# A Simple and Versatile Synthetic Route for the Preparation of Main-Chain, Liquid-Crystalline Elastomers

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ABSTRACT: A new synthetic concept has been successfully used for the preparation of main-chain, liquid-crystalline elastomers (MC-LCEs). This approach consists of a one-step, platinum-catalyzed hydrosilylation between a low molar mass divinylic nematogen and a mixture of 1,1,3,3-tetramethyldisiloxane and 2,4,6,8-tetramethylcyclotetrasiloxane (in the appropriate equimolar amount), the disiloxane being used for the polymer chain extension and the tetrasiloxane as the cross-linker. Three new MC-LCEs, **E1**, **E2**, and **E3**, were prepared accordingly for which either the mesogenic unit or the cross-linking density was changed, further proving the versatility of the method. The mesomorphic properties include smectic C ($S_C$) and nematic (N) phases as characterized by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD).

## Introduction

Liquid-crystalline elastomers (LCEs) represent a fascinating aspect in the science of macromolecular liquid crystals which has attracted much attention over the past 20 years essentially due to their exceptional properties not displayed in other high-molecular-weight systems.[1] They are composed of two subsystems: (i) the mesogenic groups which self-assemble to give the mesomorphic properties and (ii) the weak density of polymeric chains' reticulation (thus differing with anisotropic networks[2] and polymer network-stabilized liquid crystals[3]) which leads to rubber elasticity. The interest in such materials thus arises from the competition of the liquid-crystalline order and the mechanical properties. Several macromolecular systems differing in their structure have now been prepared, including mainly side-chain and side-on LCEs (SC-LCEs) with calamitic,[1] discotic,[4] and amphiphilic[5] side groups. However, it is only very recently that new structures have been obtained such as main-chain LCEs (MC-LCEs in which the mesogens are forming the backbone of a linear polymer),[6] mixed LCEs (side-chain polymer cross-linked with main-chain polymers),[7] and combined main-/side-chain LCEs (alternation of main and side groups in the polymer).[1d,8] From these studies, it appears that the thermal behavior of the un-cross-linked corresponding polymer (mesophase type and transformation temperatures) is not affected to a great extent by weak reticulation and that the rubber elasticity is preserved in the mesophase. Given this, the possibility to macroscopically orient the whole sample by the application of a mechanical stress, i.e., to couple the liquid crystalline order of the mesogenic groups with the polymer network, does appear to be one of the most fascinating properties of LCEs. As a result, a polydomain-to-monodomain transition takes place; i.e. the director of the mesophase becomes uniformly aligned throughout the whole sample with respect to the direction of the external stress.[9] If this order can be locked in by a subsequent cross-linking reaction, stable monodomains are obtained with almost perfectly oriented mesogenic groups. These LSCEs (liquid single-crystal elastomers)[10] are new, stable materials with interesting theoretical aspects[11] and with various potential applications such as artificial lenses and muscles.

In 1975, de Gennes predicted that MC-LCEs should have enhanced mechanical and optical properties in comparison to the SC-LCEs because of the direct coupling of the mesogenic units with the polymer backbone.[12] However, owing to low solubility and the high transformation temperatures found in MC-LCPs (making experimental studies rather difficult) and the difficulty to realize the corresponding MC-LCEs, this approach has not been explored to a large extent.[6] It was only very recently that an almost room-temperature nematic MC-LCE ($T_g$ = 23 °C, $T_{n,i}$ = 96 °C) was reported.[6b] This system is based on semiflexible oligoether ($T_g$ = 32 °C, $T_{n,i}$ = 100 °C),[13] the cross-linker being 2,4,6,8-tetramethylcyclotetrasiloxane. As for SC-LCEs, a reversible transition from a polydomain to a monodomain structure[9] upon stretching was observed, and thermoelastic measurements also exceeded those observed in SC-LCEs, confirming the de Gennes predictions.

