

# Switching properties in Siloxane-based Liquid-crystal Elastomer

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## Abstract

Mechanical and X-ray scattering measurements on a side-chain liquid-crystal elastomer based on a Siloxane backbone are presented. The application of a stress field to the elastomer while in the nematic phase result in a stress-induced alignment of the mesogenic units in the direction of the extension. Extensions as low as 2% result in appreciable molecular alignment. The similarities of these effects with those observed in electric and magnetic fields are outlined.

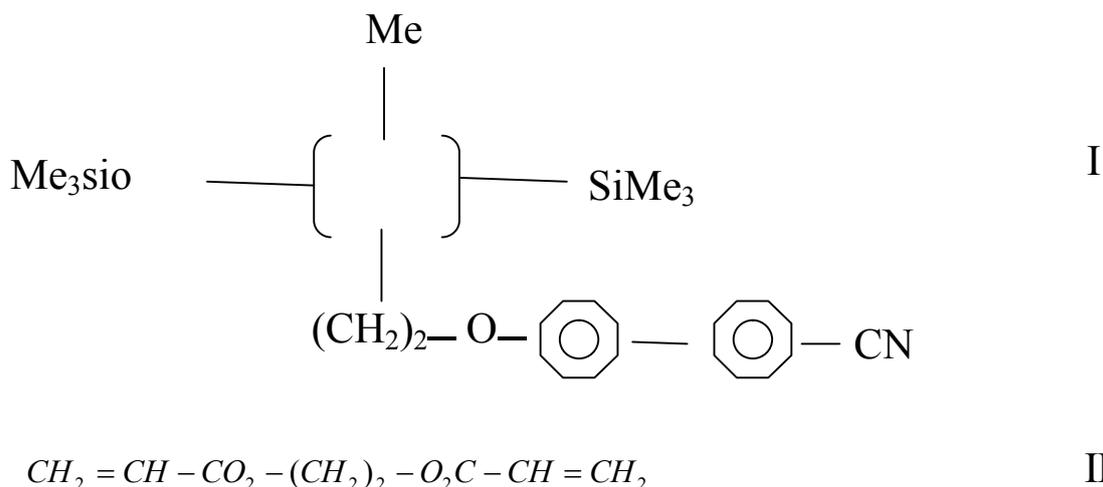
## Introduction

The design principles of side-chain liquid-crystal polymers are now well established<sup>1,2</sup>. These molecular composites comprise a flexible polymer backbone, a more or less rigid mesogenic unit, joined as a side-chain to the polymer backbone by a flexible coupling chain. By suitable chemical design, polymers can be synthesized that will exhibit<sup>3-5</sup> the well-known electric and magnetic field effects displayed by low molar mass counterparts<sup>6</sup>; i.e. a macroscopically aligned sample may be produced following the application of a suitable field\*. In these effects the electric or magnetic field couples primarily to the rigid aromatic mesogenic unit, and so, for example, in a side-chain liquid-crystal polymer, the coupling subchain and the polymer backbone are not directly affected. However, the relatively short length of any coupling chain will result in some interaction between the mesogenic units and the polymer backbone chains, as is shown by theoretical studies<sup>7</sup> and from neutron scattering experiments<sup>8,9</sup>.

We would expect the application of mechanical fields to side-chain liquid-crystal polymers to produce similar macroscopic alignment with the possibility of significant and interesting interactions between the various components of these molecular composites. However, with a conventional liquid polymer any applied static stress field will rapidly relax at rates dependent on the viscosity of the material, and thus only flow fields followed by rapid cooling generally result in orientation, as, for example, in fiber pulling. The synthesis of a crosslinked network within a liquid-crystal polymer framework to produce liquid-crystal elastomers<sup>10-12</sup> offers the possibility of applying static mechanical fields to induce molecular switching, and this communication records the preliminary results of such experiments.

