]. In addition we added crosslinkable systems (**3a**, **b**), to allow comparison with LC-elastomers [12, 14–17]. The polymers and their phase behaviour are shown in the scheme; they were

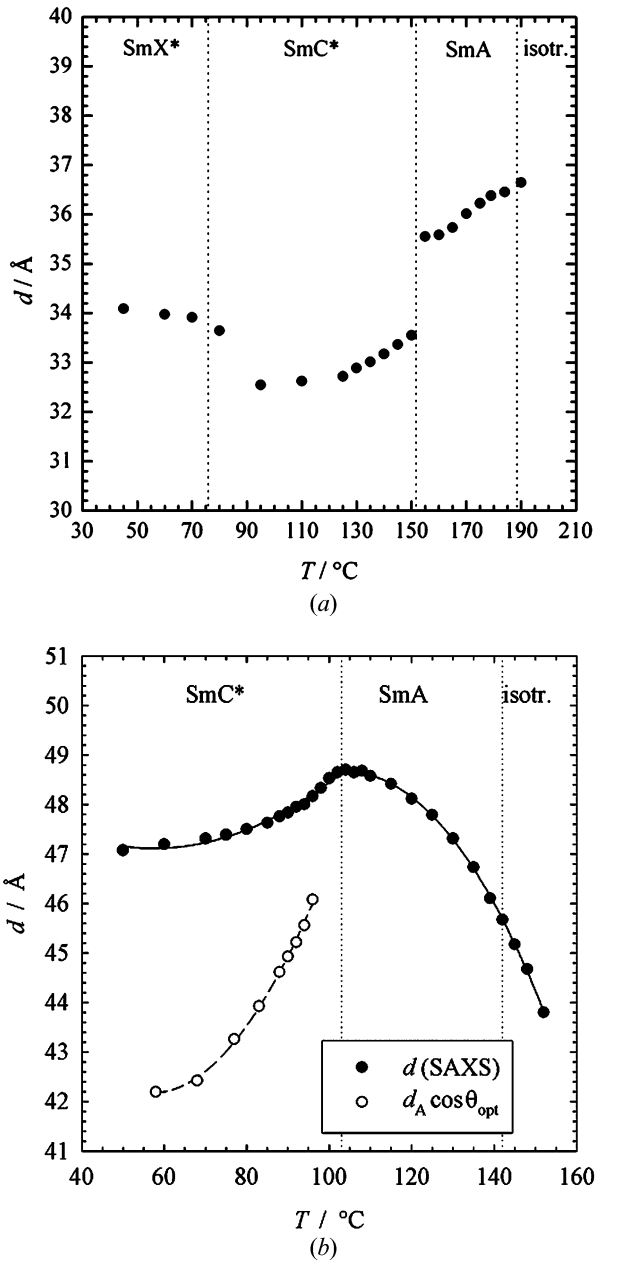

Figure 2. Temperature dependence of the layer spacing d in (a) the homopolymer **1** and (b) the copolymer **2**, compared with the expected values (○) calculated from the cosine of the optical tilt angle.