## Results and Discussion

**Concept.** On the basis of these experimental results and motivated by the possibility to study materials with new and interesting properties, an original synthetic method is proposed here. Instead of starting from a presynthesized main-chain polymer as this has been so far the case,[6] a one-pot reaction was thought of by the direct addition reaction of a divinylic mesogenic monomer to 1,1,3,3-tetramethyldisiloxane and 2,4,6,8-tetramethylcyclotetrasiloxane (in an equimolar mixture of vinyl and Si−H groups): the mesogen forms the core of the main-chain polymer, the disiloxane participates in the chain extension, and the tetracyclosiloxane is the connecting point of four polymeric chains (Scheme 1). Thus, in this approach, the synthesis only requires the preparation of a divinylic mesogenic monomer, the

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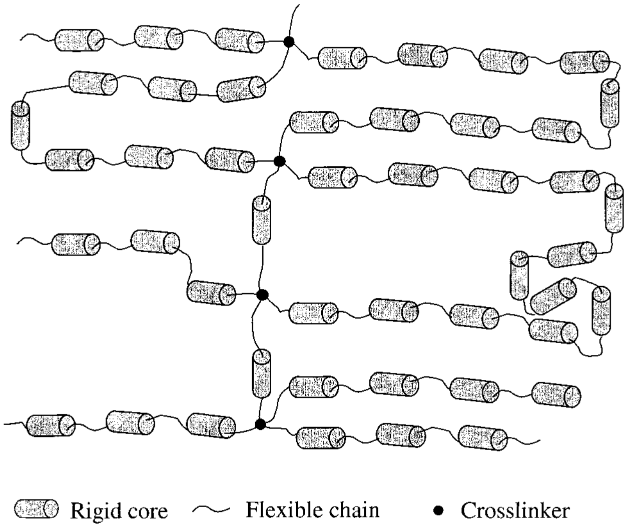
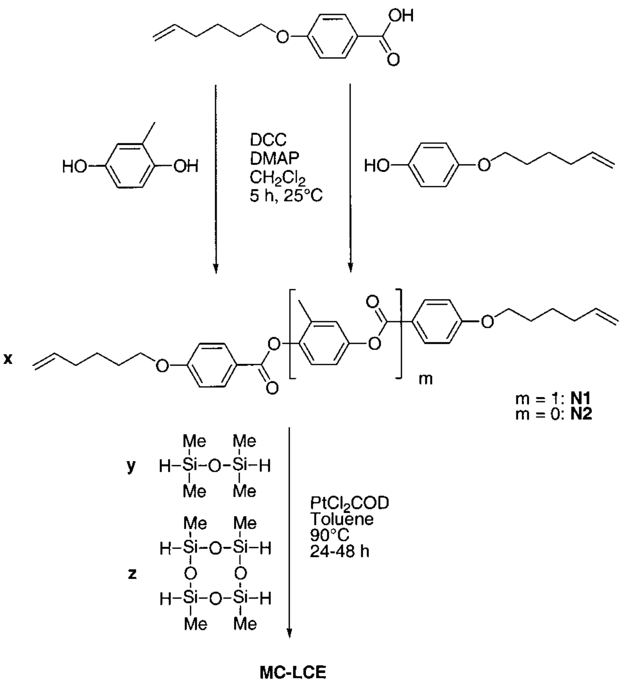
**Scheme 1. Schematic Representation of the MC-LCEs**



**Scheme 2. Reaction Scheme and Chemical Structures of the Monomers Used for the Synthesis of the MC-LCEs**



siloxanes being commercially available,[14] and the control of the cross-linking density can be more accurately monitored.

**Materials.** To test this new concept, two difunctionalized monomers were designed to yield a nematic phase at accessible temperatures, namely 1,4-bis[4-(hex-5-enyloxy)benzoyloxy]-2-methylbenzene, **N1**, and 4-(hex-5-enyloxy)benzoate−(4-hex-5-enyloxy)phenyl ester, **N2** (Scheme 2). Because of the presence of the side methyl group in the central part of **N1**, it was expected that a system favoring the formation of a nematic phase instead of smectic phases would be preferentially obtained. Indeed, the three-ring system **N1** shows as expected a broad nematic phase between 67 and 120 °C, and the two-ring system **N2** exhibits a narrow nematic phase temperature range (Crys•52•N•62•I). The nematic phase was recognized on the basis of its typical texture under polarized optical microscopy (Schlieren with $\pm{}^{1}/_{2}$ singularities and formation of droplets at $T_{N/I}$), while the DSC confirmed the transition temperatures.

