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PAPER

Unsymmetric main-chain liquid crystal elastomers with tuneable phase behaviour: synthesis and mesomorphism†

Maria Amela-Cortés,‡[a] Benoît Heinrîch,[b] Bertrand Donnio,[b] Kenneth E. Evans,[a] Chris W. Smith[a] and Duncan W. Bruce*[c]

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The synthesis of a new series of polysiloxane-based, main-chain liquid crystal elastomers (MC-LCEs) containing unsymmetric mesogenic units is described. The structure of the mesogenic monomers, spacers and cross-linkers has been varied systematically in order to tune the thermotropic behaviour of the networks. Three unsymmetric mesogens were studied, characterised by having two aromatic rings as the rigid core and two different alkoxy chains. Smectic A or nematic phases were observed, depending on the length of the alkoxy chains. These mesogens were combined with three different spacers, a flexible hexamethyltrisiloxane (**S1**) and two aromatic bis(dimethylsilyloxy)benzene with the silyl groups disposed *para* (**S2**) or *meta* (**S3**). To form the MC-LCEs, two cross-linkers were chosen, one flexible 2,4,6,8-tetramethylcyclooctasiloxane (**C1**) and a rigid, aromatic tris(dimethylsilyl)benzene (**C2**). The elastomers showed low glass transition temperatures (below 0 °C) and low clearing temperatures (between 30 and 72 °C), as such presenting liquid crystalline properties at room temperature. The transition temperatures could be tuned by a simple choice of the components; for instance, the clearing temperature decreased as aromatic spacers or cross-linkers were introduced. In contrast, the glass transition temperature did not depend on the cross-linker or mesogen used and showed only a small dependence on the structure of the spacer. The phase behaviour of the MC-LCEs was affected greatly by the spacer used and networks containing the trisiloxane spacer systematically exhibited the smectic C phase. The insertion of aromatic spacers favoured the formation of a nematic phase over a smectic phase when the flexible cross-linker, **C1**, was used. This behaviour was enhanced by the addition of the aromatic cross-linker **C3**, so that the smectic C phase was suppressed totally and only a nematic phase was observed. The synthesis of the components of MC-LCEs is presented and the structure–thermal properties relationships of the MC-LCEs are discussed.

1. Introduction

Liquid-crystal elastomers (LCEs) have attracted much attention due to their very special properties such as memory effects,[1–5] macroscopic shape changes[6–8] and shifts in phase transformations.[4,9] LCEs form part of the so-called 'shape-memory materials'[3,5,10] since they have the ability to change their shape reversibly upon application of an external stimulus, such as temperature,[11–13] light[14–17] or electrical field.[1,18–21] These unusual features were predicted by de Gennes in 1975.[22] These stimuli induce a disorder in the liquid-crystalline phase that is translated into a macroscopic deformation and, in the case of the thermally induced systems, the change in shape is attained at the liquid crystal-to-isotropic temperature. All these properties arise because of the coupling of the liquid-crystalline order with the rubber elasticity of the weakly cross-linked network,[23] leading to potential applications as sensors and actuators,[16,24–28] for example in biomedical devices such as artificial muscle.[29–31]

Over the years different architectures of LCEs have been produced, for example *side-chain LCEs* (SC-LCEs)[10,32–37] in which the mesogenic units are attached to the polymer chain *via* a flexible spacer and *main-chain LCEs* (MC-LCEs) where the mesogens are part of the polymer backbone.[3,13,28,38–53] Although SC-LCEs have been studied extensively, main-chain LCEs have recently been the subject of increasing interest since they are expected, and have shown larger spontaneous deformations than their side-chain analogues.[6,54,55] However, they present some challenges due to their synthesis and, in particular, because of

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[a] *Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. E-mail: duncan.bruce@york.ac.uk; Tel: +44 (0)1904 324085*
[b] *CNRS-Université de Strasbourg (UMR 7504), Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess BP 43, 67034 Strasbourg Cedex 2, France*
[c] *College of Engineering, Mathematics and Physical Sciences, University of Exeter, Harrison Building, North Park Road, Exeter, EX4 4QF, UK*

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‡ Present address: UMR Sciences Chimiques de Rennes, UR1-CNRS 6226, Universite de Rennes 1, Campus be Beaulieu, CS74205, 35042 Rennes Cedex, France.

their high transition temperatures, which means that they are not accessible for applications.[42]

Rather few investigations have been reported dealing with structure–property relationships of these materials, but those that have showed that small variations in the chemical composition and structure of the networks could induce significant changes in liquid-crystalline behaviour and thermomechanical response.[39,42] Therefore, in order to tune the physical properties of these materials, an understanding of the effect of the chemical structure is required.

Few MC-LCEs reported in the literature show only a nematic phase, as for example the polyether described by Bergmann *et al.*,[38] the photocross-linkable polyethyleneglycol system reported by Krause *et al.*[56] and the mixed main-chain/side-chain of Wermter and Finkelmann.[6] However, MC-LCEs derived from siloxane spacers tend to form smectic phases, in particular the SmC phase, as a result of sterically induced microsegregation between the rigid mesogenic units and the flexible siloxane parts. Indeed, SmC MC-LCEs have been reported by Sanchez-Ferrer and Finkelmann[43] and more frequently these systems show both SmC and N phases as in the cases of Donnio *et al.*,[41] Rousseau *et al.*[42] and Bispo *et al.*[39]

Here are presented a variety of new MC-LCEs (**E1** to **E15**) that show liquid crystal properties at room temperature. These MC-LCEs differ in the structure of the different components of the networks, namely, the mesogenic monomer, the spacer and the cross-linker (Fig. 1). The systematic variation of the structure of the components forming the MC-LCE will lead to systems with tailor-made properties for applications as soft actuators. The aim of this work is to understand the structure–property relationships of these systems. The mechanical properties of these materials are presented in the following paper.[57]

The elastomers are prepared from three mesogenic monomers (**M1** to **M3**), three different spacers—1,1,3,3,5,5-hexamethyltrisiloxane, **S1**, 1,4-bis(dimethylsilyloxy)benzene, **S2**, and 1,3-bis(dimethylsilyloxy)benzene, **S3**—and two silicon-based cross-linkers—cyclic tetrameric siloxane, **C1**, and the aromatic 1,3,5-tris(dimethylsilyl)benzene, **C2**. Compounds **S2**, **S3** and **C2** are not available commercially and their synthesis is described along with monomers **M1** to **M3**. Mesomorphic properties for **M1** to **M3** are reported.