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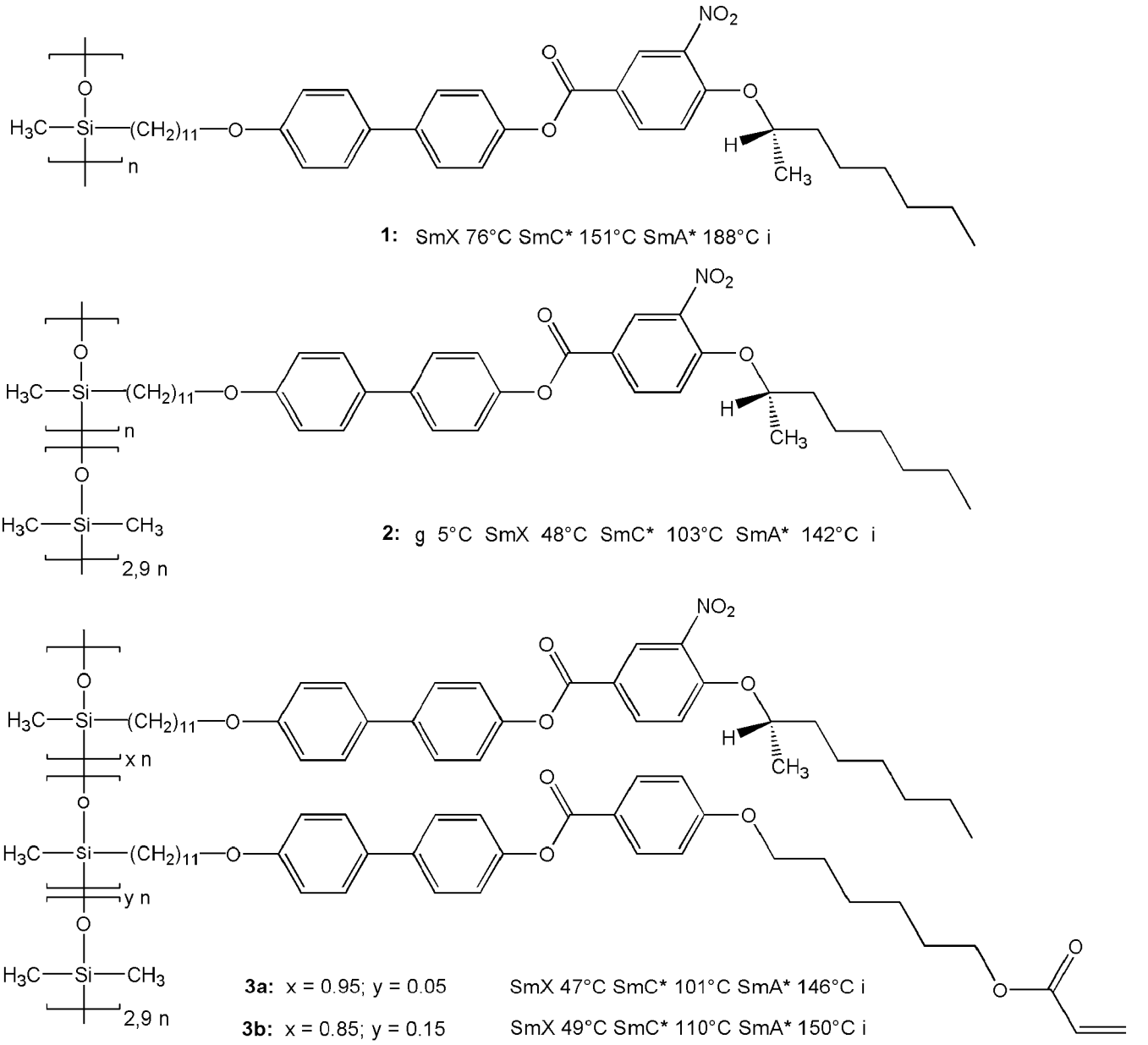

Scheme. Chemical structure of different LC-polysiloxanes with the following phase sequence: higher ordered smectic (SmX), chiral smectic C* (SmC*), smectic A (SmA) and isotropic (i).

synthesized according to ref. [15]. The 'de Vries' phases formed by copolymer **2** have been described in detail in [9].

In order to investigate the influence of the different molecular structures on the smectic phases, we carried out temperature-dependent X-ray measurements, either on thin polymer films with a theta/2theta goniometer or with a Kratky-compact camera and a position-sensitive electronic detector. At first a difference in the wide angle region is obvious. Copolymer **2** shows, in addition to the halo at 20° which corresponds to the liquid-like packing of the mesogens, an additional halo at $2\theta \approx 11°$ [10]. It corresponds to liquid-like packing in the dimethylsiloxane sublayer and is known from polydimethylsiloxane rubbers. This type of short range order demonstrates the microphase separation [10]. Both types of polymer show higher orders of small angle reflections; thus the electronic density correlation cannot be simply sinusoidal, independent of the presence of the dimethyl sublayer.

Differences are evident in the comparison of the temperature-dependent smectic layer thicknesses of homo- and co-polymers in figure 2. For copolymer **2**,

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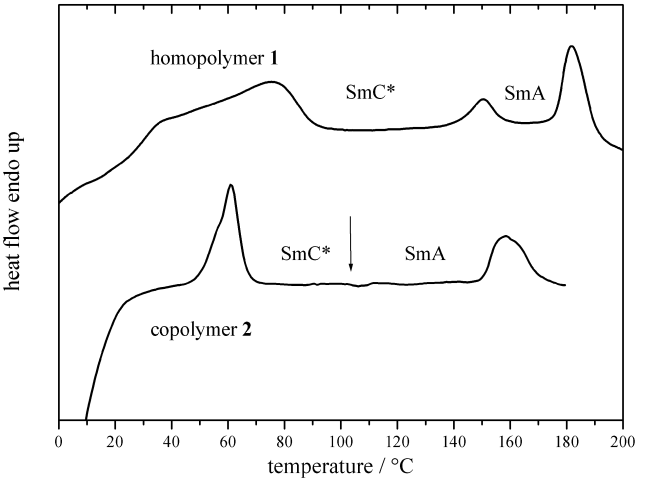

Figure 3. DSC measurements of homopolymer **1** and copolymer **2** with a heating rate of 40°C min^{-1}.

figure 2 (*b*) the results already discussed in [9] are observed.

