Liquid crystalline elastomers as artificial muscles

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Abstract: New nematic co-elastomers were synthesized which consist of a combination of nematic side- and main-chain polymers and where the liquid crystalline main-chain polymer can be considered as a macromolecular crosslinking component. By applying a mechanical field during the crosslinking process, the director of the nematic phase becomes macroscopically uniformly aligned and liquid-single-crystal elastomers were obtained. Within a narrow temperature regime, these networks can change their shape in one dimension by a factor > 3 and considerably improve the ability of being used as artificial muscles or mechanical actuators compared to the well known nematic side-chain elastomers. Networks having a non-ordered polydomain structure exhibit “soft (or semi-soft) elasticity” which is not only determined by a director reorientation process. Obviously, hairpin conformations within the main-chain segments contribute to this effect.

Introduction

Already in 1950, Kuhn demonstrated that polymer networks that are swollen with a solvent might be applicable as artificial muscles [1]. At the point of gel collapse the network changes dimensions, which causes a retractive force if, e.g., the length of the sample is held constant in one dimension. The gel collapse is due to the demixing process of the swollen network, where the collapsed gel coexists with the pure solvent. This process is determined by diffusion of the solvent within the network. Consequently the response time of such an artificial muscle is limited by the velocity of the mass transport.

Recently, liquid-single-crystal elastomers (LSCE) have been realized [2], where the liquid crystalline (LC) phase structure is macroscopically orientated in the network. At the liquid crystalline to isotropic phase transformation temperature, when the liquid crystalline network becomes isotropic and similar to a conventional rubber, the dimensions of the network change. Due to the initial anisotropic phase structure, the network shortens in the direction of the optical axis or director axis. For nematic LSCEs synthesized from nematic LC side-chain polymers, the change of length is up to about 40%. The speed of this process is determined by thermal heat conductivity of the network and not by material transport processes. If the sample thickness is limited, calculations indicate that the response time of these LSCEs is similar to that of natural muscles and mainly determined by the relaxation behavior of the polymer chains or network strands [3].
The magnitude of changes in the dimensions of nematic LSCE with temperature is determined by the coupling between the nematic state of order and the conformation of the polymer main chains. In this regard the backbone conformation of nematic side chain polymers is hardly affected, because the orientationally long range ordered, rigid rod-like mesogenic side chains only indirectly couple to the chain conformation. For nematic main chain polymers, where the mesogenic units are incorporated into the polymer main chain, large conformational changes should occur and directly be expressed in the thermoelastic behavior.

In this paper, in the first part we describe the synthesis of new nematic LSCEs that consist of a combination of LC side chains and main chain polymers. In these networks, a nematic main chain polymer of different chain length acts as the crosslinker of a nematic side chain polymer. In the second part thermoelastic measurements will reveal whether these networks exhibit an increased coupling between the nematic state of order and the chain conformation with increasing fraction of the main chain segments, and whether these networks are more efficient as thermally stimulated mechanical actuators. Finally, in the third part the stress/strain behavior of similar but macroscopically non-ordered liquid crystalline elastomers (LCE) is analyzed. Here we find a soft elasticity that can not only be explained by director reorientation processes as theoretically described by Warner et al. [4]