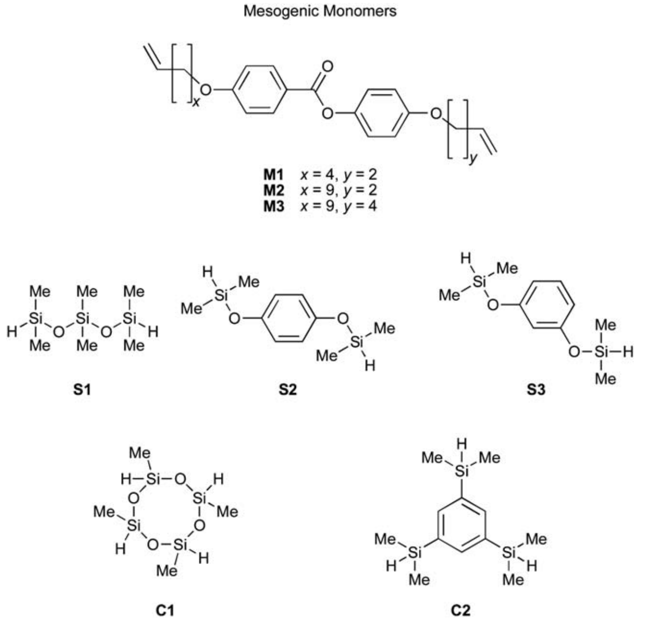


Fig. 1 Chemical structure of the different components of the LCEs, mesogenic monomers (**M1** to **M3**), spacers (**S1** to **S3**) and cross-linkers (**C1** and **C2**).

2. Experimental

2.1 Materials and apparatus

The solvent and reagents were obtained from commercial suppliers and used without further purification. Anhydrous solvents were dried by the usual procedures and used directly: CaH_2 for dichloromethane and sodium and benzophenone for toluene and tetrahydrofuran. Preparation of all compounds was carried out under atmosphere of nitrogen except for the synthesis of liquid crystal polymers and elastomers. NMR spectra were recorded on a Bruker ACF-300 spectrometer operating at 300 MHz for ^1H and 75.5 MHz for ^{13}C, and chemical shifts are reported relative to the internal standard of the deuterated solvent used. IR spectra were recorded on a Nicolet magna-IR spectrophotometer 550. Elemental analyses were recorded by a Carlo Erba EA 1110 elemental analyser.

Analysis by hot-stage microscopy was carried out on an Olympus BH40 microscope equipped with a Link-Am HFS91 hot-stage, TMS92 controller and LNP2 cooling unit. DSC data were recorded on a Perkin-Elmer DSC7 instrument using heating and cooling rates at 10 °C min^{-1}. X-Ray experiments were carried out with a Philips PW 1730 and CuK_α radiation (0.15418 nm) filtered by a graphite monochromator. The incident beam was normal to the surface of the films.

2.2 Synthesis of mesogenic monomers M1 to M3

All alkylation reactions were carried out following the Mitsunobu[58] reaction. A procedure for the synthesis of compound **3a** is given—other homologues were prepared similarly.

Synthesis of 4-(hex-5-enyloxy)benzoic acid, 3a. Ethyl 4-hydroxybenzoate **2** (2.5 g, 15 mmol) and triphenylphosphine (4.3 g, 16.5 mmol) were dissolved in THF (15 cm^3) under a nitrogen atmosphere. Then, 5-hexen-1-ol **1b** was added (1.5 g, 15 mmol) to the solution and mixed with stirring at room temperature. The mixture was cooled to 0 °C and diisopropylazodicarboxylate (3.4 g, 16.5 mmol) was added dropwise. The reaction was stirred at room temperature and was followed by thin-layer chromatography using ethyl acetate : hexane (2 : 1). After 3 h, the reaction was complete and a yellow solid appeared. The solvent was removed under vacuum and a mixture of ethyl acetate : hexane (1 : 5, 12.5 cm^3) was added, allowing the triphenylphosphine oxide and the urea formed during the reaction to precipitate. The solid formed was filtered off and the solvent was removed *in vacuo*. The orange-yellow oil obtained was purified by column chromatography with a mixture of petroleum ether (bp 40–60 °C) : acetone 95 : 5.

The ethyl ester was hydrolysed as follows. A solution of potassium hydroxide (0.84 g, 15 mmol) in ethanol (45 cm^3, 95%) was added to a solution of ethyl 4-(hex-5-enyloxy)benzoate **3** in ethanol (10 cm^3) and heated under reflux for 3 h. The mixture was then cooled to room temperature and water (15 cm^3) was added. The resulting mixture was stirred until the salt formed during the reaction had dissolved. The aqueous solution was acidified with hydrochloric acid (conc., 3 cm^3) leading to the precipitation of the desired product. The precipitate, which was a colourless solid, was filtered off and further crystallised from ethanol. Yield 2.3 g (71%).

^{1}H-NMR ($CDCl_3$): δ: 1.54 (2H, m, $-CH_2-$), 1.77 (2H, m, $-CH_2-$), 2.09 (2H, dt, $-CH_2-CH$, $J = 14.5$ Hz, 6.8 Hz), 3.95 (2H, t, $Ph-O-CH_2$, $J = 6.8$ Hz), 5.06 (1H, dd, $CH{=}CHH$, $J_{cis} = 10.3$ Hz, $J_{gem} = 3.2$ Hz), 5.11 (1H, dd, $CH{=}HH$, $J_{trans} = 17.1$ Hz, $J_{gem} = 3.2$ Hz), 5.83 (1H, ddt, $CH{=}CHH$, $J_{trans} = 17.1$ Hz, $J_{cis} = 10.3$ Hz, $J_{gem} = 6.8$ Hz), 6.87 (2H, AA′XX′, H^4, $J = 7.5$ Hz), 8.12 (2H, AA′XX′, H^3, $J = 7.5$ Hz).

^{13}C-NMR ($CDCl_3$): δ: 25.6 (OCH_2-CH_2), 28.9 ($OCH_2-CH_2-CH_2$), 33.8 ($CH_2{=}CH-CH_2$), 68.44 ($O-CH_2$), 114.6 (m-C_{ar}), 115.3 ($CH_2{=}CH$), 121.8 (C_{be}–COO), 132.8 (o-C_{ar}), 138.9 ($CH_2{=}CH$), 164 (C_{be}–O), 172.2 (COO).

