

## Toward molecular auxetics: Main chain liquid crystalline polymers consisting of laterally attached para-quaterphenyls

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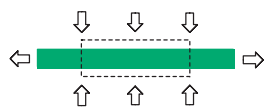
Polymers containing para-quaterphenyl rods laterally attached to the polymer main chain have been synthesized. The molecular design choices which led to use of the quaterphenyl rod to achieve auxetic response will be discussed. Preparative chemistry of the monomers will be described along with the details of the polymerization reaction. Both polyethers and polyesters were prepared. The length of the flexible alkyl main chains which link the rods plays an important role in determining whether the resulting polymers will exhibit liquid crystallinity. Polymers with longer alkyl links exhibit nematic liquid crystallinity and the rods appear to have their long axes oriented roughly parallel and along the main chain direction. X-ray scattering experiments were performed on the polymers both in the quiescent (unstretched) and the stretched states. Results from these experiments suggest that, under tensile strain, site connectivity driven rod-reorientation occurs in these materials giving rise to an increase in the interchain distance for these polymers. This increase in the interchain separation is consistent with our concept of a molecular level auxetic mechanism for this type of designed polymer.

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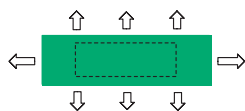
### 1 Introduction

Poisson's ratio is one of the fundamental elastic constants of a material and is a measure of dimensional change in response to an applied tensile force. Materials that exhibit a negative Poisson's ratio (NPR) expand laterally in response to an applied longitudinal strain and are termed auxetic; that is, they fatten when stretched (Fig. 1). This behavior is uncommon; rather it is rare, counter intuitive, and contrary to everyday experience. Recently, auxetic materials and structures have received much attention because of their unusual behavior and their potential for novel applications such as fasteners which resist pull-out and seals that densify and thereby seat better under compression. Auxetics derive such unique behaviour from the geometric elements and topological arrangements that constitute their structure [1]. Elastic theory allows for auxetic behaviour and places no size requirement on the structural motifs: macroscopic and microscopic levels, nano- and molecular-scale. Because there is no scaling restriction, it is possible to design auxetic materials on a molecular level and thereby achieve a high degree of control by tailoring the molecular structure: incorporating molecular elements which promote auxetic behaviour. Although,

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Conventional material



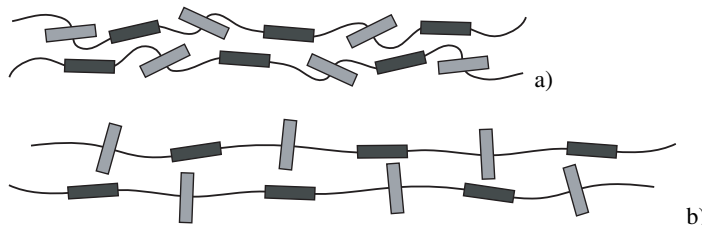
Auxetic material

**Fig. 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Dimensional response in a conventional (upper) and auxetic (lower) material when a tensile force is applied.

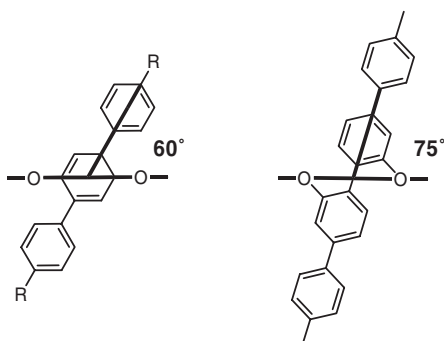
some naturally occurring inorganic crystals such as alpha-cristobalite owe their auxetic behavior to bond rotations at the atomic level within the crystalline unit cell, this discussion will be focused on bespoke organic materials for auxetic response.