## Materials

Liquid-crystal elastomers based on a siloxane backbone were produced by the free-radical copolymerization of mixtures of a mesogenic monomer I and a difunctional crosslinking unit II<sup>12,13</sup>.



A smectic liquid-crystal phase was observed in copolymers prepared with up to 13mol% of the crosslinking being to raise the glass transition (ca. 35°C for 0% of II) and to lower the smectic-isotropic transition (ca. 125°C for 0% of II). The following experiments were made on a copolymer containing 23mol% of II. Mechanical modulus measurements made in the isotropic phase coupled with spectroscopic characterization<sup>13</sup> indicates that for this composition the effective crosslink density corresponds to ca. 1%, the difference being due to chain-ends and intermolecular loops. This copolymer exhibited a glass-transition at ca. 35°C and a smectic-isotropic transition at ca. 117°C. A more detailed description of the synthesis and characterization is reported elsewhere<sup>12,13</sup>.

## Experimental

The mechanically induced alignment was achieved in a miniature tensile testing machine (Rosand Precision Ltd.) fitted with a 20N force transducer and temperature-controlled hot-air oven. Thin films of the elastomer were prepared by pressing followed by heating at 150°C to allow the material to completely relax. Samples approximately 5 mm wide by 12mm long and 0.5 mm in thickness were cut from same prepared films while still in the isotropic phase. The molecular organization of the deformed samples was monitored by using wide angle X-ray scattering procedure. These scattering measurements were made at room temperature on samples that had been rapidly cooled by an air jet from the experimental temperature. The onset of the glass transition ensured that the static molecular organization characteristic of the experimental temperature was retained upon cooling. In particular, the wide-angle X-ray scattering measurements were employed to provide a quantitative measure of the level of preferred molecular orientation  $\langle P_2 \rangle$ , where  $[P_2 = (3\cos^2 \alpha - 1)/2]^1$  and  $\alpha$  is the angle between the molecular axis and the extension direction. In essence the X-ray measurements provide an estimate of the degree of alignment of the mesogenic units. The X-ray scattered intensities were recorded by using a computer-controlled three-circle diffractometer, and the orientation parameters were derived by using procedures detailed elsewhere<sup>14-17</sup>.

## Results

The mechanical properties of these liquid-crystal elastomers in the smectic phase are both heavily temperature- and time-dependent. Figure 1 contains the essential time information. The curve shown plot force against time. Initially the sample, maintained in this example at 117°C, was continuously extended at a strain rate of  $0.01\text{s}^{-1}$ . This extension was made for 10s the force rises steeply with this extension. Upon increasing the extension, the measured force drops in an exponential manner to reach a steady level after 100-200s. We have measured the orientation parameter  $\langle P_2 \rangle$ , as indicated above, for a sample rapidly cooled from a point corresponding to the peak force detected, that is just before the cessation of extension. The orientation parameter  $\langle P_2 \rangle$  was ca. 0, indicating no preferred molecular orientation of the mesogenic units. The corresponding orientation parameter measured for a sample that had reached its equilibrium force value, i.e. after 100s, was indicates a high level of preferred orientation of the mesogenic units. In addition, the positive value of  $\langle P_2 \rangle$  creates a preferred alignment in the same direction as extension direction. The drop in the force recorded after extension has stopped may, therefore, be related to the mechanically induced alignment of the mesogenic units in the liquid-crystal elastomer.