Elemental analysis calculated for $C_{13}H_{16}O_3$: C 70.9, H 7.3; found C 70.7, H 7.4%.

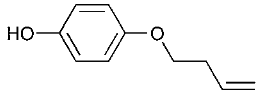
Synthesis of 4-hydroxyphenyl benzoate, 5. In a 1 dm^3 three-neck round-bottomed flask equipped with a dropping funnel, hydroquinone (20 g, 181 mmol) was dissolved in water (520 cm^3) and to that was added potassium carbonate (37.6 g, 272 mmol). The solution was outgassed by passing nitrogen through it for 15 min. After that, benzoyl chloride (23.2 g, 165 mmol) was added dropwise and the mixture stirred for 20 h at room temperature. The colourless precipitate formed during the reaction was filtered off and dried under vacuum. The desired product, **5**, was extracted from the solid by suspending the precipitate in diethyl ether (3 × 100 cm^3) and filtering the remaining solid. The solvent was then removed leading to a colourless solid, which was further crystallised from toluene. Yield = 21.22 g, 60%

^{1}H-NMR (acetone-d_6): δ: 6.77 (2H, AA′XX′, $J = 6.7$ Hz), 6.96 (2H, AA′XX′, $J = 6.7$ Hz), 7.45 (2H, dt, $J = 7.8$ Hz, $J = 7.5$ Hz), 7.58 (1H, t, $J = 7.5$ Hz), 8.01 (2H, d, $J = 7.8$ Hz), 8.45 (1H, s, –OH).

^{13}C-NMR (acetone-d_6): δ: 116.9 (o-COH), 123.9 (m-COH), 130.0 (COO), 131.2 (o-, m-C–COO), 143.8 (p-C–COO), 145.0 (p-COH), 156.5 (COH), 166.3 (COO).

CHN: calculated for $C_{13}H_{10}O_3$: C 72.9, H 4.7; found: C 73.2, H 4.5%.

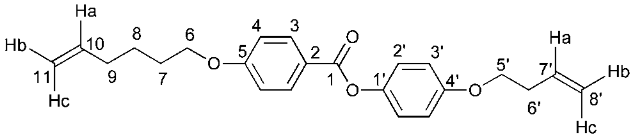
Synthesis of 4-(but-3-enyloxy)phenyl benzoate, 6a.



Compound **6a** was synthesised following the same Mitsunobu reaction as for compound **3a**. The amounts used in this case were: 4-hydroxyphenyl benzoate (10 g, 46 mmol), triphenylphosphine (13.2 g, 50.6 mmol), 3-buten-1-ol (3.36 g, 46 mmol), and diisopropylazodicarboxylate (10.2 g, 50.6 mmol) in dry THF (60 cm^3). The reaction time was 7 h at room temperature. After a mixture of ethyl acetate : hexane (1 : 5) was added, the solid that precipitated was removed by filtration. Finally, the solvent was eliminated yielding an orange oil. A yellow solid was then precipitated from ethanol (95%) at 4 °C. The intermediate benzoate ester was crystallised from ethanol and obtained in 76% yield.

A solution of potassium hydroxide (5.1 g, 91 mmol) in ethanol (60 cm^3) was poured into a solution of 4-(but-3-enyloxy)phenyl benzoate (8.15 g, 30 mmol) in ethanol (25 cm^3, 95%). The reaction was carried out under reflux for 3 h. The mixture was cooled down and then neutralised with hydrochloric acid (10%). The product was extracted from the aqueous solution with dichloromethane (3 × 40 cm^3). The organic phase was washed afterwards with sodium hydrogen carbonate solution (20%, 3 × 20 cm^3). The organic phase was combined and dried over magnesium sulfate. Finally, the solvent was removed *in vacuo* and a brown oil obtained. The compound was used in the next step without further purification. Compound **6b** was prepared similarly.

Synthesis of 4-(but-3-enyloxy)phenyl-4′-(hex-5-enyloxy)-benzoate, M1.



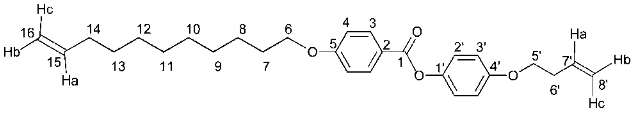
4-(Hex-5-enyloxy)benzoic acid **4** (4.4 g, 20 mmol), 4-(but-3-enyloxy)phenol **15a** (3.3 g, 20 mmol), dicyclohexyl-carbodiimide (4.1 g, 20 mmol) and 4-(N,N-dimethylamino)-pyridine (0.24 g, 2 mmol) were mixed in dichloromethane (100 cm^3) and stirred at room temperature for 24 h. The colourless solid that precipitated during the reaction was filtered off and the solvent removed *in vacuo*. The product was crystallised from ethanol. Yield 3.9 g (53%).

^{1}H-NMR ($CDCl_3$): δ: 1.52 (2H, m, H^8), 1.75 (2H, m, H^7), 2.06 (2H, m, H^9), 2.48 (2H, m, $H^{6'}$), 3.86 (4H, cs, $2H^6 + 2H^{5'}$), 4.98 (4H, $2H_b + 2H_c$), 5.72 (2H, $2H_a$), 6.75 (2H, AA′XX′, $H^{3'}$, $J = 9$ Hz), 6.79 (2H, AA′XX′, H^4, $J = 9$ Hz), 7.93 (2H, AA′XX′, $H^{2'}$, $J = 9$ Hz), 7.96 (2H, AA′XX′, H^3, $J = 9$ Hz).

^{13}C-NMR ($CDCl_3$): δ: 24.8 (C8), 28.1 (C7), 33.2, 33.0 (C9, C6′), 67.6, 67.2 (C5′, C6), 113.8 (C4), 114.8, 114.6 (C8′, C11), 116.7 (C3′), 121.3 (C2′), 122.1 (C2), 131.8 (C3), 134.0 (C7′), 138.0 (C10), 144.1 (C1′), 156.1 (C4′), 162.1 (C5), 164.9 (C1).

CHN: calculated for $C_{23}H_{26}O_4$: C 75.4, H 7.2; found: C 75.5, H 7.2%.

4-(But-3-enyloxy)phenyl-4′-(undec-10-enyloxy)benzoate, M2, yield 3.7 g, 56%.