The first proposed molecular auxetic was by Evans in 1991 [2] who suggested a chemically specific rigid carbocyclic network based on the auxetic re-entrant cell geometry of Ashby [3]. Auxetic behaviour would arise from a flexing of this network under tension. Wei and Edwards have proposed random auxetic polymer networks based on similar three-dimensional re-entrant cell geometry [4]. In addition to these ‘bond flexing’ mechanisms, molecular auxetics have been proposed [5] based on low-barrier rotational changes that would lead to polymorphic solids having significantly different volumes under strain. Wojciechowski has offered general, non-chiral, molecular proposals for auxetics based on modeling considerations [6]. While Grima has suggested a series of poly(phenylacetylene) networks involving connected rotating triangles as a potential molecular mechanism for auxetic response [7]. Baughman [8] has discussed ‘twisted chain’ structures in polymeric materials as auxetic elements. We have suggested that nematic main-chain polymers could exhibit an auxetic response when transversely attached rigid rods are incorporated in the main-chain. This site-connectivity driven rigid rod reorientation upon stretching is proposed as a mechanism for auxetic behaviour (Fig. 2).

In order to achieve NPR behavior, a desirable feature for the laterally attached rod rigidity. Any non-rigid linkages such as esters or amides may adopt a bent conformation under tensile strain and result in a shorter rod length. A unique feature of liquid crystalline polymers is the tendency for the rod-like structural elements to align roughly parallel to each other. Although there are examples of liquid crystalline polymers having interesting, atypical rod connectivity, most nematic main-chain polymers have the rod elements connected through a flexible spacer at the rod termini. These terminally attached rods will orient parallel to the stretching direction when the polymeric chain is extended. Our approach is to create a main-chain liquid crystalline polymer consisting of both terminally attached rods and laterally attached rods. The laterally attached rods will, in the quiescent (un-stretched) state, orient parallel to the terminally attached rods. However, upon stretching, the laterally attached rods should undergo a site-connectivity driven rod re-orientation to give a significant increase in the transverse dimension of the



**Fig. 2** Schematic showing how: (a) transverse-rods pre-align within surrounding liquid crystal field; and (b) anticipated re-orientation with lateral expansion after stretching.



**Fig. 3** Improvement in transverse-rod reorientation through change in site connectivity from a 1,4-phenylene to a 2,2'-biphenyl.

stretched polymer chain. The accompanying increase in inter-chain spacing upon stretching should lead to an auxetic response. It is apparent that oligo-paraphenylys are suitable for this purpose, and ter-, quater-, and penta-phenylys are good candidates.

In a previous paper, we have reported liquid crystalline polymers containing laterally attached terphenylys [9]. Due to the specific chemistry and the attachment sites on the central phenyl ring, these terphenylys make a 60 degree angle with the polymer main-chain when the polymer is fully stretched, which is the maximum limit for rotation of the laterally attached rods. In this paper, we will study a class of polymer consisting of longer laterally attached para-quaterphenyl rods that could rotate to a maximum of 75 degrees with respect to polymer main-chain when the polymer chain is fully stretched and could push the neighbouring chains further apart. Figure 3 shows the orientation between unique attachment sites of the terminally attached rods to the flexible spacer.

## 2 Experimental section

**General.** All reagents were used as received from Aldrich Chemical Co. or Lancaster Synthesis, unless otherwise specified. Tetrahydrofuran was dried by distilling from sodium benzophenone ketyl, all other solvents were used as received. Melting points were observed on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Polymer melting points and transitions were measured using a TA Instruments 2920 Differential Scanning Calorimeter (DSC) at  $10\text{ }^{\circ}\text{C min}^{-1}$  heating and cooling cycles under nitrogen. Liquid crystal phases and their transitions were partly verified on a Leica polarizing optical microscope equipped with a Mettler Toledo PP82HT heating stage. X-ray scattering was performed by a Siemens D-700 instrument ( $\text{CuK}_{\alpha}$ , 1.5418) on water quenched polymer fibers drawn from their nematic phase. Powder samples were firstly heated to their isotropic phase and cooled to room temperature.  $^1\text{H}$  NMR data was obtained using a Bruker AC-300 spectrometer. 1,10-Bis(4-hydroxyphenoxy) decane **8** was prepared according to a previously published procedure [10].