A side-chain liquid-crystal polymer may respond to a mechanical extension in two broad ways. The strain will extend the polymer network, that is the polymer backbones, and so such chains will be partially aligned. For a comparable conventional elastomer we would expect for a strain of 4 or 5 an orientation parameter of the polymer backbone. Since the liquid-crystal elastomer used here has a very short coupling chain of two methylene units, any orientation of the polymer backbone would tend to result in the perpendicular alignment in the mesogenic units and a negative value of  $\langle P_2 \rangle$ . The fact that we observe a large positive value of  $\langle P_2 \rangle$  suggests that the network alignment is not the controlling mechanism. The alternative response of the elastomer is that induced by the stress field. This will couple into the anisotropy of the mesogenic unit and may not require a high level of extension. Furthermore, we would expect anisotropy units to align their long axes in the extension direction. This is as observed for the acrylate-based elastomer in this study. Similar proposals as to the role of stress fields in the development of molecular orientation have been made in relation to non-crystalline polymers<sup>18,19</sup>. Both perpendicular and parallel alignment have been observed in an siloxane-based elastomer system with coupling chain of 3-6 methylene units<sup>11,18</sup>. An explanation of those experiments has been proposed by Schwarz<sup>21</sup> and Kock<sup>20</sup>, but the system presented in this study differs both in the chemical configuration and the mode of crosslinking. It would appear reasonable, however, to suggest that the competing mechanisms described above could produce such alternative alignments. De Gennes has highlighted the possibility of interesting mechanical properties<sup>22,23</sup> in liquid-crystal elastomers, arising through the interactions of the polymer chains via crosslinks and entanglements.

The degree of extension of the sample reported in Figure 1 was 1.1. To assess the minimum level of mechanical deformation required to induce alignment we repeated the experiment described above, but for the repeated experiment the time of continuous extension was varied to correspond to initial extension ratios from 1.03 to 2.1. The values of the final orientation parameter as measured by wide-angle X-ray scattering procedures is plotted in Figure 2 as a function of the initial extension. A plateau value of  $\langle P_2 \rangle \approx 0.45$  is reached with an initial extension of 1.3. However, most significantly even initial extensions of 1.03 resulted in an appreciable level of molecular alignment. The low values of extension, which result in a preferred molecular alignment, reinforce the view presented above that such switching arise; not from extension of the network, which would be almost imperceptible for an extension ratio of 1.03, but from the stress field applied. Varying the initial extension ratio simply results in a different initial stress level. The variation in stress level with extension may be assessed by examining the initial slope of the force-time curve in Figure 1. The particular stress level reached for any given extension will depend upon both the strain rate and

the temperature. Owing to the closeness of the glass transition, we would expect the viscosity to be heavily dependent on the temperature. So, if the temperature of operation is lowered, the initial stress will be higher for a given extension, but owing to the higher viscosity the molecular switching will occur more slowly. Conversely, raising the temperature will reduce the initial stress and hence the final level of orientation (unless the plateau level has been reached), while the rate of switching will be enhanced.

