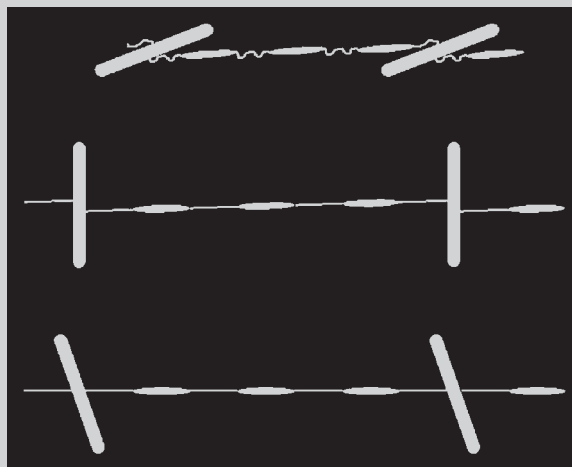


**Summary:** The morphology and deformation behaviour of a liquid crystalline polymer consisting of both laterally attached transverse rods and terminally attached rods were studied. A plaque specimen of the polymer was prepared using the melt-compression method, which exhibited highly anisotropic Poisson's ratio behaviour. In its through-thickness direction, its Poisson's ratio was approximately 0.54, and in the in-plane it was approximately 0.43. This anisotropic behaviour is explained by the anisotropic morphology of the polymer plaque resulting from its compression preparation. The high Poisson's ratio in the through-thickness direction is due to the unusual chain structure of the polymer. A simple analytical model is presented to describe the non-linear strain dependent Poisson's ratio behaviour of the material.



Representation of the arrangement of the main chain and transverse rod molecules, prior to, during, and at complete extension.

# Morphology and Deformation Behaviour of a Liquid Crystalline Polymer Containing Laterally Attached Pentaphenyl Rods

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## Introduction

Liquid crystalline polymers (LCPs) with unusual architectures have attracted much attention due to their potential scientific and technological applications.<sup>[1,2]</sup> Examples are LCPs consisting of laterally attached mesogens in their main chain.<sup>[3–7]</sup> Recently, we have proposed a molecular

design approach based on liquid crystalline polymers consisting of laterally and terminally attached rods to achieve negative Poisson's ratio or 'auxetic' behaviour.<sup>[8,9]</sup>

In common with most other materials, solid polymers usually become thinner when stretched. Thus the ratio of the transverse resultant strain to the longitudinal applied strain is negative. The Poisson's ratio is calculated as this ratio multiplied by  $-1$  so as to produce a conventionally positive Poisson's ratio. However, a few materials have a negative Poisson's ratio, termed auxetic, in which both strains are either compressive or tensile. These materials become wider when stretched and thinner when compressed. Examples of auxetic behaviour include reticulated polymer foams<sup>[10–13]</sup> and some microporous

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polymers.<sup>[10,11,14]</sup> The main problem with these materials is that their tensile stiffness and strength of these materials are relatively poor. If the auxetic behaviour could be engineered at the molecular level instead of the micro or macroscopic then other properties, such as stiffness and strength, could be controlled and improved. Efforts have been made to mimic at the molecular level the microstructures of auxetic materials in several polymer materials, based on the inverted honeycomb structure.<sup>[15,16]</sup> However to date there are no successful reports regarding synthesis of a polymer with auxetic behaviour resulting from a molecular level mechanism.

Our molecular approach to auxetic polymeric materials is based on a LCP containing both lateral and terminally attached rods, as shown in Figure 1. In a nematic phase the terminally attached mesogenic groups of the main-chain and the laterally attached transverse rods are oriented along the local nematic director. Under tensile strain the re-orientation of the transverse rods may act to push the neighboring polymer chains apart. If the laterally attached rods are long enough, the polymer chain may thus exhibit auxetic behaviour.

In a previous paper we reported on the synthesis and characterisation of LC trimers consisting of laterally attached terphenyls.<sup>[17]</sup> However, the length of the terphenyl rod was calculated to be the minimum length necessary for the polymer to exhibit auxetic behaviour. In this work we have synthesised another class of LCP based on longer laterally attached pentaphenyl rod. Here, we will also examine the morphology and deformation behaviour of an LCP containing transverse pentaphenyl rods. We also present a simple model based upon the proposed geometry of the chain and transverse rods to describe the behaviour of the material. Such models are useful in themselves as they facilitate the engineering of the molecule but they may also provide evidence of deformation mechanisms.