Experimental part

Synthesis of the elastomers

The elastomers were synthesized by a platinum catalyzed hydrosilylation reaction of poly(methylhydrogensiloxane), 1, with the side chain mesogen 4-but-3-enyloxybenzoic acid 4-methoxyphenyl ester, 2, and the nematic polyether based on 1-(4-hydroxy-4′-biphenyl)-2-[4-(10-undecenyloxy)phenyl]butane, 3, which was end-functionalized by vinyl groups (see Fig.1). This polyether was first synthesized by Percec et al. [5] and used as a main-chain polymer/crosslinker with different degrees of polymerization. The addition reaction was performed at 60° C and catalyzed with the Pt-catalyst SLM 86005 (Wacker Chemie, Burghausen, Germany). The chemical compositions of the elastomers are shown in Tab. 1. The side chain mesogen 2, PMHS 1 as functional polymer, and 3 as main-chain polymer/crosslinker were dissolved in 2.5 ml of thiophene-free absolute toluene. To exclude dust particles, the solution was filtered using a 0.45 μm Teflon filter (Millipore). After pouring the solution into a Teflon film covered centrifuge cell (49 mm diameter; 20 mm height), 15 μl of the catalyst was added. The reaction was carried out at 60° C for 12-24 h at 6000 rpm (HERMLE Z320/HAAKE F3). To obtain networks with a polydomain (PD) structure (5a - 5c), the elastomer films were removed after 24 h and deswollen on a water surface to avoid any mechanical deformation. The elastomers with monodomain (MD) structure (4a - 4d) were removed after 12 h and deswollen under a constant load. All elastomers were dried under vacuum at 80° C for at least 24 h.

Differential scanning calorimetry

DSC measurements were carried out with a Perkin Elmer DSC-7 at heating rates of 9, 16, 25 and 36 K/min. The glass transition temperature ($T_g$) and the nematic to
isotropic phase transformation temperature \((T_{n,i})\) were determined by extrapolating the heating rate to 0 K/min.

**Swelling experiments**

Swelling experiments were performed in toluene at 25°C to obtain information about the effective crosslinking density and the swelling anisotropy, \(\Delta q\), of the network. The dimensions of the elastomer samples were measured with an optical microscope (Fa. Will Strubin, Wetzlar, Germany). The swelling ratio \(q\) is the ratio of the volume of the swollen and dry elastomer. The anisotropy of the swelling \(\Delta q\) is defined as \(\Delta q = \frac{a_{\perp}/a_{||} - 1}{\text{where } a_{\perp} \text{ and } a_{||} \text{ are the extension factors perpendicular and parallel to the director, respectively, during the swelling process.}}\)

**Stress strain measurements**

Stress strain measurements were performed in a custom-made cell. All parameters including temperature were computer-controlled as previously described [4, 6]. The experiments were carried out under thermodynamical equilibrium conditions.

**X-ray diffraction experiments**

X-ray experiments were carried out with a Philips PW 1730 and Cu K\(\alpha\) radiation (0.15418 nm) filtered by a graphite monochromator. The incident beam was normal to the surface of the films. The scattered X-ray intensity was detected by the Image Plate system (Fa. Schneider, Freiburg, Germany). The order parameter, \(S\), was calculated from the azimuthal intensity distribution of the nematic intermesogen reflection at wide angles [7].

**Thermoelastic experiments**

A custom-made setup was used to measure the length of the elastomers as a function of temperature [8]. The sample was mounted in a thermostated glass column. The temperature was controlled by a Haake-F6 thermostat and measured with a Pt100 thermoresistor. The dimensions of the network were determined by a video camera where the digitized pictures were analyzed by image processing. The experiments were carried out under thermodynamical equilibrium conditions.

**Results and discussion**

**Synthesis of nematic LCE**

According to a previously described synthesis [2, 6], the nematic networks were obtained via a hydrosilylation reaction of the monofunctional side chain mesogen 2 and the bifunctional LC main chain polyether 3 with poly(methylhydrogensiloxane) 1 as shown in Fig. 1.
Fig. 1. Synthesis of the nematic LCE

To obtain a LSCE with a macroscopically uniform orientation of the director, after gelation the weakly crosslinked network was mechanically loaded with about $10^3$ N/m². Under load the hydrosilylation reaction was completed. Non-ordered LCEs were synthesized without load to complete conversion. The networks differed in the weight ratio of the mesogenic units in the main and side chains and in the degree of polymerization (DP) of 3 as indicated in Tab.1.