**2-Iodo-5-nitroanisole (1).** 2-methoxy-4-nitroaniline (30 g, 178 mmol) was dissolved in aqueous sulfuric acid ( $\text{H}_2\text{SO}_4$ -water, 40–150 mL) by heating, before cooling to  $0\text{--}5\text{ }^{\circ}\text{C}$  in an ice–water bath. To this, a solution of sodium nitrite (13.0 g, 188 mmol) in water (40 mL) was added dropwise while maintaining the temperature below  $10\text{ }^{\circ}\text{C}$  before allowing to stir for a further 20 mins. The cold solution was then poured into a solution of potassium iodide (50 g, 300 mmol) in water (150 mL) with vigorous stirring, and left to warm to room temperature for another 3 hrs. The crude solid was collected by filtration (aspirator), washed with water several times, dried in air, and finally recrystallised from ethanol to afford 41 g (82%) of **1**, mp  $129\text{--}130\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (s, 1H, ArH), 7.63 (d, 1H, ArH), 7.57 (d, 1H, ArH), 3.99 (s, 3H,  $\text{ArOCH}_3$ ).

**2,2'-dimethoxy-4,4'-dinitro-1,1'-biphenyl (2).** Bronze copper (20 g, 72 mmol) and **1** (20 g, 317 mmol) were stirred at  $200\text{--}205\text{ }^{\circ}\text{C}$ . The reaction is immediate with white smoke. The mixture was kept stirring

overnight at 200 °C before cooling to room temperature. The resulting solid is purified by Soxhlet extraction using chloroform (300 mL) for 2 days. The chloroform extracts are concentrated in volume to 100 mL by evaporation and allowed to cool. The resulting crystals were collected using filtration (aspirator) to afford 7 g (65%) of **2**, mp 245–246 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.93 (m, 2H, ArH), 7.84 (d, 2H, ArH), 7.39 (d, 2H, ArH), 3.88 (s, 6H, ArOCH<sub>3</sub>).

**4,4'-diamino-2,2'-dimethoxy-1,1'-biphenyl (3).** Hydrochloric acid (100 mL, 37%), ethanol (50 mL) and **2** (9.0 g, 29.6 mmol) were stirred and heated to 90 °C. Tin powder (20.0 g, 168 mmol) was added to the mixture in three portions over 6 hours and then allowed to stir for a further 2 hrs. at the same temperature before cooling. A solution of sodium hydroxide (75.0 g, mmol) in water (150 mL) was then slowly added; initial clearing was soon followed by precipitation. This crude solid was collected by filtration (aspirator), washed with water and dried in air. Purification by Soxhlet extraction using chloroform (300 mL) gave a solution which crystallized on cooling to afford 5.8 g (80%) of **3**, mp 196 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.70 (d, 2H, ArH), 6.25 (s, 2H, ArH), 6.14 (d, 2H, ArH), 3.58 (s, 6H, ArOCH<sub>3</sub>), 3.33 (s, 4H, ArNH<sub>2</sub>).

**4,4'-diiodo-2,2'-dimethoxy-1,1'-biphenyl (4).** Hydrochloric acid (40 mL, 37%), water (100 mL) and **3** (8.0 g, 32.8 mmol) were stirred and heated into solution for 20 mins. before cooling to 0–5 °C in an ice-water bath. A solution of sodium nitrite (7.0 g, 100 mmol) in water (20 mL) was then added dropwise while maintaining a temperature below 10 °C. After stirring for an additional 20 mins. the cold solution was poured into a rapidly stirring solution of potassium iodide (30.0 g, 180 mmol) in water (100 mL) and then allowed to warm to room temperature overnight. The crude brown solid was collected by filtration (aspirator), washed with water and dried in air. Purification by column chromatography (silica, hexane–CH<sub>2</sub>Cl<sub>2</sub>, 8:1) afford 10 g (66%) of **4**, mp 134 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.37 (d, 2H, ArH), 7.33 (s, 2H, ArH), 6.91 (d, 2H, ArH), 3.71 (s, 6H, ArOCH<sub>3</sub>).