(1) The increase of the smectic layer thickness on going from a smectic C* phase with a high optical tilt angle (30° at 60°C) into a smectic A phase seems far too low, if the smectic layer thickness is related to the cosine of the optical tilt in a first approximation. From the optical data, a thickness change of 6.5 Å is expected, however a change of only 1.7 Å (3.5%) is found.

(2) While the layer thickness hardly changes at the SmC* to SmA transitions, it changes strongly within the smectic A phase.

(3) The layer reflection does not completely disappear at the transition to the isotropic phase. Instead, some reflection can still be detected 10°C above the clearing temperature. This is an indication of some remaining microphase separation within the cybotactic clusters between mesogens and dimethylsiloxane units, still present after the mesogens have lost their orientational correlation (clearing point). This last observation leads to speculation as to whether the demixing into mesogen-rich and siloxane-rich sublayers is responsible for the unusual temperature dependence of the smectic layer thickness in the SmA phase. Could this 'confinement' stabilize the SmA phase to rather high temperatures, up to temperatures at which the orientational correlation between the mesogens is already rather weak? The result would be a smectic phase with a very low 'nematic' order parameter, which could explain the observed layer shrinkage.

For homopolymer **1**, figure 2 (*a*) the following observations were made.

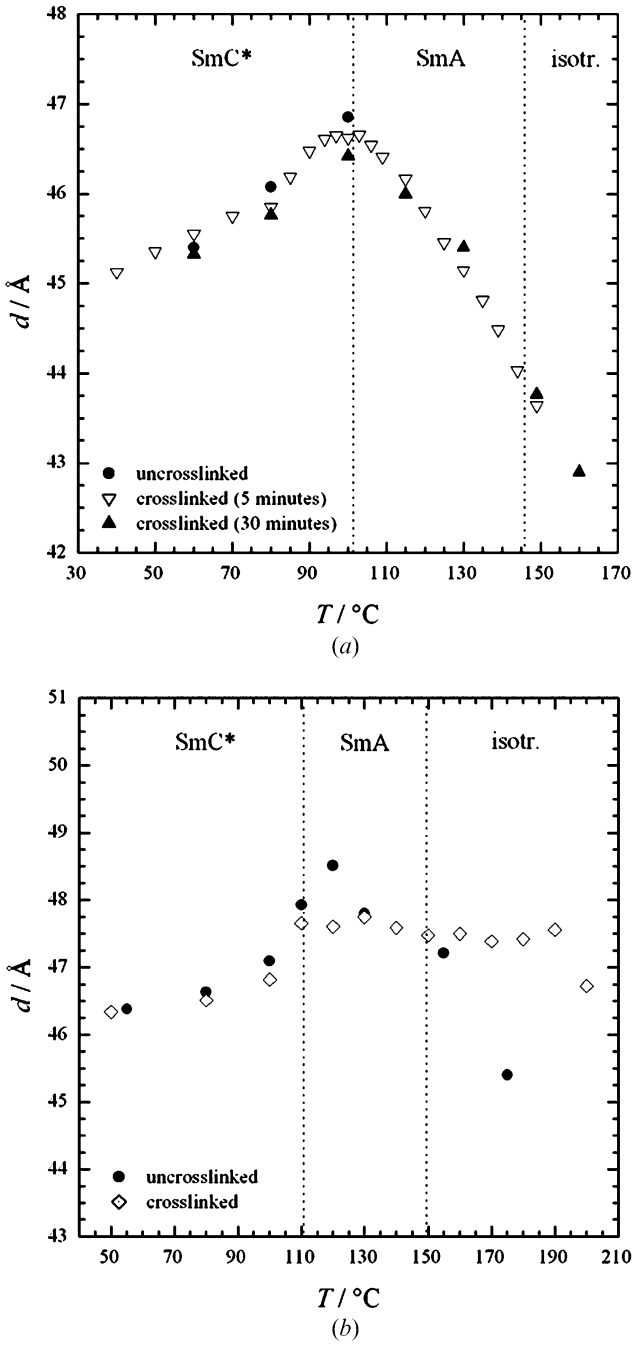

Figure 4. Temperature-dependent layer spacing *d* in the polymers (*a*) **3a** with 5 mol% and (*b*) **3b** with 15 mol% crosslinkable groups (crosslinking temperature 65°C).