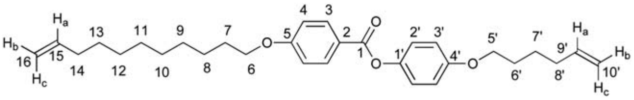


^{1}H-NMR ($CDCl_3$): δ: 1.50 (12H, m, $-CH_2-$), 1.85 (2H, m, H^7), 2.11 (2H, m, H^{14}), 2.62 (2H, m, $H^{6'}$), 4.09 (4H, cs, $2H^6 + 2H^{5'}$), 5.06 (4H, cs, $2H_b + 2H_c$), 5.09 (2H, cs, H_a), 6.98 (2H, AA′XX′, $H^{3'}$, $J = 6.8$ Hz), 7.01 (2H, AAXX′, H^4, $J = 8.8$ Hz), 7.15 (2H, AA′XX′, $H^{2'}$, $J = 6.8$ Hz), 8.19 (2H, AA′XX′, H^3, $J = 8.8$ Hz).

^{13}C-NMR (CDCl$_3$): δ: 26.4 (C7), 29.8 (C8–C13), 34.2, 34.0 (C14, C6′), 68.7, 68.0 (C6, C5′), 114.7, 114.6 (C8′, C16), 115.6 (C4), 117.5 (C3′), 122.0 (C2′), 122.9 (C3), 132.6 (C2), 134.8 (C7′), 139.6 (C15), 144.9 (C1′), 156.9 (C4′), 163.9 (C5), 165.7 (C1).

CHN: calculated for $C_{28}H_{36}O_4$: C 77.1, H 8.3; found: C 77.0, H 8.4%.

4-(Hex-5-enyloxy)phenyl-4′-(undec-10-enyloxy)benzoate, M3, yield 3.5 g, 51%.



^{1}H-NMR (CDCl$_3$): δ: 1.32 (14H, m, 7 –CH$_2$–), 1.49 (2H, m, H^7), 1.73 (2H, m, H$^{8'}$), 1.97 (2H, H^{14}), 2.06 (2H, H$^{8'}$), 3.96 (2H, t, H$^{5'}$, $J = 6.5$ Hz), 3.91 (2H, t, H^6, $J = 6.5$Hz), 4.93 (4H, 2H$_b$ + 2H$_c$), 5.75 (2H, 2H$_a$), 6.85 (2H, AA′XX′, H$^{3'}$, $J = 6.8$ Hz), 6.88 (2H, AA′XX′, H^4, $J = 6.9$ Hz), 7.02 (2H, AA′XX′, H$^{2'}$, $J = 6.8$ Hz), 8.04 (2H, AA′XX′, H^3, $J = 6.9$ Hz).

^{13}C-NMR (CDCl$_3$): δ: 25.7 (C6′), 26.4 (C7), 29.8 (C8–C13, C7′), 34.2, 33.9 (C14, C8′), 68.7, 68.6 (C6, C5′), 114.6, 114.5 (C10′, C16), 115.5, 115.2 (C3′, C4), 122.0 (C2′), 122.9 (C2), 132.6 (C3), 139.0 (C9′), 139.6 (C15), 144.8 (C1′), 157.1 (C4′), 163.8 (C5), 165.7 (C1).

CHN: calculated for $C_{30}H_{40}O_4$: C 77.7, H 8.7; found: C 77.7, H 8.9%.

Synthesis of 1,4-bis(dimethylsilyloxy)benzene,[59,60] **S2.** To a solution of hydroquinone (10 g, 91 mmol) in dry THF (15.2 cm^3) was added dropwise tetramethyldisilazane (18 g, 136.5 mmol) and one drop of chlorodimethylsilane. The reaction was carried out under reflux for 12 h, then the solvent was removed *in vacuo*. The product was obtained in the form of a colourless oil in quantitative yield.

^{1}H-NMR (CDCl$_3$, 300 MHz): δ: 0.10 (12H, d, –CH$_3$, $J = 3$ Hz), 4.76 (2H, septet, Si–H, $J = 3$Hz), 6.87 (4H, s, H^{Ar})

IR (NaCl): $\bar{\nu}$/cm^{-1} 2121 (st, ν_{Si-H}), 1256 (st, ν_{Si-C}).

1,3-Bis(dimethylsilyloxy)benzene, S3. ^{1}H-NMR (CDCl$_3$): δ: 0.10 (12H, d, –CH$_3$, $J = 3$ Hz), 4.80 (2H, septet, Si–H, $J = 3$ Hz), 6.31 (1H, s, *o*-C–OSi), 6.38 (2H, d, *m*-C–OSi, $J = 9$ Hz), 6.95 (1H, t, *m*-C–OSi, $J = 9$ Hz).

^{13}C-NMR (CDCl$_3$): δ: 0 (Me), 112.2 (*o*-C–OSi), 114.2 (*o*-C–OSi), 131.4 (*p*-C–OSi), 158.8 (C–OSi).

IR (NaCl): $\bar{\nu}$/cm^{-1} 2133 (st, ν_{Si-H}), 1257 (st, ν_{Si-C}).

Synthesis of 1,3,5-tris(dimethylsilyl)benzene,[61] **C2.** To a mixture of dimethylchlorosilane (4.73 g, 50 mmol) and magnesium (1.22 g, 50 mmol) in dry THF (15 cm^3) was added a solution of 1,3,5-tribromobenzene (3.15 g, 100 mmol) in THF (10 cm^3). The rate of the addition was adjusted to maintain a reflux. When the addition was finished the reaction was heated under reflux for 3 h. The volatiles were removed *in vacuo* and the product extracted from the solid residue of hexane (3 × 20 cm^3). The solvent was removed *in vacuo*. The product was purified by distillation under reduced pressure. Yield = 75%.

^{1}H-NMR (CDCl$_3$): δ: 0.21 (18H, d, –CH$_3$, $J = 3$ Hz), 4.29 (3H, septet, Si–H, $J = 3$ Hz), 7.58 (3H, s, H^{Ar}).

^{13}C-NMR (CDCl$_3$): δ: –2.9 (Me), 136.4 (C^{Ar}–Si), 150.0 (C^{Ar}–H).

2.3 Preparation of liquid-crystal elastomer films[41]

The reactions were performed in a customised centrifuge (Hettich, Universal 32R) equipped with a custom-made stainless steel rotor, which contained a Teflon cell with dimensions 49 mm of diameter and 20 mm height. The inner wall of the cell was coated with a Teflon film. The centrifuge was heated by a water-bath circulator (Julabo, MP-5) equipped with an immersion pump. The sample environment within the centrifuge was heated to a temperature of 60 °C, which was maintained constant.