**2'',3'-Dimethoxy-1,4'''-dimethyl-1,1':4', 1'':4'',1'''-quaterphenyl (5).** 4-Methylbenzeneboronic acid (3.0 g, 2.20 mmol), **4** (4.66 g, 1.00 mmol), barium hydroxide monohydrate (5.6 g, 29.6 mmol), and tetrakis(triphenylphosphine)palladium (0.3 g, 0.27 mmol) were dissolved in ethylene glycol dimethyl ether (120 mL) and water (8 mL), and stirred at 80 °C under an argon for 36 hrs. The mixture was then heated to reflux and filtered hot. The filter cake of crude product was dried in air and purified by column chromatography (silica, hexane–CH<sub>2</sub>Cl<sub>2</sub>, 5:2) to afford 2.2 g (60%) of **5**, mp 232 °C. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 7.66 (d, 2H, ArH), 7.64 (s, 2H, ArH), 7.32 (d, 2H, ArH), 7.29 (d, 4H, ArH), 7.24 (d, 4H, ArH), 3.82 (s, 6H, ArOCH<sub>3</sub>), 2.46 (s, 6H, ArCH<sub>3</sub>).

**1,4'''-Dimethyl-[1,1':4', 1'':4'',1'''-quaterphenyl]-2'',3'-diol (6).** With stirring, dimethyl ether **5** (2.0 g, 5 mmol) was dissolved in dichloromethane (50 mL) and cooled to –78 °C. A solution of boron tribromide (3.8 g, 15 mmol) was then added and the suspension returned to room temperature overnight. Any excess Lewis acid was destroyed with water (100 mL) of water. The dichloromethane was removed under reduced pressure, and the resulting precipitate collected by filtration (aspirator). The isolated solid was washed with water, dried in air and recrystallized from ethanol to afford 1.46 g (80%) of colorless needles of **6**, mp > 280 °C, and was used without further purification in the preparation of **7**.

**2'',3'-Bis[(10-bromodecyl)oxy]-1,4'''-dimethyl-1,1':4', 1'':4'',1'''-quaterphenyl (7).** 1,10-Dibromodecane (45.0 g, 153 mmol) and **6** (3.0 g, 7.6 mmol) were dissolved in acetone (150 mL) and heated to a gentle reflux under argon. Potassium carbonate (5.0 g, 36 mmol) was then added and the suspension refluxed for 36 hrs. The cooled reaction mixture was filtered and the filtrates evaporated under reduced pressure. The residue was purified by column chromatography (silica, hexane–CH<sub>2</sub>Cl<sub>2</sub>, 2:1), firstly with hexanes to remove excess 1,10-dibromodecane to afford 6 g (90%) **7**, mp 79 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ

7.66 (d, 2H, ArH), 7.64 (s, 2H, ArH), 7.32 (d, 2H, ArH), 7.29 (d, 4H, ArH), 7.24 (d, 4H, ArH), 3.92 (t, 4H, ArOCH<sub>2</sub>), 3.41 (t, 4H, CH<sub>2</sub>Br), 1.87 (m, 4H, ArOCH<sub>2</sub>CH<sub>2</sub>), 1.65 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>Br), 1.20–1.52 (m, 24H, CH<sub>2</sub>), 2.46 (s, 6H, Ar-CH<sub>3</sub>).