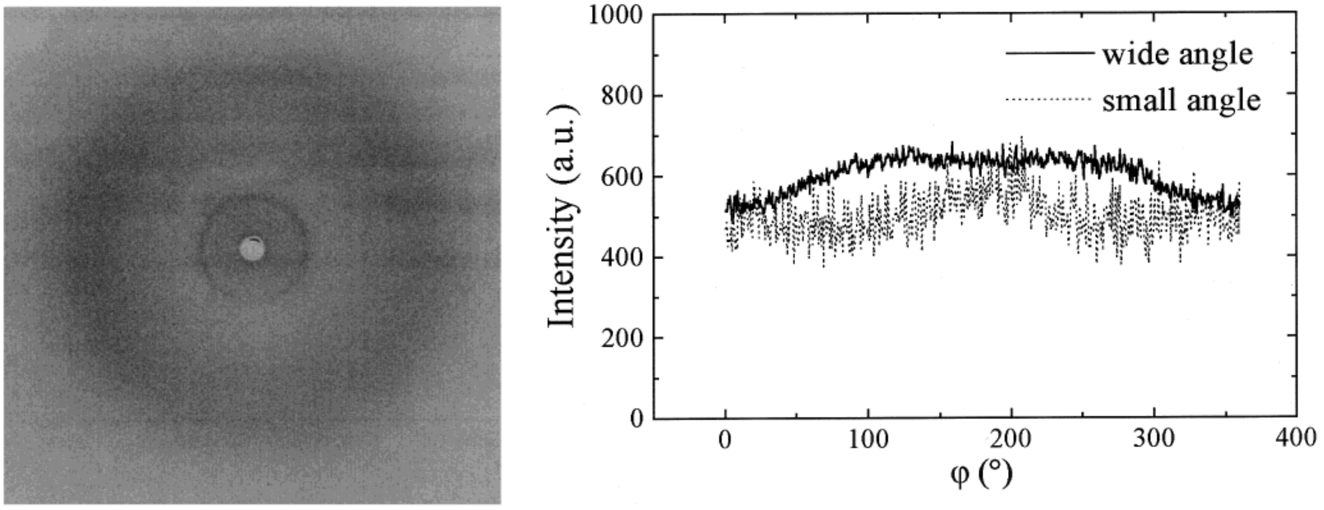
**Synthesis.** The main-chain elastomers were obtained by a one-pot, platinum-catalyzed hydrosilylation reaction of an equimolar amount of the mesogen with the same amount of 1,1,3,3-tetramethyldisiloxane and 2,4,6,8-tetramethylcyclotetrasiloxane in the spin-cast cell. This approach proved successful given that three elastomers containing the nematogens **N1** and **N2** could be prepared accordingly. The relative ratio between the disiloxane and tetracyclosiloxane was also changed.

**Characterization of the Elastomers.** To identify the mesomorphic properties of these elastomers, POM, DSC, and XRD were used.

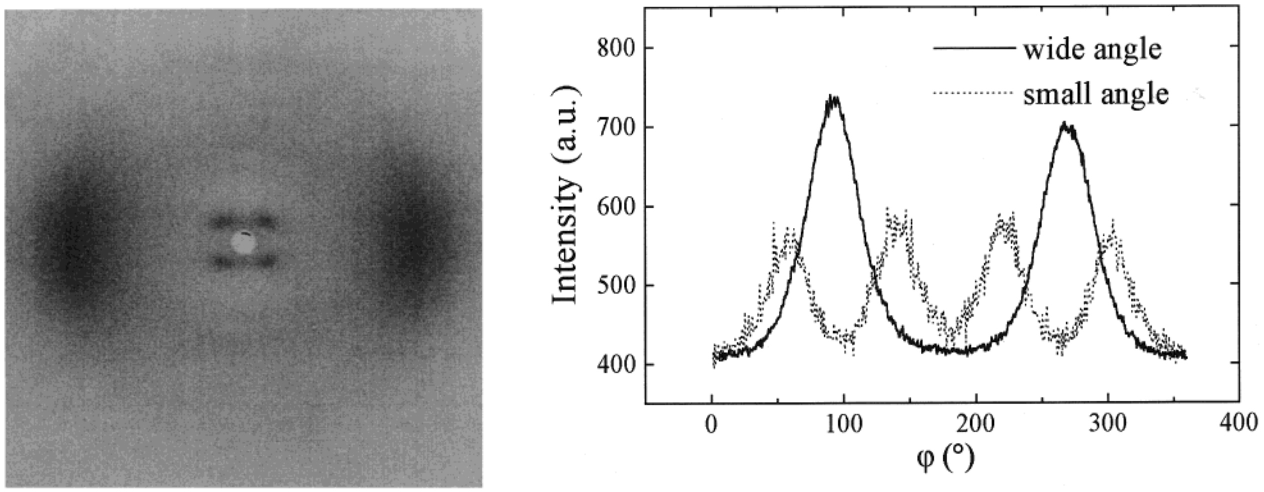
**Textures Observation by POM.** Owing to tension defects present in the thin films, it is impossible to identify the nature of the mesophase by this technique. It is however possible to determine the mesophase-to-isotropic state temperature transformation because of the observable shrinking of the film during this event. A thin piece of the elastomers was placed on a coverslip and heated on a hot-stage POM, and the clearing temperatures were determined. The measured temperatures were in complete agreement with the following DSC and XRD measurements (Table 1).