The ratio between the vinyl groups and the hydrogen of the silane was stoichiometric, with 10% of cross-linker used for all the elastomers. In this way, when the functionality of the cross-linker was four (**C1**), the mesogenic unit (2 mmol), cross-linker (0.2 mmol wrt mesogenic unit) and spacer (1.6 mmol) were solubilised in toluene (2 cm^3) and for a functionality of three, the proportions were mesogenic unit (2 mmol), cross-linker (0.2 mmol) and spacer (1.7 mmol) in dry toluene (2 cm^3).

Thus, the components were mixed in toluene and placed inside the Teflon cell. To this, a solution of [PtCl$_2$(COD)] in dichloromethane (30 μl, 1% w/w) was added before the polymerisation started. The cell was sealed and placed inside the centrifuge. The reaction was carried out for 2 to 6 hours at 5000 rpm. Once the reaction was finished, the cell was removed from the centrifuge, allowed to cool to room temperature and the swollen network was removed. From the network film, a part was cut and deswollen on a water surface to avoid mechanical deformation to form polydomain, non-oriented networks. The rest of the film was hung at one end with a clamp and the other free end of the film was loaded in order to form aligned, monodomain networks. Under these conditions, the solvent slowly evaporated from the film over 24 h. The film was then placed in an oven at 30 to 50 °C, depending on the clearing temperature, and the cross-linking reaction was allowed to run to completion over 48 h. Polydomain networks were placed in the oven without a load, while for monodomain films, the cross-linking reaction was completed under load.

3. Results and discussion

With the purpose of establishing the structure–property relationship of MC-LCEs, a matrix was constructed in which was found the structure of each component, namely mesogenic monomer, spacer and cross-linker, which have been changed systematically. The elastomers were prepared in a one-pot procedure where the mesogenic monomer, the spacer and the cross-linker are added together and thus, polymerisation and reticulation occur simultaneously. From the synthetic point of view, this technique has proved to be a powerful tool for the ready modification of the structure of the MC-LCEs. This approach has opened the door for the synthesis of a wide variety of MC-LCEs due to its versatility.[41]

In this work each monomer has been combined with each spacer and cross-linker and the influence of their chemical structure on the thermal behaviour is discussed.

3.1 Synthesis of unsymmetric mesogenic monomers M1 to M3, spacers S2 and S3 and cross-linker C2 (Schemes 1 and 2)

The synthesis of the unsymmetric monomers followed a convergent strategy. Thus, a carboxylic ester was alkylated under Mitsunobu conditions and then deprotected to give a carboxylic acid (Scheme 1), while the phenol derivative was prepared starting from the benzyl-ester-protected hydroquinone, again using Mitsunobu conditions for *O*-alkylation. After deprotection, three different monomers **M1**, **M2** and **M3** were obtained by esterification.

Spacers **S2** and **S3** were synthesised in quantitative yield by the chlorodimethylsilane-catalysed reaction between 1,1,3,3-tetramethyldisilazane and either hydroquinone (for **S2**) or resorcinol (for **S3**) in THF under reflux (Scheme 2). These compounds were obtained as colourless oils without further purification. Cross-linker **C2** was synthesised by reaction of 1,3,5-tribromobenzene with a Grignard reagent formed *in situ* from chlorodimethylsilane (Scheme 2); **C2** was obtained as a colourless liquid in 60% yield.

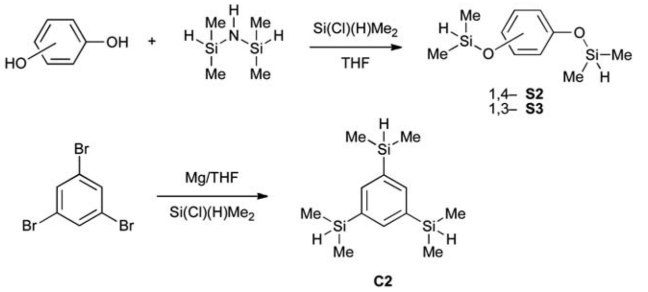
3.2 Liquid crystal properties of the unsymmetric monomers, M1, M2 and M3

The mesomorphic behaviour of the new, unsymmetric monomers was determined by polarised optical microscopy and DSC. The phase behaviour and the thermal stability depended on the length of the alkyl chain. Monomer **M1** showed the typical texture of the nematic phase by microscopy consistent with the short alkyl chain lengths. As the length of the alkyl chain increased, the formation of smectic phases was favoured and, indeed, monomers **M2** and **M3** showed focal conical textures characteristic of a smectic A phase. The thermal parameters of the three monomers were evaluated by DSC and the values for the second heating are shown in Table 1. As expected, the mesogenic monomers showed low transition temperatures and, as the length of the alkyl chain increased, the liquid crystal-to-isotropic transition temperature increased from 53.9 °C, for **M1**, to 75.6 °C, for **M3**. Regarding the thermal stability, monomers **M1** and **M2** showed similar liquid-crystalline range (10 °C) whereas for monomer **M3** the stability improved two-fold.

3.3 Preparation and characterisation of MC-LCE

MC-LCEs were prepared following a one-pot hydrosilylation reaction catalysed by [$PtCl_2$(COD)] and involving the double bonds of the mesogenic monomers and the silane group of the spacers and cross-linkers. All elastomers were prepared with 10% cross-linker **C1** or **C2** having four or three linking sites, respectively.

