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Polymeric Helices with Submicron Dimensions for MEMS Devices

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ABSTRACT

Polymer helices with submicron dimensions have been fabricated from a variety of isotropic and liquid crystalline polymers with storage moduli ranging from 38MPa to 1.9GPa (measured at 1Hz, room temperature). These helices are made using a double templating process, in which a thin film comprised of independent helical structures deposited using glancing angle deposition (GLAD) acts as the master. In our process the 'positive' structure of the master is copied into a polymer 'negative', which then itself acts as a template for the final film of polymer helices. Liquid crystalline polymers are of particular interest for use in MEMS because highly ordered liquid crystalline polymers can be actuated by exposing them to a stimulus (such as heat) that causes a decrease in order, leading to a reversible, macroscopic change in shape. The phase behavior, optical properties, and mechanical properties of planar aligned monoacrylate liquid crystalline polymers with varying crosslinker content are investigated, in order to determine the composition that will yield the largest deformations upon heating. We find that films with the lowest crosslinker content investigated (2.5%) undergo the largest reduction in birefringence as they are heated, corresponding to a loss in order. However, we also observe that the films with the highest crosslinker content investigated (10%) undergo the largest physical deformation upon heating. SEM images illustrating the deformation of liquid crystalline polymer helices as they are heated are also presented.

Keywords: MEMS, microfabrication, liquid crystalline polymers, glancing angle deposition

1. INTRODUCTION

Polymers are currently being investigated for use in MEMS devices owing to a variety of advantageous characteristics, including: low cost, ease of processing, and tunable mechanical and chemical properties^{1,2}. There are a variety of polymers that can be made to deform reversibly by varying actuation mechanisms currently being explored for use in MEMS. These include polymers that change shape in response to electric fields (electroactive polymers)^{3,4}, polymers that undergo a change in volume during electrochemical reactions (conjugated or conductive polymers)^{5,6}, and isotropic polymers that expand and contract when heated and cooled⁷. Due to the isotropic nature of these materials the direction of actuation motion must be controlled using either anisotropic stimuli (such as a directional electric field in the case of electroactive polymers), or in many cases by incorporating the material into a bilayer. In a bilayer bending motion is achieved as the active material expands or contracts with respect to another layer with a different thermal expansion coefficient. Thus the direction of motion is not dictated by the active polymer directly.

Liquid crystalline polymers are strong candidates for use in MEMS devices, as they can be made to deform reversibly with large amplitude in controlled directions⁸⁻¹¹. For example, nematic elastomers have been extensively investigated for use as artificial muscles¹². These elastomers typically consist of long strands of side or main-chain liquid crystalline molecules connected by highly flexible cross-linking groups. A high degree of nematic alignment of the mesogenic molecules can be achieved before cross-linking by applying a mechanical deformation to the system. When the material is heated towards the isotropic phase the order of the system is strongly reduced, resulting in a net physical contraction in a direction parallel to the director, and expansion in the directions perpendicular to the director. Materials with dimensions in the mm to cm range that expand reversibly to 1.6 times their original length when heated have been

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demonstrated for side-chain liquid crystalline elastomers, and even higher deformations (up to 4 times) have been achieved using main-chain liquid crystalline elastomers^{11,13}.

Alignment techniques adapted from the display industry can be used to make thin films of liquid crystalline polymers which deform much differently from the mechanically aligned samples described above. For example, thin films around 15 μ m thick in which the mesogens are arranged in a splayed configuration can be produced by polymerizing the sample between layers of polyimide, which have been treated to align liquid crystals in a planar configuration at one surface and in a homeotropic configuration at the other¹⁰. Because the director is parallel to one surface and perpendicular to the other, and the thermal expansion coefficient is dependent on orientation, one side of the film expands in the plane of the film when heated, and the other contracts, similar to a bilayer. This results in a net reversible bending motion from a flat to tightly curled state.

While the anisotropic mechanical properties and actuation mechanisms of liquid crystalline polymers make them attractive for use in MEMS, most of the work described in the literature focuses on the behavior of macroscopic samples, rather than on microfabricated ones. There is some description in the literature of microfabrication of liquid crystalline polymer for MEMS packaging, but in this case liquid crystal polymer is chosen for its moisture resistance rather than for its anisotropic properties¹⁴. Miniaturized liquid crystalline polymer tactile and flow sensors have also been patterned from commercial thin films using conventional lithographic and etching techniques². However the liquid crystalline polymer employed was designed to undergo minimal thermal expansion in an isotropic fashion, unlike in the actuator applications described above.