Tab.1 Synthesis of the elastomers

<table>
<thead>
<tr>
<th></th>
<th>1 [mmol]</th>
<th>2 [mmol]</th>
<th>3 [mmol]</th>
<th>$2/(2+3\cdot DP)\cdot 100$</th>
<th>Crosslinker in %</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>2.562</td>
<td>2.464</td>
<td>0.049</td>
<td>80</td>
<td>1.9</td>
<td>13</td>
</tr>
<tr>
<td>4b</td>
<td>2.048</td>
<td>1.930</td>
<td>0.060</td>
<td>72</td>
<td>2.9</td>
<td>13</td>
</tr>
<tr>
<td>4c</td>
<td>1.417</td>
<td>1.303</td>
<td>0.057</td>
<td>54</td>
<td>4.0</td>
<td>20</td>
</tr>
<tr>
<td>4d</td>
<td>1.210</td>
<td>1.098</td>
<td>0.056</td>
<td>43</td>
<td>4.6</td>
<td>26</td>
</tr>
<tr>
<td>5a</td>
<td>2.562</td>
<td>2.464</td>
<td>0.049</td>
<td>80</td>
<td>1.9</td>
<td>13</td>
</tr>
<tr>
<td>5b</td>
<td>1.417</td>
<td>1.303</td>
<td>0.057</td>
<td>54</td>
<td>4.0</td>
<td>20</td>
</tr>
<tr>
<td>5c</td>
<td>0.526</td>
<td>0.430</td>
<td>0.048</td>
<td>23</td>
<td>9.1</td>
<td>30</td>
</tr>
</tbody>
</table>

By varying the concentration and chain length of 3, a nearly constant crosslinking density of the different networks can be maintained, indicated by the swelling coefficients $\alpha$ (Tab.2). If we roughly neglect different solubility parameters of the corresponding homopolymers, $\alpha$ only varies between 6.5 to 6.9 although the chemical constitution of the networks has been greatly modified.
Tab.2. Characterization of the elastomers

<table>
<thead>
<tr>
<th></th>
<th>$T_g$ in °C</th>
<th>$T_{n,i}$ in °C</th>
<th>Degree of swelling, $\alpha$</th>
<th>Swelling anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>7</td>
<td>89</td>
<td>6.9</td>
<td>1.8</td>
</tr>
<tr>
<td>4b</td>
<td>8</td>
<td>86</td>
<td>6.3</td>
<td>2.9</td>
</tr>
<tr>
<td>4c</td>
<td>13</td>
<td>95</td>
<td>6.5</td>
<td>4.1</td>
</tr>
<tr>
<td>4d</td>
<td>19</td>
<td>96</td>
<td>6.8</td>
<td>4.5</td>
</tr>
<tr>
<td>5a</td>
<td>3</td>
<td>89</td>
<td>6.9</td>
<td>1</td>
</tr>
<tr>
<td>5b</td>
<td>11</td>
<td>96</td>
<td>6.5</td>
<td>1</td>
</tr>
<tr>
<td>5c</td>
<td>24</td>
<td>94</td>
<td>6.9</td>
<td>1</td>
</tr>
</tbody>
</table>

Because the main- and side-chain homopolymers exhibit nearly the same nematic to isotropic phase transformation temperature, $T_{n,i}$ varies only between 86 and 96° C for the different networks. The swelling anisotropy increases remarkably with increasing main chain mesogen ratio ($4d > ... > 4a$).

**Thermoelastic measurements**

As mentioned above, nematic side chain LSCE spontaneously and reversibly change their length with temperature up to about 40%. Detailed investigations have shown that the relative length $\lambda = L/L_0$ of the networks linearly depends on the nematic order parameter $S$ [6], where $L$ is the length of the networks in the nematic state in the direction of the macroscopically aligned director and $L_0$ the length in the isotropic state at the nematic to isotropic phase transformation. This linear relation is characterized by the cross-coupling coefficient $U$, which can be described by

$$S = - \sigma' U + (\mu/ U) \cdot \lambda$$

(1)

where $\mu$ is the elasticity modulus, $\sigma$ the mechanical field and $\lambda = L/L_{iso}$ the deformation of the LSCE caused by the nematic order. The cross-coupling coefficient $U$ mirrors the change of the conformation of the network strands between the isotropic state and the nematic state, which - in the frame of the affine network model - is directly reflected in the macroscopic dimensions of the network [4].