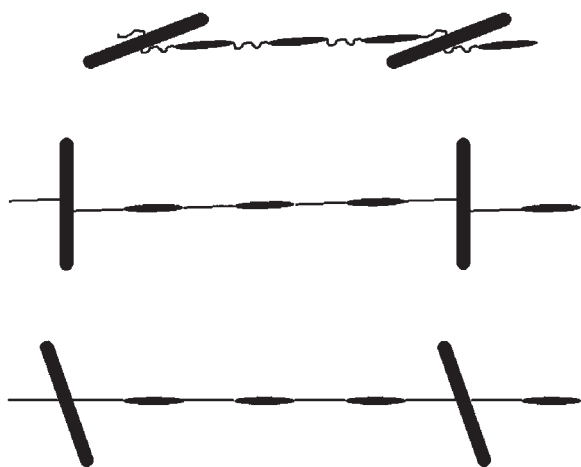


Figure 1. Representation of the arrangement of the main chain and transverse rod molecules, prior to, during, and at complete extension.

## Experimental Part

### Synthesis

Compound **1** (0.995 g, 1 mmol) and 4,4'-dihydroxy-1,10-diphenoxyalkane **2** (0.538 g, 1.5 mmol) were dissolved in 100 ml of water with sodium hydroxide (0.22 g, 5.5 mmol), then benzyltriethylammonium chloride (0.5 g, 2.19 mmol) was added. This mixture was transferred to a blender and slowly stirred while a solution of 4,4'-dichloroformyl-1,10-diphenoxyalkane **3** (1.128 g, 2.5 mmol) in 75 ml dichloromethane was added rapidly. The mixture was stirred at maximum speed for about 12 min and another 75 ml dichloromethane was added in three portions during this time. The resulting emulsion was poured into 300 ml of acetone. This mixture was stirred in 50 °C for 2 h and let cooled to room temperature. Next day the precipitated polymer was filtered and thoroughly washed with water and methanol, and then it was air dried to give pentaphenyl-rod-containing polymer **4**.

DSC: 148 °C, 203 °C (endotherms).

Polarized optical microscope: N 202 I.

FTIR (KBr): 3 424 (broad, weak), 2 920, 2 850, 1 723, 1 620, 1 512, 1 196, 1 070, 695  $\text{cm}^{-1}$ .

<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 0.98$  (t, 3H,  $\text{CH}_3$ ), 1.20–1.90 (42H,  $\text{CH}_2$ ), 2.62 (t, 2H,  $\text{ArCH}_2$ ), 3.85–4.10 (10H,  $\text{OCH}_2$ ), 6.9–8.2 (20H,  $\text{ArH}$ ).

### Polymer Characterization

The polymer samples were characterized by solution NMR ( $\text{CDCl}_3$ ) to verify the incorporation of transverse rod component, using a Bruker AC-300. Chemical shifts reflect the center of splitting patterns or envelopes. IR spectra were obtained using a Mattson Instruments Polaris FT-IR. Thermal analyses curves were obtained using a TA Instruments DSC 2920. Heating rates were 10 °C  $\cdot$  min<sup>-1</sup> unless otherwise specified. All scans were obtained using aluminium pans and nitrogen as the purge gas. Optical data was obtained using a Leica optical microscope (Laborlux 12 POLS) with a Mettler Toledo PP82HT heating stage. The nematic phase was identified from its fine-grained texture, which was opalescent when sheared. The related parent polymer, without laterally attached transverse rods is a known nematic polyester<sup>[18]</sup> having an identical grainy nematic optical texture. The difficulty in forming a classical mesophase optical texture is typical for these high molecular weight polyesters. Molecular weights of selected polymers were obtained from GPC combined with light scattering detection.