**Thermal Analysis by DSC.** A first observation that can be made is the excellent thermal stability of the samples as evidenced by the good reproducibility on successive heat−cool cycles of their thermal behavior. The data (Table 1) considered are taken from the second heating, although no apparent changes were observed between the first and second heating run. The three samples display also a comparable mesomorphic behavior. It is composed of four zones. The first zone corresponds to a glassy smectic phase. On further heating, a glass transition at $T_g$ indicates the transition from the anisotropic glass to the smectic phase. At higher temperature, a first endotherm is seen which indicates the transformation from the smectic to the nematic phase. Finally, the last endotherm is indicative of the isotropization of the sample.

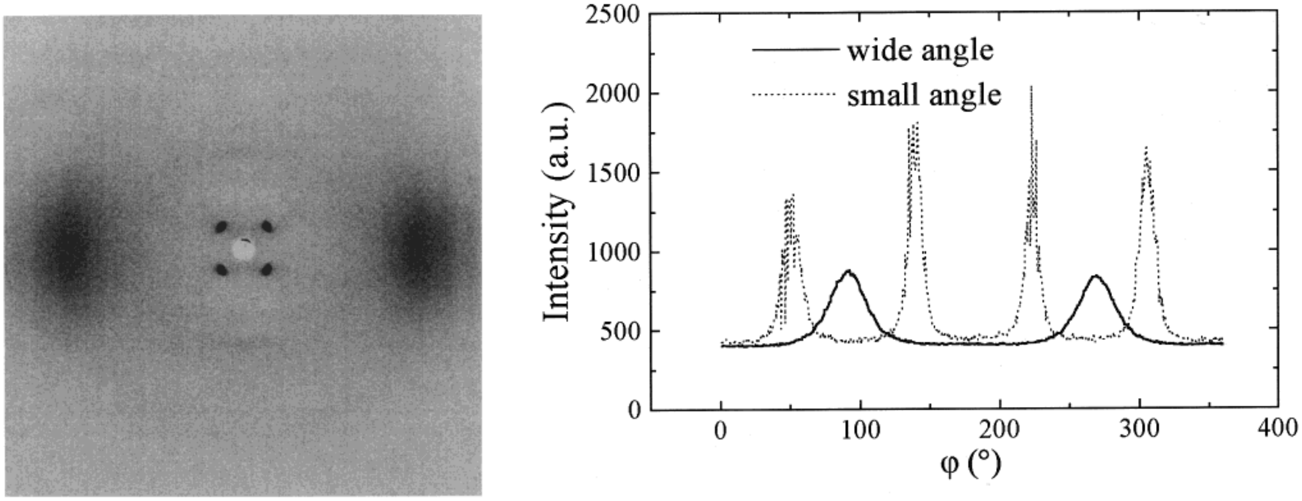
**XRD Experiments.** The mesophases of all the samples **E1**, **E2**, and **E3** were identified by XRD at different temperatures. The incident beam is perpendicular to the stress direction and to the surface of the film. Typical diffraction patterns were obtained corresponding to a smectic C phase for the low-temperature mesophase and to a nematic mesophase for the higher one. As a representative example, the X-ray patterns of the mesophases of **E2** are shown at several temperatures (Figure 1). At 153 °C, in the isotropic state, the X-ray pattern (Figure 1a) and the corresponding azimuthal intensity profiles (Figure 1a′) show two diffuse halos: one in the wide angle region, indicative of a complete orientational disorder of the mesogenic units, and another one in the small angle area, which corresponds to some degree of local positional ordering of the mesogenic units (the mesogens are chemically attached to each other through the network). On cooling, at 148 °C, the transformation to the nematic phase takes place. The inner ring transforms to a set of two diffuse scattering lines in the meridian plan, and the outer halo gives place to two large diffuse half-crescents in the equatorial plan. These changes are characteristic of a transformation to a nematic phase and to the onset of a macroscopic orientation of the mesogenic units along the stretching direction. At 110 °C, in the nematic phase



(a) T = 153°C, Isotropic state (I)



(b) T = 110°C, Nematic phase (N)



(c) T = 55°C, Smectic C phase ($S_C$)

**Figure 1.** X-ray patterns (a, b, c) and the corresponding azimuthal intensity profiles (a′, b′, c′) at different temperatures of **E2**: (a) $T = 153$ °C, in the isotropic state; (b) $T = 110$ °C, in the nematic phase; and (c) $T = 55$ °C, in the $S_C$ phase. $\varphi$ is the azimuthal angle.