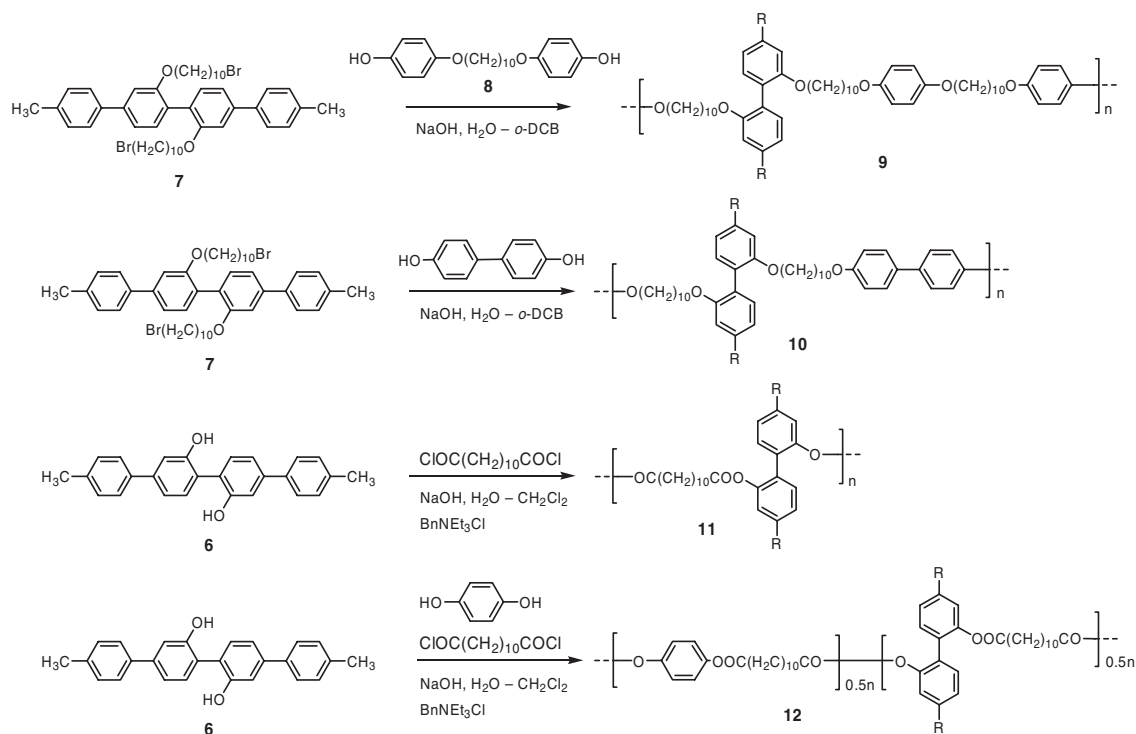
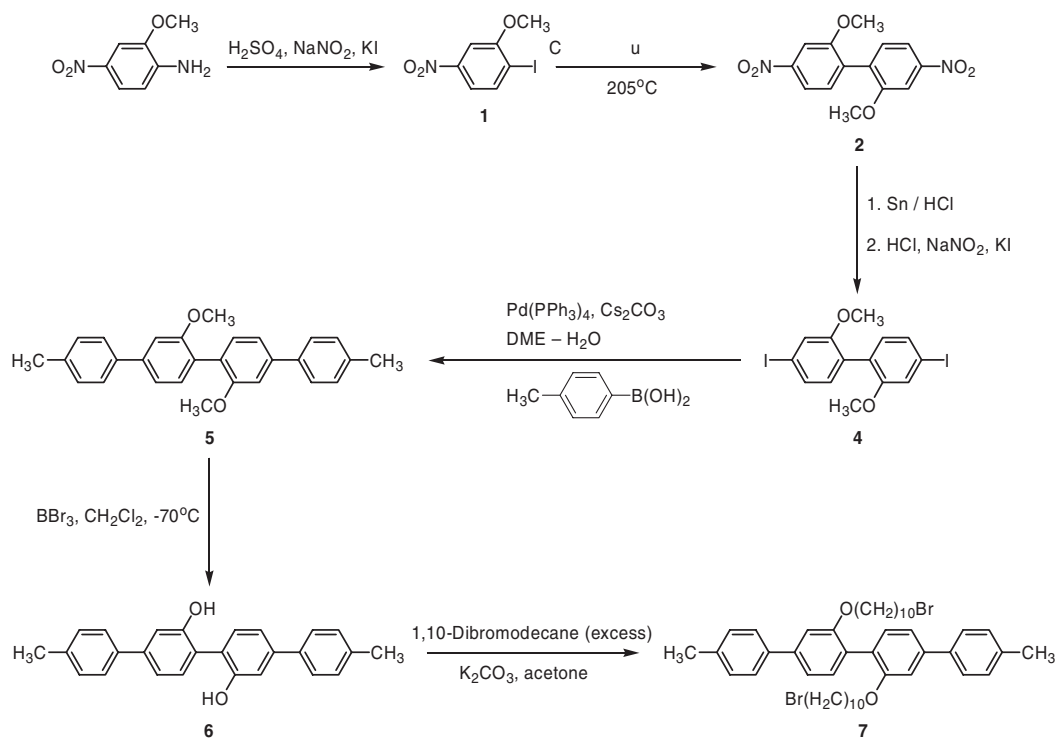
**Polyethers 9 and 10. General Procedure.** Bisphenol or **8** (1 mmol) and benzyltriethylammonium chloride (0.68 g, 3 mmol) were dissolved in aqueous sodium hydroxide (2 mL, 10 N, 20 mmol) and added to a solution of **7** (0.8 g, 1 mmol) dissolved in *o*-dichlorobenzene (2 mL). The mixture was rapidly stirred at 60 °C for 6 hrs., cooled and precipitated into methanol (100 mL). The fibrous solid was filtered (aspirator) and washed with water. The crude polymer was purified further by dissolving in chloroform and again precipitating in methanol, twice, and drying *in vacuo* to afford polyethers **9** and **10**.