The purpose of the work described in this paper is to develop microfabrication techniques to shape isotropic and liquid crystalline polymers on the microscale. We have developed a technique to manufacture polymer helices with submicron features that resemble microscopic springs, and we have demonstrated this process with a range of polymers including highly cross-linked acrylates and liquid crystalline polymers. The process used to fabricate these helices is described in section 2. In section 3 we describe the phase behavior, the optical properties, and the mechanical properties of liquid crystalline polymers with varying composition, with an emphasis on tuning these properties to maximize the deformation of these materials. In section 4 the temperature driven actuation of liquid crystalline polymer helices is illustrated using SEM images.

2. FABRICATION OF POLYMER HELICES

2.1 Microstructuring

Traditionally, fabrication techniques and materials in MEMS have been heavily adapted from those used by the microelectronics industry. These techniques are predominantly planar, and focus on patterning inorganic materials such as silicon and various metals, which are not necessarily ideal materials for use in MEMS. In order to pattern polymer helices, we have developed a two-step templating process. In the first step, a thin film with helical pores is fabricated in a templating process in which an inorganic thin film deposited using glancing angle deposition (GLAD) acts as the master. The 'positive' structure of this film is replicated into a 'negative' film (the intermediate template), which acts as the mould for the fabrication of the final polymer helices. For the case of liquid crystalline polymer helices, it is expected that the surface of the intermediate template will dictate the alignment of the liquid crystals within the pores, enabling anisotropic deformation on heating.

2.2 Glancing angle deposition (GLAD)

Glancing angle deposition (GLAD) is a physical vapor deposition process that can be used to deposit large-area thin films comprised of independent microstructures with controllable architectures^{15,16}. During this process the substrate is held at an oblique angle of incidence with respect to the vapor source, as shown in Figure 1. Provided that the vapor source is sufficiently collimated and that the mobility of the atoms arriving at the substrate is sufficiently low, some areas of the substrate are effectively 'shadowed' by material that has already been deposited, leading to the growth of independent structures. For the case of a stationary substrate, the resulting film will resemble a forest of slanted posts, with diameters ranging from 50nm to 150nm. Since the direction of growth generally tracks the direction of the source, in-plane substrate motion can be incorporated into this process in order to engineer the shape of the deposited structures. For example, if the substrate is frequently and abruptly rotated 180° during growth, the overall shape will resemble a zig-zag. If the substrate is rotated continuously the deposited film is helical in nature, where the pitch and handedness are determined by the speed and direction of rotation. In the limiting case where the pitch is

Figure 1: A schematic diagram of the GLAD set-up.

smaller than the column diameter, a 'vertical post' architecture results. Examples of some of these different types of structures are found in Figure 2. Typical materials from which GLAD films can be made include Si, Ti, Cr, SiO₂, and MgF₂.

Figure 2: SEM images of slanted post, zig-zag, and helical films deposited by glancing angle deposition.

2.3 GLAD and liquid crystals

The interaction between liquid crystals and GLAD films has been previously investigated for applications in the field of optics¹⁷. It has been shown that when nematic liquid crystals are added to a helical GLAD film this system selectively transmits and reflects circularly polarized light of opposite and like handedness, respectively, and that the wavelength of reflection is determined by the pitch of the GLAD film. A similar but much weaker effect is also seen for GLAD films without liquid crystals. This suggests that the GLAD film acts as an alignment layer for the liquid crystals. We hope to see a similar alignment for our liquid crystal polymer helices, only in this case it will be the surface of the intermediate template, which is cast from a GLAD film, that will dictate the arrangement of the liquid crystals.