### Sample Fabrication

The polymer plaque was prepared using the melt compression method. The sample was placed between two glass slides which were covered with poly(tetrafluoroethylene) (PTFE) film and the assemblage placed on a hot stage. The purpose of the PTFE film was to provide a low friction smooth surface of polymer plaque. The sample was then heated to its nematic temperature at which the polymer became translucent. The sample was then compressed by applying pressure on the upper glass slide using a 2 kg lead mass. The compression and

temperature were kept constant for 2 min, then the stage was switched off and the sample allowed to cool slowly with the lead mass remaining. The thickness of the sample was approximately 1 mm. The same plaque showed surface striations that indicated the direction of nematic flow and thus the nematic director. Two samples were prepared: a fibre was drawn out of a plaque at the nematic melt temperature by hand with a pair of forceps; and a powder sample was prepared by heating the polymer sample to its isotropic melt temperature and allowing it to cool to room temperature. The details of the monomer synthesis will be reported in a separate paper.<sup>[19]</sup>

### X-Ray Scattering

X-ray scattering tests were carried out on a Siemens Diffractometer XPD-700P with a gas filled 2-D detector at room temperature. CuK $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ , sample step =  $0.05^\circ (2\theta)$ .

### Deformation Behaviour

The mechanical behaviour of the plaque sample was characterised, in particular the Young's modulus and the Poisson's ratio. The Young's modulus is the stiffness of the material and is calculated as the slope of the linear portion of the stress strain curve. The Poisson's ratio is defined as the negative ratio of the true lateral strain to the applied true longitudinal strain.

A thin parallel sided strip was cut from the plaque in the direction in which shear was applied (in parallel to said surface striation), which we shall denote as the  $x$  axis. The second axis lying in the plane of the plaque (the in-plane direction) is the  $y$  axis, with the through-thickness direction as the  $z$  axis. The sample was held securely in a pair of specially designed grips. The grips were mounted on a universal testing machine especially for small specimens (designed and made in house). The specimen was deformed in tension for several cycles at approximately 0.01 mm/s at a stroke length of 0.1 mm. There was approximately 10 mm of specimen visible between the grips. The tests were performed at room temperature.

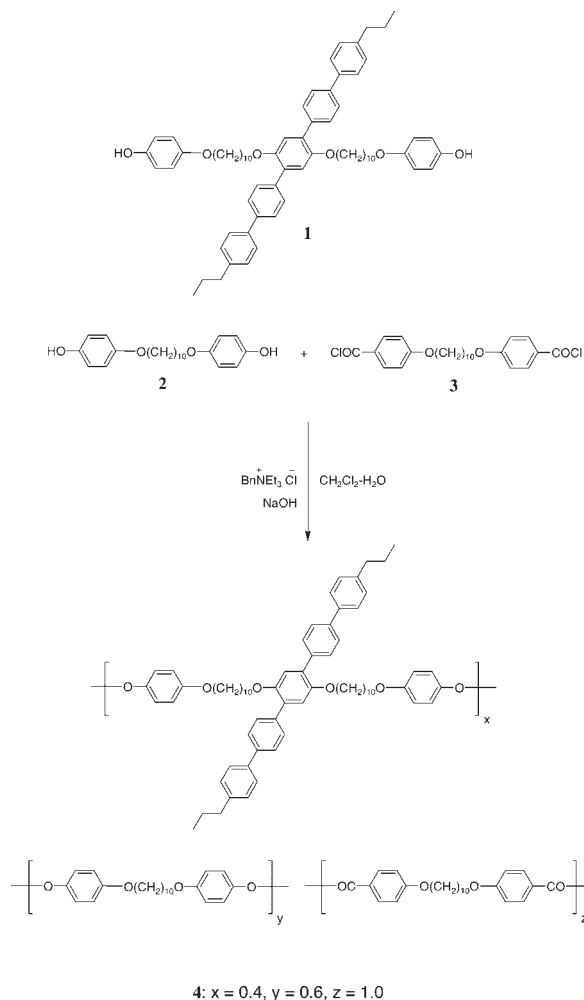
Stress was calculated as the tensile force divided by the cross sectional area of the specimen. Strains were measured indirectly via a video extensometer system ('Videoextensometer', Messphysik GmbH, Austria). The system requires a background contrasting to the specimen and contrasting markers to be mounted onto its surface. The edges of these markers are detected by the video extensometer and allow deformation in both the applied longitudinal and lateral directions to be detected.<sup>[20]</sup> True strains were calculated as

$$\varepsilon = \ln\left(\frac{l}{l_0}\right) \quad (1)$$

where  $l$  is the length and  $l_0$  its original value.