**Polyesters 11 and 12. General Procedure.** A solution of dodecanedioyl dichloride (267 mg, 1 mmol) dissolved in dichloromethane (6 mL) was added to a rapidly stirring solution of benzyltriethylammonium chloride (0.68 g, 3 mmol) and **7** (0.8 g, 1 mmol) dissolved in aqueous sodium hydroxide (8 mL, 0.37 M, 3 mmol). The mixture was stirred at room temperature for 30 mins., then precipitated into methanol (100 mL). The precipitate was filtered (aspirator) and washed with water before drying *in vacuo* to afford polyesters **11** and **12**.

### 3 Results and discussion

In earlier work we explored the use of ter- and penta-phenyl rods with lateral connectivity through a 1,4-disubstituted phenylene core (Fig. 3). In that study, we employed a parent polymer structure with known liquid crystallinity. Using this polymer we have shown [9] that in the nematic phase the laterally attached rods orient in the direction of the main chain and its terminally attached mesogens. Nominal expansions on a sub-nano scale were found by X-ray scattering as inter-chain diffraction spacings increased from the un-stretched, ordered LC state to a stretched fiber form. Only re-orientation of the laterally incorporated ter- and penta-phenyl rods could have produced this expansion, counter to the narrowing which is widely observed for polymers and is exhibited by the parent polymer with no lateral rods capable of inducing such expansion. In further consideration of the 1,4-substitution pattern of this system, it was recognized that any re-orientation of the rods could only expect to achieve a span of movement up to a maximum of 60° with respect to the main chain extension. Here we report the synthesis (Schemes 1 and 2) and properties of four polymers with varying main chain structures, but with an improved design of laterally attached quaterphenyl rod that was synthesized to improve upon the 60° limitation recognized in our earlier work. The use of a quaterphenyl with lateral connectivity through a 2,2'-biphenyl core (Fig. 3) should allow for an increased span of movement in re-orientation up to a maximum of 75° from the axis of the main chain. However, the polymers reported here contain one further difference: they have no terminally linked mesogens, only laterally attached quaterphenyl rods linked through non-mesogenic alkyl chains. This then raises the question as to how these laterally attached rods manage to organize their nematic phase.

Property changes observed in small molecules as a result of structural alterations can reveal insights into the behaviour of the corresponding polymers. Laterally functionalized rod **5** with its methoxy groups at the 2,2' positions, for instance, is a highly crystalline material with a melting temperature of 232 °C that does not exhibit any liquid crystallinity. When the methoxy groups are substituted with a decyl chain, the resulting quaterphenyl **7** has a lower melting temperature of 79 °C, but remains crystalline. However, when **7** is combined with bisphenol **8** the resulting polymer exhibits liquid crystallinity. The absence of liquid crystallinity in **5** can be attributed to its highly anisotropic shape and conjugated para-quaterphenyl structure, which promotes a strong lateral intermolecular attraction and high melting point. However, investigation also shows that when **5** contains a small amount of impurity (about 5% impurity according to NMR), the mixture exhibits a monotropic nematic liquid crystal phase as consequence of melting point depression indicating the pro-liquid crystalline character of the quaterphenyl rod system.