(1) The smectic layer thickness changes abruptly by 2 Å (finally 3 Å) at the phase transition SmC* to SmA. Although a decrease of 4.8 Å is expected from an optical tilt angle of about 30°, 10°C below the phase transition, this corresponds much more to the classical situation in tilted smectics, where

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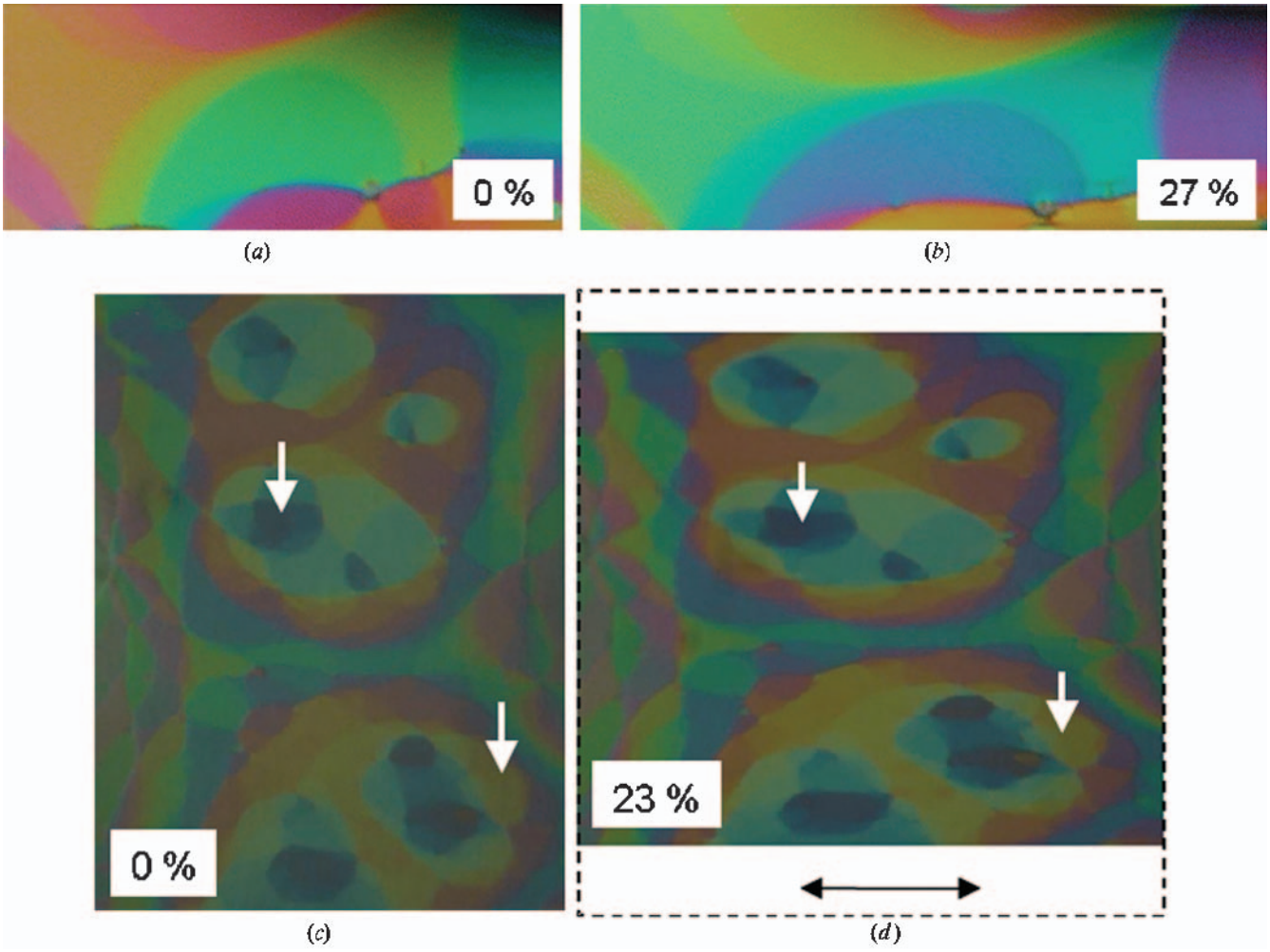

Figure 5. Reflection colors from thin films of LC-polysiloxane elastomers with (*a*, *b*) co- and (*c*, *d*) homo-polymer backbone. For the copolymer the thickness of the film shrinks during stretching (change of reflection colour from *a* to *b*); for the homopolymer the film thickness stays constant up to a stretching of 23% (*c* to *d*).