The elastomers prepared were analysed by the estimation of the sol content and the degree of swelling. The sol content estimation gives an idea of the effectiveness of the cross-linking reaction since the chains that do not form part of the network are soluble in certain solvents and can be extracted from the swollen network. As such, the higher the sol content, the lower the reticulation. In these networks, the sol content varied between 5 and 25 wt% (Table 2); previous work has shown that the mesomorphic properties of MC-LCEs are not affected by sol content,[39] and this is the case here too. Elastomers **E1** and **E2** showed the lowest sol contents of 6 and 5 wt%, respectively, although overall the synthesised elastomers showed a sol content in the range described in the literature for these systems.[39,41] This high soluble content can be due to the purity of the precursor olefins and side reactions, as explained by Sanchez-Ferrer and Finkelmann,[43] who avoided this problem by using a high-purity terminal vinyl ether. Regarding the swelling ratio (*q*), two

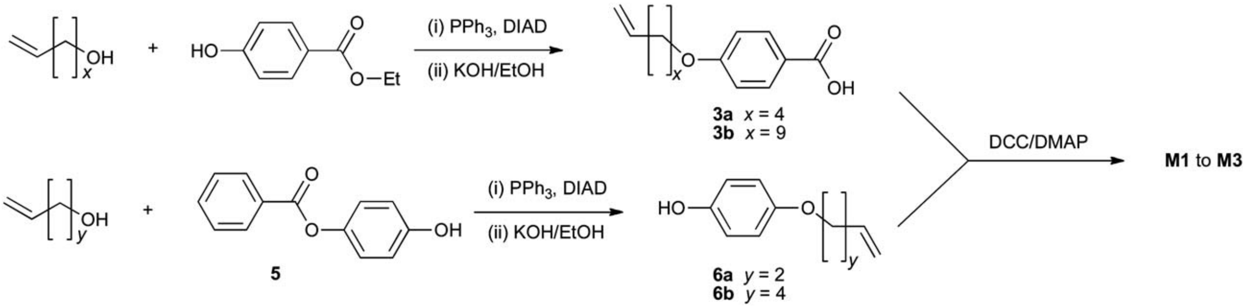


Scheme 2 Reactions for the synthesis of the siloxane spacers **S2** and **S3** and cross-linker **C2**.

Table 1 Transition temperatures of the mesogenic monomers

Monomers	Thermal behaviour[a]
M1	Cr 43.5 (60.1) N 53.9 (3.9) Iso
M2	Cr 57.9 (63.4) SmA 66.2 (4.1) Iso
M3	Cr 54.2 (72.3) SmA 75.6 (13.6) Iso

[a] Transition temperatures (°C) and enthalpies (ΔH in J g^{-1}) in parentheses. Data correspond to the second heating: Cr, crystal phase, SmA, smectic A phase, N, nematic phase, and Iso, isotropic liquid.



Scheme 1 Synthetic route for the synthesis of the mesogenic monomer.

Table 2 Transition temperatures of the elastomers prepared with different monomers, spacers and cross-linkers

Elastomer	Components[a]	Swelling ratio[b]/q	Sol content/wt%	Thermal behaviour[c]
E1	**M1**·**S1**·**C1**	4	3	g −26 SmC 30 (4) Iso
E2	**M2**·**S1**·**C1**	3	5	g −24 SmC 72 (8) Iso
E3	**M3**·**S1**·**C1**	4	10	g −27 SmC 71 (15) Iso
E4	**M1**·**S2**·**C1**	—	—	g −4.8 Iso
E5	**M2**·**S2**·**C1**	4	10	g −6 SmC 44 N 53 (8) Iso
E6	**M3**·**S2**·**C1**	4	24	g −9 SmC 60 (12) Iso
E7	**M1**·**S3**·**C1**	—	—	g −22 SmC 43.6 (3) Iso
E8	**M2**·**S3**·**C1**	4	25	g −14 SmC 37 N 50 (7) Iso
E9	**M3**·**S3**·**C1**	—	—	(g −9.2) Cr 83 Iso[d]
E10	**M2**·**S1**·**C2**	7	20	g −22 SmC 63 (11) Iso
E11	**M3**·**S1**·**C2**	—	—	(g −11) Cr 82 Iso[d]
E12	**M2**·**S2**·**C2**	6	18	g −7.2 N 31.6 (8) Iso
E13	**M2**·**S3**·**C2**	9	25	g −16 N 30.6 (7) Iso
E14	**M3**·**S2**·**C2**	6	22	g −13 N 47.5 (10) Iso
E15	**M3**·**S3**·**C2**	—	—	(g −3)Cr 79.6 Iso[d]

[a] Relative composition as set out in the text. [b] Swelling ratio is defined as $q = \alpha^2_{\perp} \times \alpha_{\parallel}$, where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the stretching factors parallel and perpendicular to the stretching direction. [c] Transition temperatures (°C) and enthalpies (ΔH in J g^{-1}) in parentheses. Data correspond to the second heating: g, glassy phase. [d] Note that for elastomers **E9**, **E11** and **E14**, a melting point is measured on first heating, after which cooling leads to the formation of a glassy phase. The crystalline state is not recovered in subsequent thermal cycles. Elastomers **E4**, **E7** and **E9** were not obtained in film form.

different groups of networks can be distinguished depending on the cross-linker used. Elastomers cross-linked with **C1** (functionality of four, **E1** to **E9**) showed a swelling ratio of four, while with **C2** (functionality of three, **E10** to **E15**), the swelling ratio was higher and varied between 6 and 9. These results are in agreement with those found in the literature for MC-LCEs[6,39,41] and suggest an anisotropic swelling behaviour for monodomain networks. Thus, for a monodomain, the network swells more in the direction perpendicular to the stretching direction than in the parallel.

3.4 Thermal properties of MC-LCEs

As described in the literature, MC-LCEs show systematically both SmC and N phases.[38–43] That the SmA phase of the monomer is replaced by a SmC phase in the polymer is accounted for by the tilt enforced to compensate for the much greater cross-sectional area of the siloxane chain compared with an alkyl chain. The liquid-crystalline properties of the new MC-LCEs showed not only that mesogenic units dictate their behaviour but also that the spacer and the cross-linker used had a major effect on the stability and identity of the mesophases. The liquid crystal properties of the networks prepared are summarised in Table 2.

The remaining elastomers exhibited a second-order transition, between −27 and −6 °C, corresponding to the glass transition temperature (T_g) and were liquid-crystalline at room temperature. The results show that T_g depended strongly on the flexibility of the spacer, but much less so on the mesogenic monomer used. As expected, for the most flexible spacer, **S1**, the networks showed the lowest T_g (−27 to −24 °C; **E1** to **E3**). The value of T_g increased as the more rigid, aromatic spacers **S2** and **S3** were used. Networks containing spacer **S2** (**E4** to **E6**) showed the highest T_g, which was attributed both to the rigid nature of the spacer and its overall linear shape (1,4-disubstitution), allowing good organisation of the polymer chains. T_g was much lower for elastomers **E7** to **E9** that use the non-linear spacer **S3**, as the 1,3-disubstituted component led to less well organised packing. On the other hand, T_g was not affected by the nature or connectivity of the cross-linker.