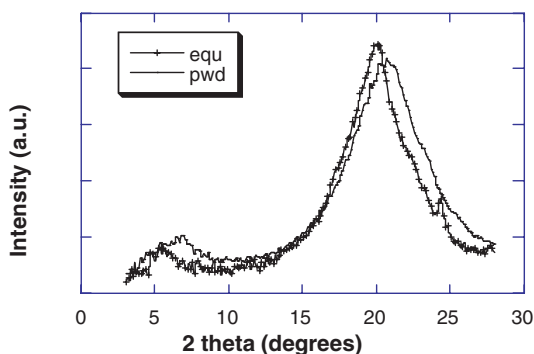


When **7** is linked to form a polymer, the resulting polymer exhibits a liquid crystalline phase; the polymerization process providing the additional order that leads to the liquid crystallinity observed for polymers **9** and **10**. This is the stabilizing macromolecular effect in liquid crystals. This additional ordering in the polymer fortunately permits the incorporation of such long, otherwise non-mesogenic rods, and thereby gives the required ordering of these rods along the liquid crystal director of the main chain: our proposed pre-requisite for auxetic polymer design.

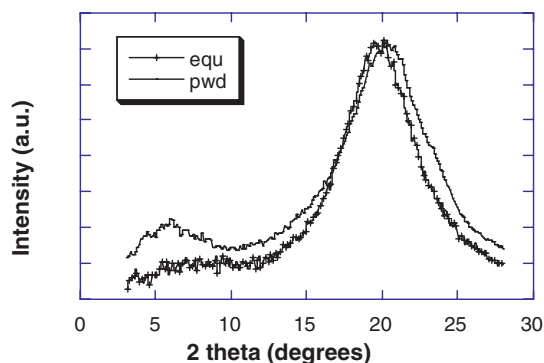
The phase behaviours for all four polymers were studied using DSC and polarizing optical microscopy. Polymers **9**, **10** and **12** exhibit liquid crystallinity while polymer **11** does not. Microscopy studies indicate that polymers **9**, **10** and **12** exhibit a distinct birefringence at their isotropic-mesophase transition which resembles that of a nematic liquid crystalline polymer (LCP). Powder and fiber X-ray scattering of these polymers at room temperature confirm that they are unlikely to be smectic LCPs since there is no distinct low angle scattering which could be characterized as scattering from a smectic layer.

The structural difference between **9** and **10** is their main chain. Polymer **10** has a mesogenic rigid 1,1' biphenyl, while polymer **9** has a flexible bisphenol incorporating an extra decyl spacer. Polymer **10** displays greater stability in its mesophase with a nematic-isotropic (clearing) temperature of 115 °C while that for polymer **9** is significantly lower at 64 °C. Clearly the added rigidity favours the formation of a mesophase. Our observations with the small molecule quaterphenyl rods have shown that only when these precursors are linked together as a polymer can they exhibit liquid crystallinity. This linking of small pro-liquid crystalline rods to form a polymer chain, together with a small increase in rigidity, promotes the formation of a nematic phase and indicates that the polymer chain direction is likely the nematic director. As a result, we can conclude with some confidence that, in the unstretched state, our laterally attached rods orient in the polymer chain direction. Further support for the orientation of the laterally attached quaterphenyl rods within the polymer comes from the study of the relation between the length of linkage and the liquid crystallinity of the resulting polymers. Polymer **11** has the shortest spacer of the four polymers: only a ten-carbon chain between any two neighbouring quaterphenyls. The thermal analysis and microscopy of **11** gives a melting temperature of 160 °C on heating but no mesophase. Harvard CPK models show that the length of the ten-carbon alkyl chain is only around 15 Å while the length of laterally attached quaterphenyl rod is about 18 Å, thereby restricting rod orientation along the polymer chain direction. If the polymer liquid crystallinity were a result of quaterphenyls lying normal to the polymer chain direction, polymer **11** would be the most likely LC (smectic) candidate, simply because of the higher concentration of laterally attached rods oriented adjacent to each other in such compact proximity. In confirmation of this, if the spacer is lengthened by random copolymerization with hydroquinone to give **12**, there appears a monotropic nematic phase at 72 °C. This relation between the length of spacer linkage and liquid crystallinity provides strong evidence that the formation of nematic phases for these polymers is as a consequence of quaterphenyl rod orientation along the polymer chain direction.