2.4 GLAD and MEMS

Microhelices and microcantilevers fabricated using the GLAD technique have been previously explored for use as resonant devices in MEMS-type applications¹⁸. Microhelices have been shown to behave like micro-scaled springs, undergoing much larger deformations in response to an applied force than solid films of the same material. The stiffness of a SiO helical film was determined to be up to 10³ times lower than for a dense SiO film. However, one limitation of

using GLAD-type structures as resonant devices is the high modulus of the materials from which the structures can be made. The materials that can be easily deposited using GLAD are limited to those that can be deposited by physical vapor deposition processes such as sputtering or evaporation, including elemental materials such as Ti, Ni, and C or simple compounds such as SiO_x and MgF_2 . These materials generally have storage moduli in the range of tens to hundreds of GPa. It has been suggested that materials with lower moduli such as polymers may be more suitable for study as resonant devices.

2.5 Intermediate template fabrication

In order to make polymer spring-like structures, an intermediate template consisting of a solid thin film with helical pores is required. This thin film is the 'negative' three-dimensional image of a 'positive' GLAD film. An appropriate alignment layer can therefore be fabricated in a replication process in which the GLAD film acts as the master or mould. This 4-step process is illustrated schematically in Figure 3.

Figure 3: Schematic diagram of the intermediate template fabrication process. (a) GLAD film master. (b) The GLAD film is filled in with the material that will form the intermediate template. (c) The second material is etched-back in order to allow access to the master film. (d) The GLAD film is etch-removed, leaving the intermediate template.

In the first step of the process a GLAD film with the desired helical architecture is deposited, typically by evaporation of SiO_2 (Figure 3a). In the second step this film is filled in with another material, which will comprise the intermediate template (Figure 3b). This can be accomplished using a variety of materials and techniques, for example nickel can be deposited by electrodeposition (provided that the GLAD film is deposited on a metal electrode), or solution processable polymers such as spin-on glass can be spin coated into the film^{19,20}. Since this material typically both coats the GLAD film and forms a supplementary layer on top, in the third step of the process the excess material is etch-removed (Figure 3c). In the final step the master film is removed by wet-etching, leaving a solid film with microstructured helical pores (Figure 3d). For our system we have selected a standard lithographic photoresist as the intermediate template for a number of reasons. Photoresist can easily be spin-coated to form a uniform layer with a high degree of repeatability. Additionally, exposed photoresist is soluble in a variety of organic solvents, and can therefore be removed after it has fulfilled its function as an intermediate template.

Microstructured intermediate templates made from electrodeposited nickel and a spin-coated multifunctional acrylate blend (dipentaerythritol pentaacrylate and ethylene glycol dimethacrylate) are shown in Figure 4.

Figure 4: Examples of microstructured intermediate templates. Left: Electrodeposited nickel. Right: Spin-coated polymer.

2.6 Fabrication of isotropic polymer helices

Fabrication of isotropic polymer helices from a variety of multifunctional acrylates has been demonstrated²¹. These helices were made using a templating process in which the intermediate template described in section 2.5 acts as the mould, as illustrated schematically in Figure 5.

Figure 5: Fabrication of polymer helices from the intermediate template (a). (b) The intermediate template is filled with a solution of monomers, which is subsequently polymerized. Both layers are then removed from the original substrate, and the intermediate template is dissolved. (c) The sample is flipped over, and the large cap of excess polymer acts as the new substrate.

In this process a mixture composed of acrylate monomers and photoinitiators is added in vacuum to the intermediate template, filling the pores and forming a large cap on top. The mixture is then polymerized by exposure to UV light in N_2 . The intermediate template/acrylate layer is removed from the substrate, and the intermediate template is dissolved in isopropyl alcohol. The remaining acrylate layer is flipped over, and the large cap provides mechanical support for the helices. Samples sizes are typically on the order of a few cm^2 .

Isotropic polymer helices have been fabricated from the following four acrylates: pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate (a mixture of tetra, penta and hexaacrylates), and a dipentaerythritol pentaacrylate/hexaacrylate mixture. An example of tetraacrylate helices is shown in Figure 6.

Figure 6: Isotropic polymer helices, made from pentaerythritol tetraacrylate.

The moduli of solid thin films of the four different multifunctional acrylates was measured using dynamic mechanical analysis (DMA, Q800, TA Instruments). Samples were prepared by polymerizing the monomers in glass cells approximately $100\mu m$ thick, in which the cell thickness was controlled by 2 layers of tape and 1 layer of glue containing $18\mu m$ spacers. The samples were removed from the glass cells and measured in tension using a thin film clamp at room temperature. The thickness of each sample was measured using a micrometer. The results are shown in Figure 7.