## Results and Discussion

The chemical structure of the polymer in this study is shown in Scheme 1. This polymer is a random copolyester with a molecular weight of about 100 000 as determined by the



Scheme 1. Phase transfer catalysis polycondensation of polymers.

light scattering method. The synthesis and characterisation of this class of polymers is reported in a separate paper.<sup>[19]</sup> This polymer exhibits a very sharp and intense liquid crystalline transition at  $203^\circ\text{C}$  on heating and a slight undercooled transition on cooling at about  $196^\circ\text{C}$ . Polarised light microscopy indicates that the polymer exhibits a nematic phase which is similar to its parent polymer (without laterally attached transverse rods). The polymer also shows a very weak crystallisation transition at about  $100^\circ\text{C}$  indicating very little crystallinity, as shown in Figure 2.

The results of the X-ray scattering tests on the plaque (un-oriented, 'powder') and fiber are shown in Figure 3. The powder scattering is dominated by a broad scattering at about  $20.5^\circ (2\theta)$ , which represents the intermolecular inter-chain interaction among non-bonded atoms in the polymer. The negligible crystallinity of the polymer can be attributed to the bulky nature of the laterally attached transverse rods, and the random chain structure of the polymer. In the low angle region at approximately  $6^\circ (2\theta)$  the powder shows only weak scattering. The scattering from the equator

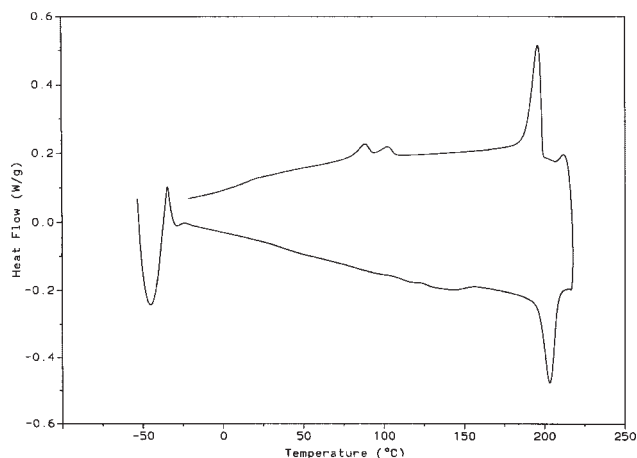


Figure 2. The DSC data showing weak crystallisation transition at approximately 100 °C.

represents the inter-chain interactions, and hence the distance among non-bonded atoms between the polymer chains. In the low angle region there is a four-point off-equatorial scattering with a medium intensity. The position of this four-point scattering corresponds to the weak low angle powder scattering. The four-point off-equatorial scattering indicates that the polymer is likely to have fluctuating regions of inter-digitated order consistent with a cybotactic nematic arrangement.

The position of the peak equatorial scattering is at  $19.5^\circ$  in the drawn fiber and  $20.5^\circ$  in the powder specimen, a shift of approximately  $1^\circ$ . These angles mean that the  $d$  spacings from the equatorial scattering of the fiber and powder specimens are  $4.55 \text{ \AA}$  and  $4.33 \text{ \AA}$  respectively, an increase of approximately 5%. The polymer specimen without the laterally attached rods, the parent polymer, shows a more normal decrease in inter-chain distance upon drawing into a fiber.<sup>[8]</sup> The equatorial scattering in Figure 4 also indicates that the material is becoming more ordered during the drawing process. The distribution of intensity is narrower in the drawn fiber than in the powder specimen.

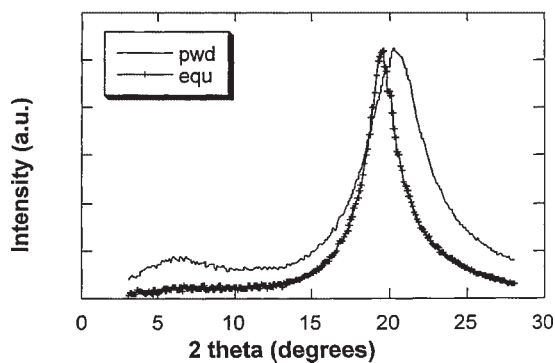


Figure 3. The X-ray diffraction results for the plaque and fibre specimens.