For nematic side chain polymers the nematic order of the rigid rod-like mesogenic side groups only indirectly couples to the orientation of the chain segments. But if the rigid, mesogenic segments are inserted into the network chains, the nematic order will directly cause an anisotropic chain conformation. Compared to nematic side chain LSCEs, with increasing fraction of the LC main chain segments in the networks, an increase in the thermoelastic response and cross-coupling coefficient, $U$, is expected.

The experimental results of the thermoelastic measurements of the networks are summarized in Fig. 2 where the spontaneous deformation, $L/L_{iso}$, of the networks is determined as a function of the reduced temperature $T_{red} = T/T_{n,i}$. For the network $4a$ that contains 20 mol-% of mesogenic main chain monomer units of 3, actually a pronounced increase of the thermoelastic response is observed compared to the networks that are crosslinked with conventional crosslinkers [2]. At $T_{red} = 0.85$ the
elastomer is extended by a factor of 1.8 in the director direction compared to the isotropic state which is about twice as much as the pure LC-side chain network. On increasing the mole fraction of the main chain segments to 28 mol-% ($L/L_{iso} = 2.25$) and to 46 mol-% ($L/L_{iso} = 2.9$) and finally for 4d to 57 mol-% of the main chain polymer with DP = 26, we obtain a remarkable spontaneous deformation of $L/L_{iso} = 3.8$. This is, to our knowledge, the largest, thermally stimulated spontaneous and reversible deformation of a solid ever observed. The lengthening of the networks in the direction of the director causes a decrease of the dimensions perpendicular to the director. This is confirmed by 4c and is shown in Fig. 3 where $L/L_{iso}$ and the perpendicular dimension $L_{per}/L_{iso}$ is measured as function of the temperature. From these results we obtain the relative volume $V_{rel}(T) = (L\cdot L_{per}^2)/L_{iso}^3$ which remains constant within the accuracy of the experiment.

Fig. 2. Thermoelastic experiment of 4a - 4d (load 6·10³ N/m²)

Fig. 3. Thermoelastic behaviour of 4c parallel and perpendicular to the director
The results of the thermoelastic experiments are summarized in Fig. 4 where \( \frac{L}{L_{iso}} \) at \( T_{\text{red}} = 0.85 \) is shown as a function of the mole fraction of 3. Interestingly, an almost linear relation exists within this mole fraction region. A linear extrapolation to the pure (hypothetical) network without any main chain units 3, however, results in \( \frac{L}{L_{iso}} < 1 \), which cannot be explained. The extrapolation to the pure main chain polymer would give \( \frac{L}{L_{iso}} = 6 \). To determine the cross-coupling coefficient \( U \), the nematic order parameter of the networks has to be determined as a function of temperature. According to previous measurements, \( S(T) \) has been analyzed by X-ray measurements and the results are summarized in Fig. 5.

![Graph](image1.png)

**Fig. 4.** \( \frac{L}{L_{iso}} \) versus ratio of monomer units (MU) in the main chain at \( T_{\text{red}} = 0.85 \)

![Graph](image2.png)

**Fig. 5.** Order parameter \( S \) as function of \( T_{\text{red}} \) for 4a - 4d

Within a small temperature regime of \( 0.95 < T_{n,i} < 1 \), the order parameter strongly increases and equals about 0.7 for all networks at lower temperatures (\( T_{n,i} < 0.9 \)).
The continuous course of \( S(T) \) and analogously for \( L/L_{iso}(T) \) indicates that the networks behave super-critically with respect to the nematic to isotropic phase transformation as is well known for side chain LSCEs [6]. The correlation \( S(\lambda) \) as summarized in Fig. 6 yields straight lines within the accuracy of the experiment. With Eq. (1) and the moduli from stress/strain measurements that will be reported in a forthcoming paper, we obtain the cross-coupling coefficients summarized in Tab. 3.