(Figure 1b,b′), the two half-crescents are smaller and confined in the equatorial plan and the two diffuse lines give way to a set of four Braggs peaks. This indicates that the nematic phase has its director perfectly aligned

**Table 1. Elastomers' Characteristics: Composition, Thermal Behavior, Phase Transformation Temperatures (°C), and Corresponding Change of the Isobaric Specific Heat ($\Delta C_p$/J g$^{-1}$ °C$^{-1}$ for the Glass-to-Mesophase Transformation) or Phase Transformation Enthalpy ($\Delta H$/J g$^{-1}$ for the Mesophase-to-Mesophase and Mesophase-to-Isotropic Liquid Transformations) in Parentheses**

| elastomer | nematogen | disiloxane (% mmol) | tetrasiloxane (% mmol) | thermal behavior[a] (from POM, DSC, XRD) |
|---|---|---|---|---|
| **E1** | **N1** | 90 | 5 | g·7.5 (0.3)·$\mathrm{S_C}$·74 (2.1)·N·151 (3.8)·I |
| **E2** | **N1** | 60 | 20 | g·4 (0.3)·$\mathrm{S_C}$·69 (1.7)·N·148 (3.4)·I |
| **E3** | **N2** | 60 | 20 | g·9 (0.8)·$\mathrm{S_C}$·67 (11.5)[b]·N·73 (−)·I |

[a] Abbreviations: g = anisotropic glass, $\mathrm{S_C}$ = smectic C phase, N = nematic phase, I = isotropic liquid. The transformation temperatures were extrapolated to 0 °C min$^{-1}$ heating rate. [b] Cumulated enthalpy for the $\mathrm{S_C}$-to-N and N-to-I phase transformations (unresolved peaks).

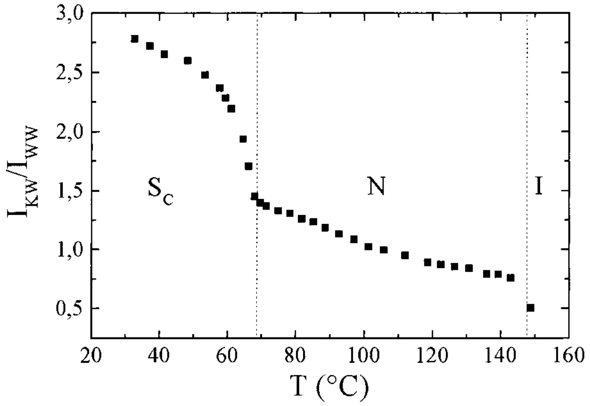


**Figure 2.** Variation of the ratio between the intensity of the small angle reflexes, $I_{\mathrm{KW}}$, and the intensity of the wide angle reflexes, $I_{\mathrm{WW}}$, as a function of temperature for sample **E2**.

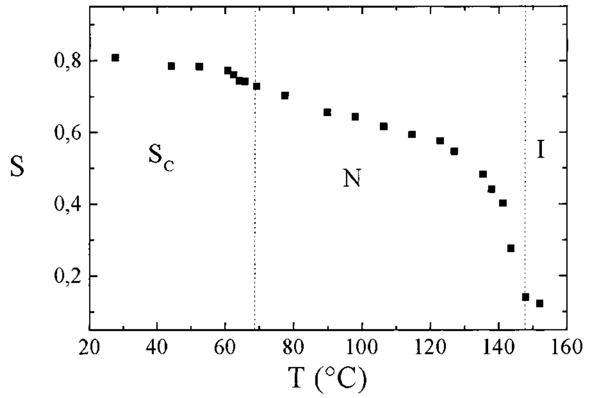


**Figure 3.** Variation of the order parameter, *S*, with temperature for sample **E2**.

perpendicular to the X-ray beam and parallel to the surface of the film (Figure 1b). In other words, the mesogenic subunits are macroscopically aligned parallel to the axis of the applied stress. One can also notice the presence of smectic fluctuations within the nematic phase, their domain size increasing on cooling. On further cooling, the nematic monodomain undergoes another phase transformation at 69 °C. The wide angle half-crescents remain still diffuse but are narrower, and the small-angle Braggs peaks become sharper, indicative of a layered phase, namely a smectic C phase (Figure 1c,c′). The tilt angle (angle between the layer normal and the director) is ca. 45°, suggesting a Chevron structure.