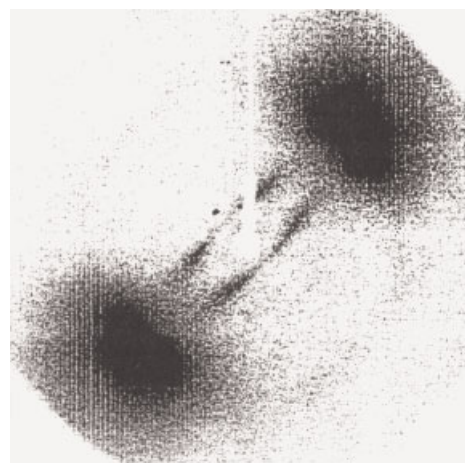


Figure 4. The four-point off-axis X-ray scattering pattern.

The likely implication of this increase in inter-chain polymer chain packing distance between the plaque melt and the drawn fiber was that the fiber became wider at the same time as it was extended during drawing out of the melt. It was not possible to measure strains during this process. Because the fiber specimen during this drawing process is probably undergoing plastic (permanent) deformation rather than elastic (recoverable) deformation, this phenomenon does not, in itself, indicate a negative Poisson's ratio as this can only be demonstrated during purely elastic deformation. It does however strongly suggest that the desired transverse rod rotation mechanism is functioning, at least at this temperature in this fiber.

X-ray scattering patterns in the through-thickness direction and the in-plane direction were obtained. It was observed that in the through-thickness direction the scattering showed some preferred orientation whilst the in-plane direction scattering shows a Debye ring, indicating a random packing of polymer chains. Figure 5 shows the integration of the X-ray scattering data from the through-thickness direction along  $2\theta$  ( $10\text{--}28^\circ 2\theta$ ). It was concluded

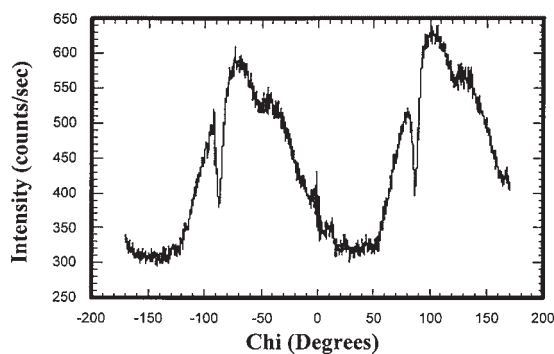


Figure 5. The integration of the X-ray scattering data from the through-thickness direction along  $2\theta$  ( $10\text{--}28^\circ 2\theta$ ).



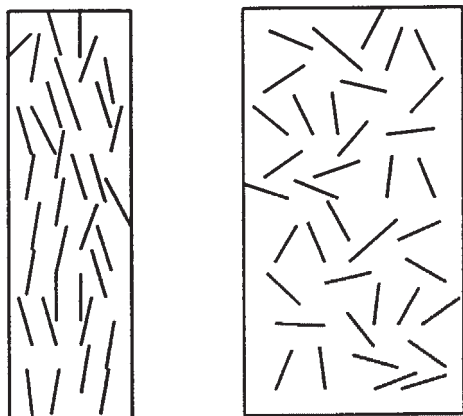


Figure 6. Schematic of our proposed packing structure in the through-thickness (left) and in-plane (right) directions.

that the polymer exhibits preferred orientation. Figure 6 shows a schematic diagram of our proposed packing structure of the polymer in the through-thickness and in-plane directions. The lines represent the polymer chains or at least the directors of the nematic domains.

The deformation behaviour of the plaque specimens are shown in Figure 7. The specimen was only loaded along the axis in which the plaque was sheared, in which presumably the molecules were aligned, defined as the  $x$  axis. The Poisson's ratios,  $\nu_{xy}$ ,  $\nu_{xz}$ , were 0.43 and 0.54 respectively, and the Young's modulus was 0.55 GPa. Predictions from a simple analytical model described below are also shown as solid lines.