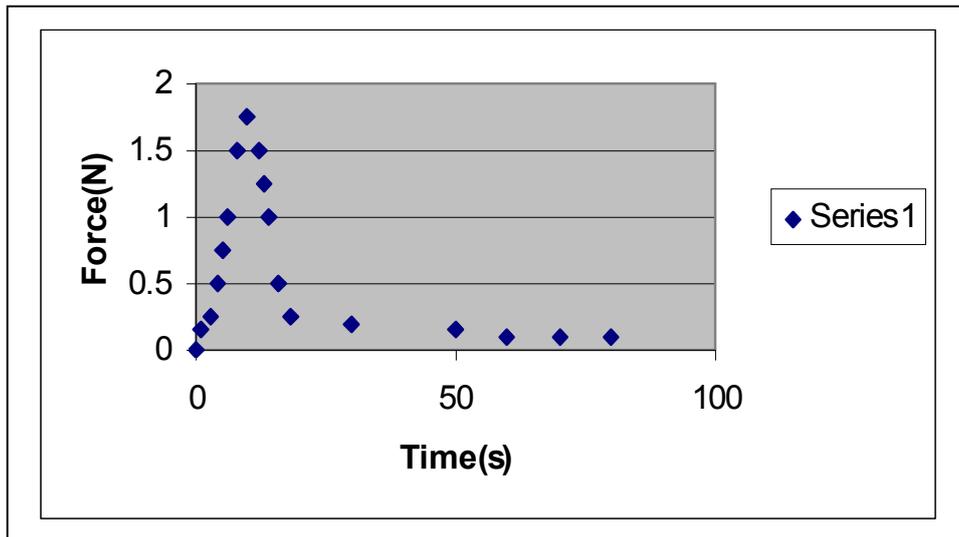
## Discussion

We suggest the following as the mechanism of switching. The extension of the material, owing to the crosslinking and heavy entanglement density as a result of the side-chains, causes a rapid rise in the stress level. The stress field, which we can view either as a tensile stress in the direction of the extension or as a compressive stress normal to the extension direction, is sufficient to operate on the anisotropic mesogenic units, the stress being relieved by preferential alignment of those side-chains in a direction parallel to the extension direction. The molecular reorientation results in anisotropic dimensional changes, in particular a dilation of the sample length<sup>11,20</sup>, and hence a drop in the stress. If we remove the stress field completely, but maintain the sample in the smectic phase, the molecular alignment switches off albeit on a timescale at least an order of magnitude slower than the switch on. The loss of a preferred molecular alignment results in a shortening of the sample to its original length. The speed of switching on after the sudden application of a stress field will depend on the stress level and the viscosity of the polymer. Thus, this mechanically induced alignment parallels that which may be induced by using electric or magnetic field, but which couples via the anisotropy of the mesogenic unit rather than its dielectric or diamagnetic susceptibility anisotropy.

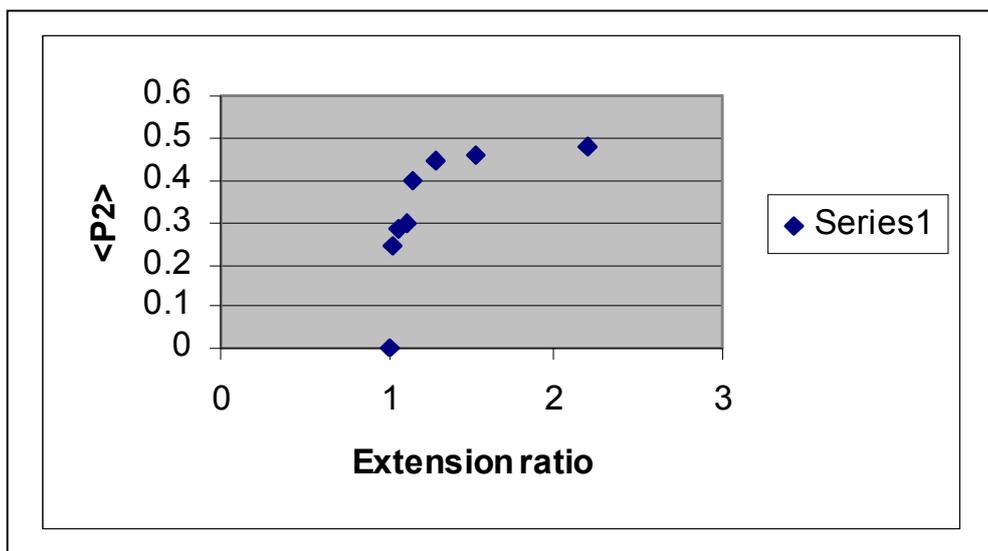
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**Fig. 1** A plot of force versus time for an siloxane-based liquid-crystal elastomer deformed at 85°C, i.e. in the smectic state. The sample was extended continuously for 10s . The remainder of the curve corresponds to the measured force on the sample held at constant extension of 1.1. The orientation parameter  $\langle P_2 \rangle$  was measured by using wide-angle X-ray scattering techniques as described in the text.



**Figure 2** The measured orientation parameter  $\langle P_2 \rangle$  for samples of the Liquid-crystal elastomer subjected to the initial extension induced on the ordinate, at 117°C and at a strain of  $0.01s^{-1}$ . The samples were allowed to reach a steady-force value while held at the indicated extension, before the orientation measurement was made.