The intensity ratio between $I_{\mathrm{KW}}$ and $I_{\mathrm{WW}}$, where $I_{\mathrm{KW}}$ is the intensity of the small-angle layer reflexes and $I_{\mathrm{WW}}$ the intensity of the wide angle reflexes, represented in Figure 2 as a function of temperature, corroborates these observations. This ratio decreases drastically at the $\mathrm{S_C}$-to-N phase transformation and at the clearing of the sample. The three parts of the diagram correspond to the $\mathrm{S_C}$ phase (up to 69 °C), to the nematic phase (between 69 and 148 °C) showing the presence of cybotactic groups within the mesophase, and then to the isotropic state. The order parameter, *S*, was estimated from the wide-angle interchain scattering as previously described.[6b,9b,15] The variation of *S* as a function of temperature (Figure 3) is also in complete agreement and shows the persistence of the nematic monodomain over a large temperature range. It is found to decrease through a succession of plateaus as the temperature is raised, these plateaus corresponding to different molecular organizations. Finally, it drops down instantly at the approach of the clearing temperature. In all cases, the consistency of the transformation temperatures is verified.

## Conclusion

We reported on a rapid and easy pathway for the synthesis of MC-LCEs, which does not require the preparation of a prepolymer, and thus the control of the corresponding parameters such as the polymolecularity and the degree of polymerization. This approach presents other interesting aspects, such as the wide possibilities for structural variations, thus providing many possibilities to modify the phase behavior and the transformation temperatures by straightforward structural modifications. For instance, one can decrease the mesogenic content (which can be varied from 100% to 0%, still not yet achieved) by the introduction of, for example, 1,3-divinyltetramethyldisiloxane or make use of other mesogenic subunits (calamitic, discotic, chiral, amphiphilic, or mixtures). These modifications will most certainly have profound effects on the properties of the resulting elastomers. This concept is therefore a powerful and competitive tool for the realization of a wide variety of MC-LCEs not yet reported in the literature. These systems may be suitable, once all the property—structure relationships established, for several types of applications, one of them being the artificial muscles.[16] Some other physical experiments such as the birefringence and thermoelastic measurements are currently being carried out, and the promising results will be reported in a forthcoming paper.

## Experimental Section

**Synthesis. Monomers. N1** and **N2** were prepared by DCC-based-catalyzed esterifications.[17] 1,3-Dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), dichloro(1,5-cyclooctadiene)platinum(II) ($\mathrm{PtCl_2COD}$), and 2-methyl-hydroquinone were used as purchased. Toluene was made thiophene-free by distillation over sodium. The synthesis of the 4-[hex-5-enyloxy]benzoic acid and 4-(hex-5-enyloxy)phenol has been described elsewhere.

**Elastomers.** The synthesis of the elastomers follows the procedure of standard hydrosilylation reactions and was carried out in concentrated solution (1 mL per 1 mmol). A thiophene-free toluene solution (1 mL) of the monomer (*x* mmol equiv), chain extensor ($y$ mmol equiv), and cross-linker ($(x - y)/2$ mmol equiv) was filtered using a 0.5 $\mu$m Millipore filter and filled into a centrifuge cell with a diameter of 5 cm and a height of 1 cm. The catalyst (25−40 $\mu$L per mmol of mesogen of a 1% w/w solution of $PtCl_2COD$ in $CH_2Cl_2$) was then added. The reaction was carried out under centrifugation (5000 rpm) at 90 °C for 24−48 h. Prior to the reaction launch, the inner wall of the cell was coated with a Teflon film in order to remove the gel formed at the end of the reaction. The cell was removed from the centrifuge and allowed to cool to 25 °C, and the swollen gel was cautiously removed from the cell. The gel was then hung at one end with a clamp and left for 30 min at room temperature. In these conditions, the solvent slowly evaporates, giving rise to a LCE film. In the meantime, the other free extremity of the film was carefully loaded (ca. 3 g) in order to align the sample. Thereafter, it was annealed for 24 h at 30 °C under high vacuum and the unfinished cross-linking reaction allowed going to completion. The LCEs (polydomains and monodomains) thus prepared were stable.

**E1. N1**: 528.7 mg (1 mmol); disiloxane: 124.6 mg (0.9 mmol); tetrasiloxane: 12 mg (0.05 mmol); toluene: 1 mL; catalyst: 40 $\mu$L; $T$: 90 °C; $t$: 48 h.