The deformation behaviour raises some questions about why the polymer has an anisotropic Poisson's ratio, and why it exhibits a positive Poisson's behaviour in mechanical tests when it seems from X-ray scattering data that the inter-chain distance increased during the fiber drawing process. The anisotropic Poisson's ratio of the specimen

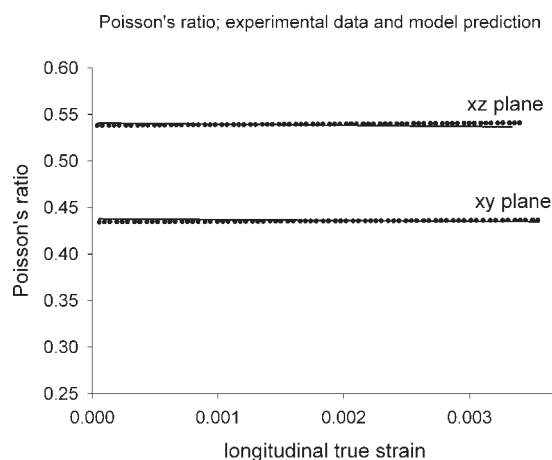


Figure 7. The Poisson's function of the plaque in the  $x$ - $y$  (in-plane direction) and  $x$ - $z$  (through thickness) planes (●). The model predictions for these two planes are also shown (—).

might be expected as a result of the orientation of the polymer chains; the sample preparation involved compression of the nematic melt between PTFE-coated glass slides and resulted in a differential rod flow direction that gave anisotropic structure to the sample plaque. It is, therefore, reasonable to expect that if the Young's modulus could be measured in the through-thickness direction it might also reveal a comparative anisotropy. There may be several reasons why the material exhibited a positive Poisson's ratio in the mechanical tests. The mechanical tests were performed at room temperature whereas the fiber was drawn slightly below its nematic-isotropic temperature. At the higher temperature the chains are less rigidly held together than at room temperature. The transverse rod rotation mechanism may be able to operate at this higher temperature but not at room temperature. We feel this is the most likely explanation.

Also, neighboring polymer chains are likely able to slip past each other under tensile strain, this will act to progressively reduce the cross section of the specimen, and thereby counteract any transverse rod rotation in producing auxetic behaviour. Shorter spacers in the polymer main-chain may circumvent this by encouraging the spacers to tighten and lever transverse rod rotation before many of the polymer chains themselves slip past each other. Lastly, the transverse rod rotation mechanism may be functioning as intended, except that the initial angle between the transverse rod and the main chain polymer molecule may be obtuse rather than acute. If this were so the transverse rods would rotate inwards towards the main polymer chain rather than away. Figure 8 is a diagram of the possible geometry of the main chain and transverse rod molecules. The side rods make an angle  $\theta$  with the main chain, which may be acute (as shown) or obtuse. It is possible to fit the model described below to this experimental data using such an obtuse value for  $\theta$ . However, we feel it is unlikely that the transverse rods would lie at a large obtuse angle in the nematic phase.

It may be possible to predict some of the behaviour of this and other polymers using simple geometrical models.<sup>[11,17,21]</sup> This technique has proved successful with macro and microporous polymers, where elements of the internal structure were able to undergo large rotations. The main polymer chain and side rods may be thought of as stiff

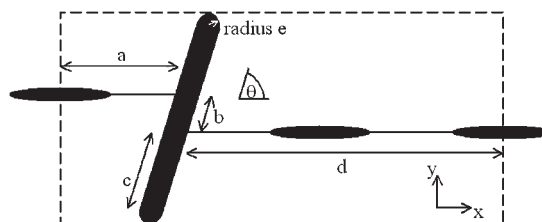


Figure 8. The geometric model of the polymer molecule. The transverse rods chains lie at angle ( $\theta$ ) to the main chain. The unit cell is outlined in the dashed line.

rods connected by compliant pin joints, based upon the geometry shown in Figure 1. A tensile force extending the chain will exert a moment on the side rod and result in rotation of the side rod about the chain. The structure shown in Figure 8 can be thought of as a unit cell which when tessellated in a plane forms a continuous network whose behaviour are similar to that of the unit cell. The Poisson's ratio of a material consisting of such a network can then be calculated from the unit cell. The unit cell has an initial dimensions  $x_0$  in the  $x$  axis and  $y_0$  in the  $y$  axis.