Figure 7: Storage modulus of multifunctional acrylate thin films (100 μ m thick), measured at room temperature.

All four films behave as glassy polymers, with storage moduli on the order of only a few GPa. This is much lower than the modulus of SiO (92GPa)¹⁸, which is the material used to make the helical films that were studied as resonant devices. These polymer springs are therefore expected to be much more compliant.

2.7 Fabrication of liquid crystalline polymer helices

Liquid crystalline polymer helices can be fabricated in a similar process as the isotropic polymers described in section 2.6, with some minor modifications. Since the liquid crystalline monomer mixture is crystalline at room temperature, it is first heated into the isotropic region (61°C), and applied to the intermediate template. The intermediate template and monomer mixture are then cooled into the nematic region (53°C). It is expected that the alignment of the liquid crystals will be dictated by the surface of the pores of the intermediate template. The mixture is then polymerized by exposure to UV light in N₂. The polymer layers are removed from the substrate as described in the previous section, and the intermediate template is dissolved in isopropyl alcohol. Again the large cap of excess liquid crystal material acts as the substrate. SEM images of liquid crystalline polymer helices and the template from which they were made are shown in Figure 8.

Figure 8: Left: Photoresist intermediate template. Right: Liquid crystalline polymer helices.

3. LIQUID CRYSTALLINE POLYMER

3.1 Composition of liquid crystalline polymer

The liquid crystalline monomers used in our work are shown in Figure 9:

Figure 9: Liquid crystalline monomers. Phase transitions on heating are also shown.

Each of these molecules has acrylate groups on one or two ends that can be polymerized by free radical polymerization in the presence of an appropriate photoinitiator (Irgacure 369, CIBA) and UV light. The first molecule is a monoacrylate with a liquid crystalline phase. The second molecule, C6M, is a liquid crystalline diacrylate that acts as a crosslinker, joining together the long polymer chains of monoacrylates. A schematic drawing of a film composed of monoacrylates and diacrylates is shown in Figure 10, where the monoacrylates are shown as light colored molecules and the diacrylates are shown as dark colored molecules.

Figure 10: Schematic drawing of a planar-aligned liquid crystalline polymer film, composed of mono- and diacrylate molecules.

The liquid crystals in Figure 10 are shown in a highly ordered planar configuration, where the long axis of each molecule points in the same direction in the plane of the film (along the director). This type of polymer film can be made by using layers of rubbed polyimide to align liquid crystalline monomers, which are then polymerized in the nematic phase. Actuation can be achieved by heating the sample towards the nematic to isotropic transition point, thereby reducing the order of the liquid crystals in the system. Theoretically, this loss in order should result in a macroscopic change in shape of the material, since the material should expand in a direction perpendicular to the director, and contract in the direction along the director, as illustrated in Figure 11.

Figure 11: Schematic drawing of the deformation of a planar-aligned liquid crystal film on heating due to the reduction in order.

In order to achieve large deformations a number of conditions must be met. In the nematic phase of the polymer the liquid crystals must be highly ordered to ensure that they can undergo a significant change in orientation when they are heated. The crosslinker content must be high enough to couple the change in orientation of the liquid crystalline molecules to an overall deformation of the polymer chains. Conversely, if the crosslinker content is too high the network will be rigidly locked into place and the isotropic phase will be completely suppressed.

To maximize the order of the system in the nematic phase, we found that it was necessary to add a small component of non-liquid crystalline monomer to our system. This molecule is shown in Figure 12.

Figure 12: Non-mesogenic monoacrylate.

Without the presence of this molecule, a smectic phase that is not present in the monomer mixtures forms in polymers with low crosslinker concentrations. As the nematic monomers polymerize the resulting polymer forms a smectic phase, resulting in inhomogeneous samples. Even though order is increased on a local scale because the polymer is smectic rather than nematic, overall the order of the bulk material is disrupted. Thus 495 is added to prevent the smectic phase from forming. The role of the 495 molecule can be demonstrated using differential scanning calorimetry (DSC, Q1000, TA Instruments), which maps the heat flow into and out of a sample as it is heated and cooled. Peaks in the DSC curves generally indicate that a phase transition is taking place. DSC curves were collected for a series of polymerized samples with constant crosslinker content (5%) and varying ratios of 495 to 716p, as shown in Figure 13. The curves shown are from the second heating cycle, since the first heating cycle was used to eliminate the thermal history of the sample. Samples were heated and cooled at a rate of 10°C/min.