**E2. N1:** 528.7 mg (1 mmol); disiloxane: 83.1 mg (0.6 mmol); tetrasiloxane: 48.1 mg (0.2 mmol); toluene: 1 mL; catalyst: 30 $\mu$L; $T$: 90 °C; $t$: 48 h.

**E3. N2:** 384.6 mg (1 mmol); disiloxane: 83.1 mg (0.6 mmol); tetrasiloxane: 48.1 mg (0.2 mmol); toluene: 1 mL; catalyst: 25 $\mu$L; $T$: 90 °C; $t$: 36 h.

The structure of **E1** and **E2** cannot be known with accuracy because the cross-links are formed statistically according to the chemistry used. However, by FT-IR, the conversion of Si−H to Si−C has been checked on a thin elastomer film, that is after the annealing procedure, and was found to be larger than 95%. The degrees of swelling of the three elastomers (which is an indirect measure of the network density[18]) were measured in a saturated atmosphere of toluene and were found to show rather high values. For **E1**, **E2**, and **E3** the values are 7.6, 7.5, and 5.8, respectively. The sol ratios are 22% for **E1**, 21% for **E2**, and 18% for **E3**.

**DSC.** The measurements were performed with a Perkin-Elmer DSC 7. Two heat−cool cycles were systematically run for all the samples. For the monomers the two heat−cool scans were recorded at 5 and 10 °C $min^{-1}$ using 5.5 mg of **N1** and 7.4 mg of **N2**. For the elastomers, they were recorded at 16 and 25 °C $min^{-1}$ using 22.7 mg of **E1**, 18.6 mg of **E2**, and 22.2 mg of **E3**. The glass transition temperatures ($T_g$) and the phase transformation temperatures were determined by extrapolating to 0 °C $min^{-1}$ heating rate.

**XRD.** X-ray experiments were carried out with a Philips PW 1730 and Cu K$\alpha$ radiation. The incident beam was normal to the surface of the films. The scattered X-ray intensity was detected by the Image Plate system. The order parameter, $S$, was calculated by an azimuthal scan applied to the nematic intermesogen reflections.[15]