Mesomorphic behaviour: effect of spacer structure. Compared to the mesomorphic behaviour of the liquid crystal monomers shown in Table 1, reticulation favours the formation of SmC phase. The mesomorphic behaviour of the LC networks depended greatly on the spacer used. Networks containing trisiloxane spacer **S1** (**E1** to **E3**) formed a SmC phase due to the segregation between rigid cores of the mesogenic molecules and the flexible spacer. Elastomers containing mesogenic monomers **M1** (**E1**, **E4** and **E7**) and **M3** (**E3**, **E6** and **E9**) formed smectic C phases and, depending on the aromatic spacer used (**S2** for **M1** and **S3** for **M3**), the formation of liquid crystal phases was suppressed.

The family of elastomers that contained **M2** as the mesogenic monomer was shown to be more variable in the phase behaviour and the phase formed depends on the spacer. The elastomers that contained **S2** were smectic C, but interestingly as aromatic molecules were added as spacers (**S2** and **S3**, **E5** and **E8**), the networks tended to form a nematic phase above the smectic C.

Concerning the clearing temperature and the phase stability, different trends were observed since both depended on the mesogenic monomer and the spacer used. The addition of trisiloxane spacer **S1** stabilised the liquid-crystalline phase in the case of monomer **M2** (from 66.2 °C for monomer to 72 °C) and had little effect on the elastomer containing **M3** (entries 2 and 3). In the case of monomer **M1**, the introduction of spacer **S1** (elastomer **E1**) lowered the clearing temperature from 53.9 °C for the monomer to 30 °C for the elastomer. Thus, the introduction of an odd parity alkoxy chain may have affected the stabilisation of the mesophase. Interestingly, when the more rigid aromatic spacers **S2** and **S3** were used, the clearing temperature fell. Moreover, elastomers **E6** and **E8** showed the same mesomorphism.

Mesomorphic behaviour: effect of the cross-linker structure. In order to compare and verify the trends observed in the previous section, the same study was carried out for elastomers cross-linked with the more rigid aromatic cross-linker, **C2** (which possesses a functionality of three), and mesogenic monomers **M2** and **M3** (Table 2, **E10** to **E15**).

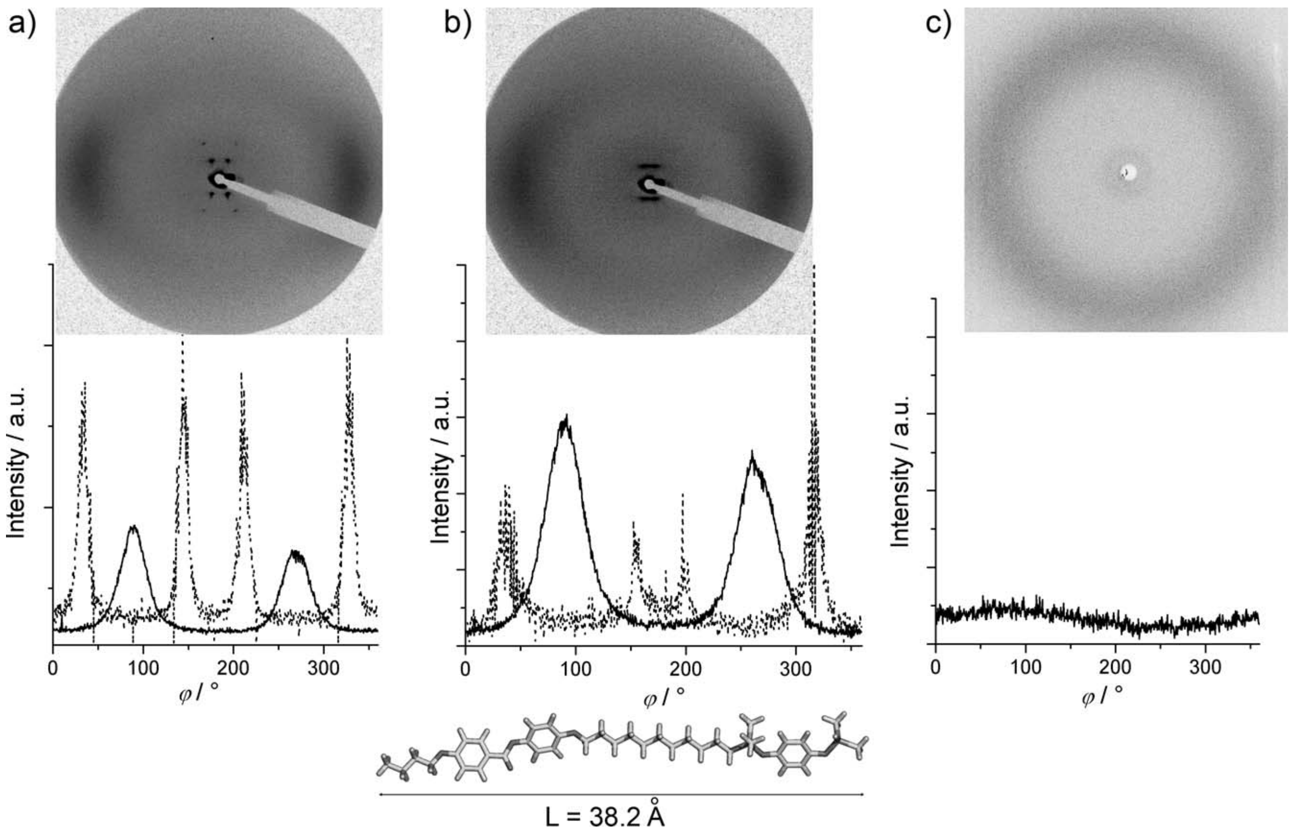


Fig. 2 X-Ray diffraction patterns for elastomer **E5**: (a) SmC phase at room temperature, (b) nematic phase at 50 °C, and (c) isotropic phase at 59 °C. Radial variation, φ, of the intensity of the small angle (dotted line) and wide angle (solid line) reflections corresponding to the X-ray patterns.

The most noticeable result was that cross-linker **C2** favoured the formation of the nematic phase, the exception being **E10** (which used flexible spacer, **S1**), where a SmC phase was found. Regarding the clearing temperature and phase stability, aromatic cross-linker **C2** had little effect on the clearing temperature compared to the monomer **M2** (66.2 °C). Also, it was observed that the addition of aromatic spacers **S2** and **S3** (for elastomers **E12**, **E13** and **E14**) destabilised the mesomorphic phase, compared to that of the monomer **M2** or **M3** (66.2 °C and 75.6 °C, respectively) and clearing temperatures as low as 30 °C were found. Elastomers **E11** and **E12** exhibited the same mesomorphism.