$$x_0 = a + d - \left( (b^2 + 4e^2)^{\frac{1}{2}} \cdot \cos \left( \theta + \arctan \frac{2e}{b} \right) \right) \quad (2)$$

$$y_0 = (b + 2c) \sin \theta + 2e \quad (3)$$

A small change in the length  $x$ ,  $dx$  results in a small change in the width  $dy$

$$dx = \sin \left( \theta + \arctan \frac{2e}{b} \right) \delta \theta \quad (4)$$

$$dy = (b + 2c) \delta \theta \cos \theta \quad (5)$$

Thus the engineering strains in the  $x$  and  $y$  axes are

$$e_x = \frac{dx}{x_0} = \frac{\sin \left( \theta + \arctan \frac{2e}{b} \right) \delta \theta}{a + d - \left( (b^2 + 4e^2)^{\frac{1}{2}} \cdot \cos \left( \theta + \arctan \frac{2e}{b} \right) \right)} \quad (6)$$

$$e_y = \frac{dy}{y_0} = \frac{(b + 2c) \delta \theta \cos \theta}{(b + 2c) \sin \theta + 2e} \quad (7)$$

and the true strains are

$$\varepsilon_x = \ln(1 + e_x) \quad (8)$$

$$\varepsilon_y = \ln(1 + e_y) \quad (9)$$

Thus the true strain Poisson's ratio is

$$\nu_{xy}^{tru} = (\nu_{yx}^{tru})^{-1} = \frac{-\ln \varepsilon_y}{\ln \varepsilon_x} \quad (10)$$

The values of the parameters  $a$ ,  $b$ ,  $c$ ,  $d$  and  $e$  were taken from a physical model made of the polymer chain molecule;  $a = 23$ ,  $b = 5$ ,  $c = 20$ ,  $d = 66.8$  and  $e = 5.2$ . The initial value of the angle  $\theta$  was altered so that the predicted Poisson's ratio matched the experimental data for both the width ( $xy$ ) and thickness ( $xz$ ) planes. The values of  $\theta$  found to give the best match were  $90.14^\circ$  and  $90.17^\circ$  for the  $xy$  and  $xz$  planes respectively, see Figure 7. The model's prediction of Poisson's ratio versus strain is very sensitive to changes in the angle  $\theta$  when near to  $\theta = 90^\circ$ . It is unlikely that in reality the initial value of  $\theta$  will be near to  $90^\circ$ , due to energetic and

packing considerations, but more likely to be either minimal or maximal. The X-ray diffraction patterns do not show strong indications of the side rod at  $90^\circ$  to the main chain. It is likely then that the Poisson's ratios observed in these samples at room temperature are not due to rotation of the side rods and are more likely due to the usual interactions of the main chains and the domains. The model shows that in order to obtain a large negative Poisson's ratio the side rods must lie at an acute angle to the main chain and be free to rotate and push against the main chains, possibly indicated by a reduced  $T_g$ . The authors have recently synthesized liquid crystalline polymers incorporating transverse rods with poly(dimethylsiloxane) flexible spacers and crosslinks that give elastomers with a low  $T_g$ .<sup>[19]</sup>

The values measured for Poisson's ratio are large; near to 0.5. However as the samples show a strong orientation along the  $x$  axis, as would be expected of a liquid crystal material, it is probable that this would give rise to the high values of Poisson's ratio.

## Conclusion

The structure and deformation behaviour of a liquid crystalline polymer consisting of laterally and terminally attached rods has been studied. A plaque specimen prepared by the melt compression method had marked anisotropic Poisson's ratio behaviour which could be explained by its structure. The specimen had a Poisson's ratio of 0.43 along its primary axis in the in-plane and 0.54 along the primary axis in the through-thickness direction and a Young's modulus of 0.55 GPa. It is clear from the X-ray diffraction of both unoriented (powder) and stretched (fiber) preparations that expansions on a molecular level are taking place that lead to an increase in inter-chain distances upon stretching. In this case, it is likely that transverse rods in the main-chain are rotating to create this effect by pushing neighbouring polymer chains apart. However, this promising expansion observed on the molecular scale has not lead to a room temperature negative Poisson's ratio. It is thought that polymer chains are allowed to slip past each other under tensile strain so as to progressively reduce the cross-sectional area of the bulk samples, thereby counteracting any molecular-scale expansions observed from transverse rod rotation. We have shown that a polymer based on laterally attached transverse rods is a promising approach to achieving auxetic behaviour in a material at the molecular level. By tailoring the chain structure through improved synthetic design, and by modifying fabrication conditions, preparation of a polymer with a bulk auxetic response at large strains may be possible.

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