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(17) **N1**: 4-[Hex-5-enyloxy]benzoic acid (5 g, 22.7 mmol), 2-methylhydroquinone (1.4 g, 11.3 mmol), DCC (4.7 g, 22.7 mmol), and DMAP (280 mg, 2.3 mmol), $CH_2Cl_2$ (50 mL), room temperature, stirred for 48 h. Crystallization in EtOH. Yield: 3.6 g (60%). DSC (°C): cryst·69.5 (22.2 kJ $mol^{-1}$)·N·159.3 (3.1 kJ $mol^{-1}$)·I. $^1H$ NMR ($CDCl_3$, 299.87 MHz): 8.09 ($H_{be}$, AA′XX′, $|J|$ 7.4, 2 H), 8.07 ($H_{be}$, AA′XX′, $|J|$ 7.4, 2 H), 7.11 ($m$-$H_{hy}$, d, $|J|$ 8.6, 1 H), 7.05 ($p$-$H_{hy}$, dd, $|J|$ 8.6, $|J|$ 3.2, 1 H), 7.02 ($o$-$H_{hy}$, d, $|J|$ 3.2, 1 H), 6.93 ($H_{be}$, AA′XX′, $|J|$ 7.4, 2 H), 6.91 ($H_{be}$, AA′XX′, $|J|$ 7.4, 2 H), 5.77 ($-C\mathit{H}{=}CH_2$, ddt, $^{trans}J$ 18.0, $^{cis}J$ 12.0, $^3J$ 6.0, 2 H), 4.98 ($-CH{=}C\mathit{H}H$, dd, $^{trans}J$ 18.0, $^{gem}J$ 3.0, 2 H), 4.93 ($-CH{=}CH\mathit{H}$, dd, $^{cis}J$ 12.0, $^{gem}J$ 3.0, 2 H), 3.98 ($-OC\mathit{H}_2-$, t, $^3J$ 6.0, 4 H), 2.18 ($-CH_3$, s, 3 H), 2.08 ($CH_2{=}CH-C\mathit{H}_2-$, m, 4 H), 1.78 ($-O-CH_2-C\mathit{H}_2-$, m, 4 H), 1.53 ($-C\mathit{H}_2-$, m, 4 H). $^{13}C$ NMR ($CDCl_3$, 75.41 MHz): 163.84, 163.45 (2 $-\mathit{C}OO-$), 162.42 ($\mathit{C}_{be}-O-$), 147.36 ($o$-$\mathit{C}_{ar}-O-$), 145.97 ($m$-$\mathit{C}_{ar}-O-$), 137.28 ($-\mathit{C}H{=}$), 131.20 ($\mathit{C}_{be}$), 130.68 ($Me-\mathit{C}_{ar}$), 121.81 ($o$-$\mathit{C}_{ar}$), 120.54 ($\mathit{C}_{be}-COO-$), 120.37 ($m$-$\mathit{C}_{ar}$), 118.95 ($p$-$\mathit{C}_{ar}$), 113.81 (${=}\mathit{C}H_2$), 67.03 ($-O-\mathit{C}H_2-$), 32.28 ($-\mathit{C}H_2-CH{=}CH_2$), 27.45 ($-O-CH_2-\mathit{C}H_2-$), 24.17 ($-\mathit{C}H_2-$), 15.33 ($-\mathit{C}H_3$). **N2**: 4-(Hex-5-enyloxy)benzoic acid (4 g, 18.2 mmol), 4-(hex-5-enyloxy)phenol (3.5 g, 18.2 mmol), DCC (3.8 g, 18.2 mmol) and DMAP (225 mg, 1.8 mmol), $CH_2Cl_2$ (50 mL), room temperature, stirred for 24 h. Crystallization in EtOH. Yield: 4.5 g (63%). DSC (°C): cryst·52 (22.0 kJ $mol^{-1}$)·N·61 (0.6 kJ $mol^{-1}$)·I. $^1H$ NMR ($CDCl_3$, 299.87 MHz): 8.05 ($H_{be}$, AA′XX′, $|J|$ 7.6, 2 H), 7.03 ($H_{ph}$, AA′BB′, $|J|$ 6.8, 2 H), 6.89 ($H_{be}$, AA′XX′, $|J|$ 7.6, 2 H), 6.85 ($H_{ph}$, AA′BB′, $|J|$ 6.8, 2 H), 5.77 ($-C\mathit{H}{=}CH_2$, ddt, $^{trans}J$ 18.0, $^{cis}J$ 12.1, $^3J$ 6.2, 2 H), 4.99 ($-CH{=}C\mathit{H}H$, dd, $^{trans}J$ 18.0, $^{gem}J$ 3.0, 2 H), 4.93 ($-CH{=}CH\mathit{H}$, dd, $^{cis}J$ 12.1, $^{gem}J$ 3.0, 2 H), 3.99 ($-OC\mathit{H}_2-$, t, $^3J$ 6.4, 2

H), 3.91 ($-\mathrm{OC}\mathit{H}_2-$, t, $^3J$ 6.4, 2 H), 2.09 ($\mathrm{CH_2{=}CH{-}C}\mathit{H}_2-$, m, 4 H), 1.77 ($-\mathrm{O{-}CH_2{-}C}\mathit{H}_2-$, m, 4 H), 1.54 ($-\mathrm{C}\mathit{H}_2-$, m, 4 H). $^{13}$C NMR (CDCl$_3$, 75.41 MHz): 163.80 ($-\mathit{C}\mathrm{OO}-$), 161.88 ($\mathit{C}_{\mathrm{be}}-\mathrm{O}-$), 155.23 ($\mathit{C}_{\mathrm{ph}}-\mathrm{O}-$), 142.94 ($\mathit{C}_{\mathrm{ph}}-\mathrm{OCO}-$), 137.01, 136.86 ($-\mathit{C}\mathrm{H}{=}$), 130.70 ($\mathit{C}_{\mathrm{be}}$), 120.95 ($\mathit{C}_{\mathrm{ph}}$), 120.28 ($\mathit{C}_{\mathrm{be}}-\mathrm{COO}-$), 113.58 ($\mathit{C}_{\mathrm{ph}}$), 113.37, 113.23 ($={\mathit{C}}\mathrm{H}_2$), 112.75 ($\mathrm{C}_{\mathrm{be}}$), 66.69, 66.56 ($-\mathrm{O}-\mathit{C}\mathrm{H}_2-$), 31.91, 31.85 ($-\mathit{C}\mathrm{H_2{-}CH{=}CH_2}$), 27.21, 27.02 ($-\mathrm{O{-}CH_2}-\mathit{C}\mathrm{H}_2-$), 23.81, 23.74 ($-\mathit{C}\mathrm{H}_2-$).

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