In the absence of 495, the polymer undergoes 2 distinct phase transitions, from smectic to nematic at around 70°C, and from nematic to isotropic at just over 130°C. When just 5% of the 716p is replaced with 495, the smectic to nematic transition effectively disappears, indicating that the smectic phase is suppressed. At increasing concentrations of 495, the nematic to isotropic peak decreases in magnitude and shifts to lower and lower temperatures, suggesting that the nematic phase is becoming destabilized, and the overall order of the liquid crystals is being reduced. Therefore in our systems we keep the ratio of 716p to 495 constant at 19:1 in order to suppress the smectic phase while maintaining as much order as possible.

Figure 13: DSC curves for varying ratios of 716p to 495, with a constant crosslinker content of 5% (2nd heating cycle).

DSC can also be used to measure the effect of changing the crosslinker concentration of the sample, as shown in Figure 14. For 0% crosslinker the smectic phase is again seen, indicating that the crosslinker itself also reduces some of the order in the system. As the crosslinker content is increased the peaks become broader, indicating that the transitions occur more gradually as a function of temperature. However, at very high content (100%) the nematic to isotropic transition is absent, and the polymer retains its nematic ordering at very high temperatures. The amount of crosslinker must therefore be kept low (<10%) in order to ensure that the material will deform when heated.

Figure 14: DSC curves for varying amounts of crosslinker and constant ratio of mesogenic to non-mesogenic monomer (19:1 ratio of 716p to 495), (2nd heating cycle).

Increasing the crosslinker concentration also increases the modulus of the material. Without the inclusion of the crosslinker, the polymerized monoacrylate is a viscoelastic fluid, with a modulus of around 38MPa (as measured using DMA, Q800, TA Instruments, 1Hz, 30°C). As the content of crosslinker is increased to 10%, the modulus at room temperature increases to around 85MPa. The relationship between crosslinker content and modulus is shown in Table 1. These measurements were made on samples 55μm to 67μm thick that were polymerized in a planar configuration between glass slides coated with rubbed polyimide. All measurements were made in the direction parallel to the long axis of the liquid crystals. For all samples the modulus is strongly dependent on temperature, since the glass transition temperature for these materials is around or just above room temperature. Therefore the modulus falls off rapidly as each sample is heated.

Crosslinker	Modulus at 30°C
0%	38MPa
2.5%	48MPa
5%	69Mpa
10%	85MPa

Table 1: Storage modulus as a function of crosslinker content.

The modulus of a thin film ~18μm thick composed entirely of crosslinker was also measured parallel to the long axis of the liquid crystals and was found to be 1.5GPa. It should therefore be possible to vary the modulus of this system from 38MPa to 1.5GPa by varying the crosslinker content.

3.2 Predicting deformation in planar thin films from optical measurements

It is difficult to predict how liquid crystalline polymer helices will deform when heated, since the deformation is strongly dependent on how the liquid crystals are aligned in the material, which is not trivial to determine. As a first approximation however, we can predict how we expect a monodomain planar-aligned thin film to deform by examining the optical properties of a liquid crystalline film polymerized in a cell in which a glue containing 18μm spacers provides a gap between layers of rubbed polyimide.

A uniaxial liquid crystalline polymer thin film in which all of the molecules are aligned along a single director in the plane of the film exhibits anisotropic optical properties, owing to the anisotropy of the mesogenic units. Liquid crystals have one index of refraction in the direction parallel to their long axis (the extraordinary index n_e), and another index in the directions perpendicular to this axis (the ordinary index n_o). The birefringence of a material ($\Delta n = n_e - n_o$) can be determined by placing the film at a 45° angle between crossed polarizers, measuring the transmission as a function of wavelength, and fitting the resulting curve to the two-term Cauchy equation. Since the birefringence is dependent on the alignment of the liquid crystals, it is expected to decline as the polymer is heated and the order is reduced. This is indeed observed for the free-standing films with 10% and 2.5% crosslinker (and 19:1 ratio 716p to 495), as shown in Figure 15:

Figure 15: Change in birefringence as a function of temperature for free-standing thin films 16-18μm thick.