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the long axis of the mesogens rises at the transition into the SmA phase.

(2) On further increase of temperature, the layer thickness does not decrease within the SmA phase, instead it rises slightly.

(3) The smectic layer reflection abruptly disappears at the transition into the isotropic phase.

As a result, there is no hint of a 'de Vries' phase transition in the homopolymer **1** and no sign of a microphase separation (as expected). The transition between the SmC* and SmA phases seems to be of first order. This is in agreement with DSC measurements (figure 3), which show the transition very clearly already at slow heating rates. By contrast, for the copolymer the transition has never been detected by DSC measurements.

Finally we include the crosslinkable copolymers **3a**,**b** and the LC-elastomers prepared from them by polymerization [15] in the investigation. They differ from copolymer **2** only by the substitution of 5 or 15% of the mesogens with acrylate groups. Since the phase transition temperatures change with the content of crosslinkable acrylate groups, they are shown separately in figures 4 (*a*) and 4 (*b*). It is evident that the uncrosslinked copolymers show the same behaviour as the unmodified copolymer **2**. Again, the change of the smectic layer thickness is too small at the SmC* to SmA transition and too large within the smectic A phase. If polymer **3a** with 5 mol% of crosslinkable groups is crosslinked, this behaviour is unaffected. Thus weak crosslinking, which transforms a soluble polymer into a soft solid, has no influence on the layer spacing and its temperature dependence.

For polymer **3b** with 15 mol% of crosslinkable groups, things are slightly different, see figure 4(*b*). After crosslinking within the SmC* phase at 70°C, the smectic layer thickness is unchanged in the LC-elastomer. However, the temperature dependence of the smectic layer thickness is smaller for the crosslinked system than for the as yet uncrosslinked polymer **3b**. Both the increase of the layer thickness (on heating towards the SmC*–SmA transition) and the subsequent decrease (on heating within the SmA phase) is reduced. In addition, some remnant of the small angle reflection can now be seen up to 50°C above the clearing transition. This is expected for a network, which tends to maintain the state in which it was formed. For highly crosslinked thermosets it is known that they maintain their structure up to thermal decomposition. For slightly crosslinked systems (polymer **3a**) the effect was within the limits of accuracy. Polymer **3b** is an intermediate case: in agreement with earlier work on LC-elastomers [15], it is soft enough to respond to thermal change and to switching in electric fields, but at the same time tries to retain some memory of the state and structure during crosslinking.

Since LC-elastomers show the same properties as the uncrosslinked polymers it is adequate to relate differences between LC-elastomers prepared from homo- and co-polysiloxanes to differences in the nature of their smectic phases. Finkelmann has reported that in stripes of smectic LC-elastomers (in his case from homopolymers), the thickness parallel to the smectic layer normal is constant during stretching (Poisson ratio of 0) [18, 19]. This corresponds to a high smectic layer compression modulus for siloxane hompolymers, as compared with the entropy elasticity moduli. We observe that this thickness actually decreases in free-standing films from copolymers during stretching, the Poisson ratio being close to 0.5 [12]. It is natural to assume that differences in the total smectic film thickness are directly related to differences in the compressibility of the individual layers. Thus, the observations indicate a rather low smectic layer compression modulus for siloxane copolymers, as compared with their entropy elasticity. In the same set of experiments, this thickness was constant for free standing films of the elastomers prepared from corresponding homopolymers [12].

Both effects can be clearly seen in figure 5. For the copolymer films, the reflection colours of a submicrometer thin film change during elongation; for the homopolymer they remain rather constant, at least for small strain. Since we can assume that the entropy elasticity does not differ substantially between both types of elastomer, the magnitude of the smectic layer compression modulus obviously depends on the molecular structure. It may be speculated, whether the smectic layer compression modulus is so low for the polysiloxane copolymers because (1) the siloxane sublayer can be easily deformed, or (2) because it is easier to change the layer thickness in a SmA–SmC* phase transition of the 'de Vries' type under lateral stress. Since the mesogens are already tilted, a small change of the tilt will have a strong first order effect on the overall thickness in this case, whereas the coupling of the tilt angle to the layer thickness in an untilted smectic structure is only of second order.

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