Tab. 3. Cross-coupling constants

<table>
<thead>
<tr>
<th>( \Delta S/\Delta (L/L_{iso}) )</th>
<th>( E ) in N/m(^2)</th>
<th>( U = E/m ) in J/m(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>0.99</td>
<td>2.1( \cdot )10(^4)</td>
</tr>
<tr>
<td>4b</td>
<td>0.65</td>
<td>2.2( \cdot )10(^4)</td>
</tr>
<tr>
<td>4c</td>
<td>0.38</td>
<td>10.0( \cdot )10(^4)</td>
</tr>
<tr>
<td>4d</td>
<td>0.26</td>
<td>16.0( \cdot )10(^4)</td>
</tr>
</tbody>
</table>

As already identified from the thermoelastic measurements and beginning with the pure LC-side chain network, \( U \) strongly increases by more than one order of magnitude with the mole fraction of LC main chain segments in the elastomers.

Fig. 6. Order parameter \( S \) as function of \( L/L_{iso} \) for 4a - 4d

With respect to the question as to whether these networks are suitable as mechanical actuators, the thermomechanical response of 4d is examined for three different loads (Fig. 7). While within the regime of the isotropic to nematic transformation, the samples behave similarly to each other, the final elongation at lower reduced temperatures is clearly affected by the load which indicates the efficiency of the actuator. Here additional experiments have to carried out in order to elucidate the load dependent properties of the elastomers.
From nematic side chain elastomers exhibiting a polydomain structure it is well-known that a mechanical field causes a director orientation [6]. Following this process with stress/strain measurements, after a linear $\sigma(\lambda)$-regime, at $\lambda_1$ the director reorientation sets in which is accompanied by a plateau formed of the $\sigma(\lambda)$ curve. According to the model of Warner for an ideal nematic network, the plateau characterizes the “soft elasticity” of the network [4]. Director reorientation does not affect the conformational entropy of the network strands. Consequently above $\lambda_1$ the elongation of the network is only due to the rotation of the director of the nematic domains towards the direction of the mechanical field without changing the retractive force. When this process is terminated at $\lambda_2$, the network exhibits a monodomain structure. Above $\lambda_2$ the stress/strain curve yields the modulus $E$ parallel to the director. The width of the plateau between $\lambda_1$ and $\lambda_2$ is determined by the anisotropy of the chain conformation imposed by the nematic state of order and is characterized by the coupling coefficient. As established by the thermoelastic measurements, with increasing amount of main chain segments within the networks the coupling coefficient becomes larger. In a similar way the width of the plateau between $\lambda_1$ and $\lambda_2$ should become broader with the monodomain appearing at $\lambda_2$. These mechanical properties are analyzed using the polydomain networks. In Fig. 8 the stress strain relation is shown for a constant reduced temperature of $T_{\text{red}} = 0.95$. Actually, after a narrow regime between $1 < \lambda \leq 1.3$, above $\lambda_1$ a plateau-like behavior is observed, where the slope of the $\sigma(\lambda)$ curve slightly increases from $< 500$ N/m$^2$ to $1.3 \cdot 10^4$ N/m$^2$ depending on the chemical constitution. Most interestingly compared to the corresponding pure side chain elastomers is that a clear threshold for $\lambda_2$ can not be identified, where for $\lambda > \lambda_2$ a linear $\sigma(\lambda)$ relation identifies the modulus of the ordered monodomain parallel to the director. Instead of this, an exponential increase of the slope is observed as already found for the pure main chain elastomer [9]. On examining the temperature dependence from the $\sigma(\lambda)$ curves, another unexpected result is identified which is shown in Fig. 9 for the elastomers 5c.
Fig. 8. Stress strain behavior of 5a - 5c ($T_{\text{red}} = 0.95$). Inset: $\sigma$ vs. $\lg \lambda$ of 5c

Fig. 9. Stress strain behavior of 5c at different temperatures

With increasing temperature, the regime of semi-soft elasticity $\lambda_1$ and $\lambda_2$ becomes extended and while $\lambda_1$ stays constant within experimental error, $\lambda_2$ increases significantly. These results are summarized in Tab. 4.