A steady decline in birefringence is seen as the films are heated. Above 140°C the birefringence in the 2.5% crosslinker film is too low to be measured, indicating that the liquid crystals are in an isotropic phase. At the temperatures measured a transition for the 10% film was not observed.

The change in birefringence can be related to an overall change in length of the film by first determining the order parameter S . S is a measure of how well the liquid crystals are aligned with the respect to the director, and can be related to the orientation of the liquid crystals using the following equation: $S = 1/2(3\langle\cos^2\theta\rangle - 1)$, where θ is the angle between the director and the long axis of the liquid crystal. Once the order parameter is estimated at an initial and final temperature from the optical data, it can be used to determine the average alignment of the liquid crystals in the sample with respect to the director. In an ideally ordered state $S = 1$, and all of the liquid crystals are perfectly aligned with the director. In this case $\langle\cos^2\theta\rangle = 1$. In a perfectly isotropic state $S = 0$, and $\langle\cos^2\theta\rangle = 1/3$.

The change in length of the film can be estimated from $\cos\theta$. In the perfectly ordered state all liquid crystals are aligned with the director, $\cos\theta = 1$, and the overall length can be taken as L_o . In the isotropic phase $\langle\cos\theta\rangle = 0.577$, giving an overall length of around $0.6L_o$, or a contraction of around 40%. However, for our films the liquid crystals will not be perfectly aligned, so the contraction is expected to be less. The initial order parameter can be estimated using equation [1]²²:

$$S = \left(\frac{\tilde{a}}{a_{\parallel} - a_{\perp}} \right) \frac{n_e^2 - n_o^2}{\tilde{n}^2 - 1} \quad [1]$$

where $\tilde{n}$ is the average index of refraction in the ordered phase, and can be determined from the equation: $\tilde{n}^2 = (n_e^2 + 2n_o^2)/3$, and $\tilde{a}$, $a_{\parallel}$ and $a_{\perp}$ are the average, parallel and perpendicular electronic molecular polarizabilities of the liquid crystals. For the 2.5% film n_o was measured using an Abbe Refractometer ($n_o = 1.511$), and this value is assumed to be constant with temperature up to the clearing point. The extraordinary index of refraction n_e can therefore be calculated from the data represented in Figure 15. The polarizability term $(\tilde{a}/(a_{\parallel} - a_{\perp}))$ in the above equation can be estimated using the Haller method²³: $-\log[(n_e^2 - n_o^2)/(\tilde{n}^2 - 1)]$ is plotted against $-\log(1 - T/T_c)$, and the data is fit with a linear curve, which is then extrapolated to $T=0$, where $S = 1$. Equation [1] can then be solved for the polarizability term, which is found to be 2.49. The Haller plot is shown in Figure 16.

Figure 16: Haller plot for 2.5% crosslinker film (19:1 ratio of 716p to 495). This plot is used to estimate $(\tilde{a}/(a_{\parallel} - a_{\perp}))$ for the film.

Using this information the order parameter at room temperature for the 2.5% film is calculated to be 0.72, so if the sample is heated all of the way to the isotropic phase the maximum contraction will be 32%.

3.3 Measured deformation in planar thin films

The deformations in planar thin films can be measured using thermal mechanical analysis (TMA, Pyris), in which the ends of the films are clamped and the length of the sample is measured as it is heated and cooled. Samples around 70 μm thick were prepared by polymerizing a monomer mixture between pieces of glass coated with rubbed polyimide, and separated by a spacer. The increased thickness of the samples made them tougher and easier to handle than the thinner films used in optical characterization. However, the large gap between alignment layers may also have reduced the alignment of the liquid crystals far from the surface, leading to an overall reduction in order parameter, thereby reducing the maximum change in dimension achievable.

The deformation as a function of temperature was measured for films containing 5% and 10% crosslinker (and a 19:1 ratio of 716p to 495). Both films were clamped such that the deformation was measured in a direction parallel to the director, and the samples were therefore expected to contract when heated. The second heating curve for each sample is shown in Figure 17. These deformations are fairly reversible, since non-reversible deformations such as relaxation took place during the first heating cycle.