For the systems described in the literature and for the networks described here, the formation of SmC or both SmC and N phases was independent of whether the mesogenic monomer had two or three aromatic rings, the length of the alkyl chain and/or the degree of substitution in the ring. Comparing these systems with those containing mesogens with two aromatic rings,[41,43] in all cases it was found that clearing temperatures were between 50 and 70 °C. In these networks, this temperature can be tuned by modification of the spacer and/or the cross-linker, and temperatures as low as 30 °C have been found. As reported in the literature,[39] the use of rigid cross-linkers destabilises the mesomorphic phase in these systems also.

Concerning the siloxane spacer, the present materials showed the same behaviour as the systems described by Rousseau *et al.*,[42] where trisiloxane spacer **S1** and an aromatic 1,4-substituted siloxane spacer, similar to **S2**, were used. They observed that the use of the trisiloxane spacer formed a SmC phase, whereas using the aromatic spacer, a nematic phase was observed above the SmC phase. Here, the presence of a nematic phase was promoted by changing the cross-linker from a flexible siloxane to a more rigid aromatic unit.

3.5 XRD measurements

The mesophases of the elastomers were characterised by small-angle X-ray diffraction (XRD) for aligned samples, with the incident beam being normal to the surface of the films and the stretching direction. XRD patterns at different temperatures for **E5** are shown in Fig. 2; other data are found in the ESI†.

For all elastomers that showed a SmC phase, a pattern characteristic of a layered structure was observed as indicated by the presence of the inner reflection at low angles corresponding to the layer spacing (ESI†); the outer reflection corresponded to the side-to-side distance between mesogens. As the film was stretched uniaxially to form a monodomain, the mesogens become oriented in the direction parallel to the applied external stress, observed by the presence of two diffuse crescents in the wide-angle range (d-spacing = 4.5 Å) (Fig. 2a). At small angles, four, sharp reflections typical of a smectic C phase were observed, in which the layer normal was tilted at an angle with respect to the mesogens, suggesting a chevron-like structure§ (Fig. 3). The sharp reflections were indicative of a very high

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§ This has also been modelled as a conical arrangement in ref. 44. The two are rather similar.

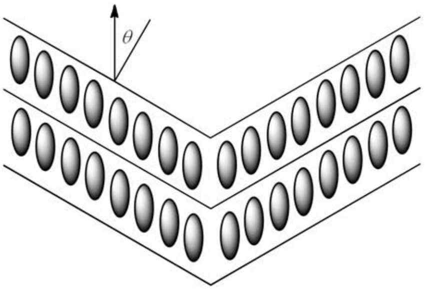

Fig. 3 Aligned 'chevron-like' structure of SmC phase.

Table 3 X-Ray data for elastomers containing cross-linker **C1**[a]

Elastomer	Phase(s)	d_m/Å	d_{001}/Å	d_{002}/Å	l_{cal}/Å	θ_{calc}/°	θ/°
E5	SmC, N	4.5	30.4	15.0	38.2	37	33
E6	SmC	4.5	33.9	16.3	40.5	33	37
E2	SmC	4.3	30.1	—	34.9	30	30
E3	SmC	4.3	31.6	15.5	35.6	27	26
E8	SmC, N	4.4	31.5	15.0	38.2	35	37

[a] d_m: *d*-spacing between mesogens; d_{001} and d_{002}: interlayer distances measured from X-ray data; l_{cal}: interlayer distances from geometry optimisation; θ_{calc}: calculated, and θ: measured tilted angle from X-ray experiments.

degree of alignment, while the fact that there are four of them points to the chevron structure rather than a true monodomain. When the sample was heated to 50 °C in the nematic phase, the sharp inner reflections give way to diffuse lines, corresponding to the presence of smectic fluctuations within the nematic phase, their domain size decreasing on heating (cybotactic groups, Fig. 2b). The mesogens orientation along the stretching direction is maintained in the mesophase as evidenced by the two large diffuse half-crescents confined in the equatorial plan (*i.e.* the nematic director is aligned perpendicular to the X-ray beam and parallel to the surface of the film, Fig. 2b).

The interlayer distance obtained from the low-angle distribution for the elastomers cross-linked with **C1** varied between 30.1 and 33.9 Å for d_{001} and between 15 and 16.3 Å for d_{002}, in agreement with those distances reported in the literature.[42] The tilt angles, θ, calculated from the azimuthal intensity distribution at low angle, were between 26 and 37°.

These tilt angles are in the same range to those reported in the literature[39,41–43] (θ = 30–45°). The measured tilt angles θ are in good agreement with the theoretical values of θ_{calc}, calculated from the fully extended chain conformation tilted at the angle θ (Fig. 2, Table 3).

4. Conclusions

A series of new unsymmetric MC-LCEs having different chemical composition have been synthesised. The mesogenic monomer, the spacer and the cross-linker have been varied systematically with the purpose of determining the structure–properties relationships of these systems.

The MC-LCEs studied showed that small changes in the chemical structure either of the mesogenic monomer, the spacer or the cross-linker had an important effect on the thermal behaviour of the networks. Unsymmetric monomers did not favour the formation of the nematic phase as might have been expected, rather a SmA phase was formed when a long alkyl chain was used.

The MC-LCEs were liquid-crystalline over a wide temperature range, showing low T_g values and low clearing temperatures (up to 72 °C). The elastomers that contained the flexible spacer (**S2**) systematically presented the smectic C phase. The introduction of an aromatic ring into the spacers (**S4** or **S5**) promoted the formation of the nematic phase. That an aromatic group should have such an effect was reinforced by the observation that the use of an aromatic cross-linker (**C2**) also gave rise to elastomers that showed only a nematic phase. On the other hand the presence of a more rigid spacer and/or cross-linker destabilised the mesomorphic phase and thus clearing temperatures as low as 30 °C were found.

In this report, it is shown that the mesomorphic behaviour of the MC-LCEs can be tuned by the chemical composition of the components, namely the mesogenic monomer, the spacer and the cross-linker and the accessible working temperatures found make them good candidates as sensors and actuators. The effect of the structure and thus the mesomorphic behaviour on the mechanical and thermomechanical properties of the new unsymmetrical MC-LCEs will be discussed in the following paper.

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