For the pure side chain elastomers, $\lambda_2$ marks the end of the polydomain/monodomain transition with strain [6]. This can be measured by the overall order parameter $S$ as a function of $\lambda$, where $S = S_n S_D$, and $S_n$ and $S_D$ are the nematic order parameter and the director order parameter, respectively. To evaluate whether this also holds for the coelastomers, $S$ has been measured as function of $\lambda$ and $T$ by X-ray measurements.
Tab.4. Stress strain and X-ray data for 5a - 5c compared to pure main chain (MC) and side chain (SC) elastomers

<table>
<thead>
<tr>
<th>Elastomer</th>
<th>$T_{\text{red}}$</th>
<th>$E_1$</th>
<th>$E_2$</th>
<th>$E_3$</th>
<th>$\lambda_1$</th>
<th>$\lambda_2$</th>
<th>$\lambda_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>0.95</td>
<td>2.2·10^4</td>
<td>&lt;500</td>
<td>1.5·10^4</td>
<td>1.2</td>
<td>2.3</td>
<td>1.7</td>
</tr>
<tr>
<td>5b</td>
<td>0.95</td>
<td>3.7·10^4</td>
<td>1600</td>
<td>3.8·10^4</td>
<td>1.3</td>
<td>2.8</td>
<td>1.8</td>
</tr>
<tr>
<td>5c</td>
<td>0.95</td>
<td>6.7·10^4</td>
<td>1.3·10^4</td>
<td>4.9·10^4</td>
<td>1.3</td>
<td>4.0</td>
<td>1.9</td>
</tr>
<tr>
<td>5c</td>
<td>0.92</td>
<td>9.4·10^4</td>
<td>1.9·10^4</td>
<td>23.0·10^4</td>
<td>1.4</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>0.91</td>
<td>23.0·10^4</td>
<td>&lt;1000</td>
<td>34.0·10^4</td>
<td>1.3</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>5c</td>
<td>0.88</td>
<td>27.6·10^4</td>
<td>3500</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SC</td>
<td>≈1.1</td>
<td>≈10^4</td>
<td>&lt;&lt;10^3</td>
<td>≈10^4</td>
<td>=1.1</td>
<td>1.2-1.4</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>MC</td>
<td>1.2-1.3</td>
<td></td>
<td></td>
<td>10^5-10^6</td>
<td>10^5-10^6</td>
<td>1.2-1.4</td>
<td>1.6-5.0</td>
</tr>
</tbody>
</table>

The results are summarized in Fig. 10 for the networks 5a - c measured at $T_{\text{red}} = 0.95$. As expected, for all networks $S$ increases almost linearly with $\lambda$, but surprisingly for $1 < \lambda < 1.5$ with the same slope. Even more remarkable is that $S_D$ becomes unity for 5a at $\lambda_M = 1.8$ while $\lambda_2$ was identified as 2.3 from stress strain measurements. This discrepancy between $\lambda_M$ and $\lambda_2$ markedly increases from 2.3 to 4.0 with increasing content of the LC main-chain segments. Simultaneously the order parameter of the monodomain networks increases from $S_n = 0.6$ to 0.8 as expected from former measurements on LC side- and main-chain polymers [6, 9]. From these results we have to conclude that for these elastomers containing LC main-chain polymers, the regime of semi-soft elasticity is not only determined by director reorientation. Even above $\lambda_M$, where the monodomain with $S_D = 1$ exists, the networks exhibit a soft mechanical response on elongation up to $\lambda_2$.
The soft mechanical response of the networks in the regime $\lambda_M < \lambda < \lambda_2$ might be explained by the well-known fact that the conformations of nematic main chain polymers considerably deviate from the conformations of the backbone of side chain polymers. While the latter are assumed to exhibit a statistical chain conformation that is deformed by the anisotropic nematic molecular field towards an overall prolate shape, the monomer units of the LC-main chain polymers are directly ordered in a nematic fashion as schematically sketched in Fig. 11.