Figure 17: Contraction of liquid crystalline polymer films parallel to the director as a function of temperature.

Surprisingly, the 10% film achieved a larger contraction than the 5% film (~16% at 160°C vs. ~8%). This unexpected trend was also confirmed by measuring the length of free-standing films heated on a hotplate. These results are in contradiction with the optical data, which predicts that a larger change in order parameter (and therefore a larger deformation) should be achievable in films with lower crosslinker content. However, we suspect that the films with lower crosslinker content are actually deforming less because the change in alignment of the liquid crystals is not sufficiently coupled to the network (non-affine deformation). This would mean that while the liquid crystals are indeed undergoing a decrease in order as they are heated, the loosely joined strands of monoacrylates are not sufficiently connected together for this to result in a macroscopic change in shape of the film. Further work is required to verify this hypothesis.

4.0 ACTUATION OF LIQUID CRYSTALLINE POLYMER HELICES

Preliminary measurements of the deformation of liquid crystalline polymer helices have been made by heating helical samples while imaging them using scanning electron microscopy (SEM, Philips XL 30 ESEM- FEG). The samples were coated with approximately 10nm of gold for imaging, which may impede deformations. However, this layer of gold is critical to achieve high-resolution images and to prevent the beam from damaging the sample.

SEM images of a sample consisting of a 19:1 ratio of 716p to 495 with 10% crosslinker are shown at room temperature and 86°C in Figure 18. Both images are at identical magnification. The helices on the right are visibly compressed with respect to the helices on the left. For these images the sample was scanned in the direction perpendicular to the film thickness in order to ensure that the apparent change in thickness was not due to drifting of the sample during imaging. The overall compression is estimated to be ~5%, which is slightly higher than the change in dimension of the planar aligned sample shown in Figure 17 (~3%). Careful inspection of the area around which the images were taken indicates that the samples were not burned during imaging, and the contraction therefore did not result from exposure to the electron beam.

Figure 18: Heating of helical samples composed of a 19:1 ratio 716p to 495, with 10% crosslinker. Left: At room temperature (~25°C). Right: Heated to 86°C.

A similar experiment was conducted with a 2.5% sample, only this time the sample was heated to 133°C. The image quality is slightly degraded in the last image since a faster scanning time was used to prevent the image from becoming distorted by drift during imaging. Nonetheless, the compression is visible. A slight change in the angle between the sample and the beam occurred during imaging. This can be seen in the SEM images since more of the top layer of the sample is visible in the image at room temperature. From these images we can estimate that the angle between the cross-section of the helical film and the beam shifted from around 70° to around 88° during heating. However, this change in angle is not responsible for the apparent reduction in thickness, since the apparent thickness has a cosine dependence, and should actually be higher when the sample is more perpendicular to the beam. If anything the actual change in thickness could be up to 5% higher than it appears. From the images in Figure 19 the apparent overall contraction from room temperature is ~9.5% (or ~4% from 25°C to 90°C).

Figure 19: Heating of helical samples composed of a 19:1 ratio of 716p to 495 and 2.5% crosslinker. Left: At room temperature (~25°C). Middle: 90°C. Right: 133°C. (Note: the scale is identical for all images).

Further work is required to quantitatively characterize the change in thickness and pitch of the helices, and to demonstrate the reversibility of this deformation.

5. CONCLUSIONS

We have demonstrated a templating technique for patterning polymers into three-dimensional helices with submicron dimensions. This process was demonstrated with glassy high modulus isotropic acrylates, as well as with rubbery liquid crystalline polymers whose modulus could be tuned by varying the ratio of diacrylate to monoacrylate molecules. The anisotropic properties of liquid crystalline polymer are of interest for MEMS since materials with specific director orientations can be used to design actuators that will deform in specific directions when stimulated. In this paper we have focused on temperature-responsive materials that deform reversibly when heated and cooled. Planar thin films have been shown to contract along the director when heated, as a result of a reduction in order. The contraction of films with varying crosslinker content were compared, and it was found that films with lower crosslinker content contracted considerably less than expected based on the reorganization of the liquid crystals that was observed optically. This may be due to insufficient coupling of the liquid crystals with the polymer network. Microstructured liquid crystalline polymer helices were also found to contract in a spring-like manner when heated.

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