Powder scattering from **9** and **10** (Figs. 4 and 5); show that both polyethers are amorphous in structure, and that this can be attributed to the laterally attached quaterphenyl rods producing a glassy nematic phase. The powder scatterings centre at 20° (2θ). At low angles, any scattering is weak for both **9**



**Fig. 4** (online colour at: [www.pss-b.com](http://www.pss-b.com)) X-ray scattering profiles of polymer **9** containing laterally attached transverse rods. The equatorial (equ) scattering of the oriented polymer at  $2\theta = \sim 20$  degrees reflects the interchain distance after stretching. The powder (pwd) scattering at this angle reflects the interchain distance of the unstretched polymer.



**Fig. 5** (online colour at: www.pss-b.com) X-ray scattering profiles of polymer **10** containing laterally attached transverse rods. The equatorial (equ) scattering of the oriented polymer at  $2\theta = \sim 20$  degrees reflects the interchain distance after stretching. The powder (pwd) scattering at this angle reflects the interchain distance of the unstretched polymer.

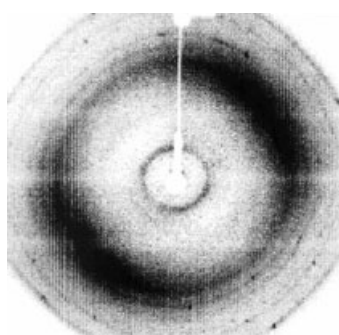
and **10** and centered about  $6.7^\circ$  and  $6.1^\circ$  ( $2\theta$ ) respectively. It is, however, unlikely the low angle peaks indicate smectic layering. This is because the low angle scattering is not well defined and the intensity is very weak compared with the amorphous halo for the polymers. The low angle scatterings are more likely due to density fluctuations between laterally attached rigid rods and the flexible main chain.

Fiber patterns of polymers **9** and **10** are shown in Figs. 6 and 7 respectively. Both show strong equatorial scattering at about  $20^\circ$  ( $2\theta$ ); diffraction arcs representing inter-chain interactions between non-covalently bonded atoms. The observed four-point off-equatorial scatterings are very weak, corresponding to low angles and indicating that the polymers have an inter-digitated rod packing structure consistent with our rod re-orientation mechanism. Their weak intensity can be attributed to the distorted packing structure of the polymers.

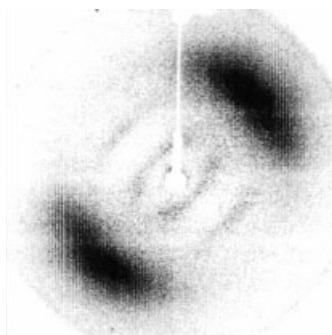
To determine whether or not the laterally attached *p*-quaterphenyl rods might achieve a negative Poisson's ratio we examined their molecular structure through inter-chain distance measurements before (powder diffraction) and after (fiber diffraction) stretching. Considering a material with a fixed number of polymer chains in cross-section, if the material has NPR property, the inter-chain interaction distance of the material should increase under tensile strain. Figures 4 and 5 show the powder scatterings and the equatorial scatterings (i.e. the equatorial scatterings from fiber patterns) of the two polymers. It can be seen that the equatorial scatterings of both polymers move to a lower angle compared with their corresponding powder scatterings, which indicates that the inter-chain distances of the polymers increase when stretched, consistent with our predictions.

#### 4 Conclusions

Polymers containing laterally attached para-quaterphenyl rods have been synthesized where the length of the flexible spacer linking them plays an important role in influencing any resulting liquid crystallinity.



**Fig. 6** X-ray scattering from polymer **9** fiber containing laterally attached transverse rods.



**Fig. 7** X-ray scattering from polymer **10** fiber containing laterally attached transverse rods.

In this case, spacers longer than the quaterphenyl allow for a nematic liquid crystalline phase to form, the laterally attached rods lying in the direction of the polymer main chain. The polymers assume an interdigitated packing structure. Under tensile stress (orientation), the inter-chain distances increase for polymers containing laterally attached quaterphenyl rods, suggesting the possibility of a negative Poisson's ratio or auxetic response for this polymer design.

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