![Fig. 11. Sketch of hairpin conformations (refer to the text)](image)

It is assumed and concluded from detailed X-ray and SANS measurements on the corresponding linear homopolymer 3 that the chains are not linearly extended but the conformation entropy enlarged by “hairpins” within the chain [10, 11]. This is illustrated in Fig. 11 for chains having one or two hairpins. From this picture we can also immediately conclude that a chain with one hairpin can be elongated by a maximum factor of 2, with 2 hairpins by a factor of 3 etc. without loosing the hairpin or decreasing the conformational entropy. With this picture in mind, the $\sigma(\lambda)$ behavior of the polydomain networks might be explained. In the regime $\lambda_1 < \lambda < \lambda_M$ the elongation of the network causes director reorientation as theoretically explained by Warner. This process, in the ideal case, costs no entropy for the change of the conformation of the network chains. Above $\lambda_M$ where the network exhibits macroscopically uniform orientation of the director, hairpins still exist within the networks due to the LC main chain segment. In the first step, elongation of the network will simply shift the hairpins along the main chain as indicated in Fig. 8 and finally the hairpins will disappear. The first step is not connected with a conformation change of the backbone (but concentration of the hairpins towards the chain ends) and also causes a "soft" mechanical response of the network. Consistent with this idea is the fact that the regime $\lambda_M < \lambda < \lambda_2$ broadens with increasing concentration of the main chain segments in the network 4a to 4d. The distribution of the position of the hairpins along the network strands, of course, results in a progressively increasing number of the undeformed elastomers of elongated chains under deformation. This might explain the almost exponential increase of the modulus with $\lambda$, as shown in Fig. 8, which completely differs from the $\sigma(\lambda)$ behavior of pure nematic side chain elastomers. Correspondingly, the extraction of $\lambda_2$ is rather difficult. The inset in Fig. 8 presents $\sigma(\lg \lambda)$, where we can roughly identify two linear regimes. From this graph, we evaluated $\lambda_2$ as indicated. It is obvious that a clear physical picture is missing for this procedure.
Conclusion

A new type of LC coelastomer has been synthesized containing LC side chain and LC main chain polymers as network strands. The ratio of mesogenic segments in the main and side chain was varied to analyze the efficiency of the main chain segments on the thermoelastic behavior of the LSCE. Due to the direct coupling of the LC main chain segments to the network anisotropy, a remarkable increase of the thermoelastic response is observed with an increase of their concentration. Compared to the length of the networks in the isotropic state, an elongation of up to a factor of almost 4 occurs in the nematic state in the direction of the director. To our knowledge this is the largest thermal expansion behavior ever observed.

As previously discussed, already the thermo-mechanical response of pure nematic side chain LSCE is interesting with regard to these networks being used as artificial muscles [4] or mechanical actuators. Our results clearly indicate that nematic networks with LC main chain polymers improve this ability considerably. Very recently for side chain LSCEs a remarkable photo-elastic response was demonstrated [12]. By applying the concept demonstrated in this paper it should be straightforward to improve the photo-elastic response of these systems.

This paper was partly presented at the ACS-Meeting, San Francisco 2000 [13].

Acknowledgement: Support from Deutsche Forschungsgemeinschaft, SFB 428 and Fonds der Chemischen Industrie is gratefully acknowledged.