Main-Chain Liquid Crystalline Elastomers: Monomer and Cross-Linker Molecular Control of the Thermotropic and Elastic Properties

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ABSTRACT: In this study, we report on the design and synthesis of new main-chain liquid crystal elastomers (MC-LCEs), i.e., LCEs with the mesogenic groups inserted in the main-chain, and on their mesomorphic and mechanical properties. We proposed and tested various approaches to produce in a simple way MC-LCEs exhibiting systematically the nematic phase, preferably within an accessible temperature range and ideally with a room-temperature activity, and for which systematic smectic mesophases formation and stability would be reduced. The first approach consisted in the straight modification of the nematic monomer core by methylation of the central ring to reduce the side-by-side molecular interactions, but still preserving the molecular anisotropy to promote nematic materials. As for the second approach, it implied the incorporation within the reticulated network of bulky and anisotropic cross-linkers, with the expectation to disfavor the tendency for lamellar phase formation by limiting the microsegregation between the plastifying segments and rigid parts. All the elastomeric systems reported here exhibited a room-temperature mesomorphic behavior; in all cases, both SmC and N phases were systematically observed. Particularly relevant, a low-temperature nematic behavior was strongly promoted over the formation of smectic phases with elastomers containing discotic cross-linkers. In contrast, the degree of methylation appeared to have almost no influence on the mesophase nature, but contributed to a substantial reduction of the transition temperatures. The impacts of these structural modifications on the mechanical properties were also evaluated. For instance, elastomers with anisotropic cross-linkers have a more reduced stretching ability and are slightly more fragile than those with flexible (and deformable) ones and do not form as stable monodomains either. The results of these investigations are reported, the mesomorphic and elastic properties are discussed in correlation with the molecular structures of the components, and also some aspects connected to the synthesis are evoked.

Introduction

Liquid crystal elastomers (LCEs) have been the subject of increasing research and are developed as promising functional materials due to their remarkable properties and, in particular, to their exceptional elastic behavior,[1,2] first predicted by de Gennes,[3] and to the fact that, unlike conductive polymers and gels, they do not need a solvent to actuate and exert traction.[4,5] Indeed, LCEs are materials with uncommon elastic properties that combine the orientational ordering properties of liquid crystalline systems (enthalpic contribution) with the rubbery elasticity of polymer networks (entropic effect).[6] Their ability to change their shape and size significantly (and reversibly) by inducing disorder in the liquid crystalline structure at the nematic-to-isotropic (N−I) phase transformation (triggered by temperature) or in response to other external stimuli (electric field,[7] light[8]) make them particularly attractive in order to be potentially incorporated into actuating materials that can mimic muscle performances (contraction/elongation cycles)[9–11] or integrated into electronics (SHG, lasers).[12] The contraction length, the stress, and the speed of the response of these materials are the three important parameters to optimize for successful implementation in a wide range of applications including robotics, microfluidics, and microelectromechanical systems (MEMS). Ideally, and this is a real challenge for their utilization in these applications, LCEs with well-ordered and immobilized single nematic monodomains at room temperature are required. However, before considering possible applications, important fundamental and theoretical efforts are essential to improve our understanding of the physical properties and chemical requirements for these types of systems.

There are two main families of LCEs, resulting from the weak cross-linking of linear polymers:[13–18] the main-chain type with the mesogens inserted within the polymeric backbone[19–24] and the side-on type with the anisotropic units attached as side groups to the polymer chain.[8,13–17,25–30] Other structural variations including main-chain/side-chain mixed and combined LCE structures[31–33] or LC H-bonded polymer forming transient networks[34] have also been prepared. Side-chain LCEs (SC-LCEs), the first to be obtained, and since the most studied,[13–17,35,36] produce mainly large smectic temperature domains when the side groups are attached in the end-on fashion, while those with laterally attached mesogens (side-on) exhibit preferentially a small temperature-range or a metastable nematic phase,[8d,37] temperature domains that can be tuned by the use of two types of cross-linkers, in various proportions,[38] or by changing the chemical nature of the side-on group (fluorinated chains).[39] Similarly, both SmC and N phases are simultaneously produced with MC-LCEs, with a slight tendency to show a broad temperature-range nematic phase.[20–22,40] The presence of mesogenic units inserted within the polymeric backbone should however theoretically lead to a stronger coupling between the polymeric chain orientation, network strain, and the intrinsically high liquid crystalline orientational order than SC-LCEs and thus to a great enhancement of the mechanical properties. This

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was shown experimentally only recently by Wermter and Finkelmann in their study on a nematic monodomain of a LCE based on mixed main- and side-chains.[32] They showed that increasing the proportion of the main-chain component versus the side-chain one resulted in increasing elongations with values reaching about 300% at the isotropic state-nematic phase transition compared to the average value of 50% for the mean elongation observed for pure SC-LCEs.

Encouraged by these results, we proposed and tested various approaches to produce in a simple way MC-LCEs exhibiting systematically the nematic phase within an accessible temperature range, and for which smectic mesophases formation would be discouraged. The first approach consists in the systematic modification of the nematic monomer core by methylation of the central rigid part to reduce the side-by-side molecular interactions auspicious to smectic phase stabilization on the one hand but still preserving the molecular anisotropy to promote nematic materials on the other hand. The second approach implies the incorporation within the network of rigid, anisotropic cross-linkers to disfavor the lamellar ordering by breaking the lamellae and reducing the microsegregation between the plastic and rigid parts.

Results and Discussion

In the first part, the preparation and thermal properties of a set of four monomers is presented, and the influence of the degree of methylation and symmetry of the central core on the thermotropic properties of the resulting main-chain polymers (MC-LCPs) and related elastomers is discussed. In the second part, various types of cross-linkers, differing in their branching multiplicity, rigidity, core geometry and molecular symmetry are described and the impact of their insertion within the corresponding elastomers on some physical properties (mesomorphic and elastic) evaluated. All the systems prepared exhibited mesomorphic behavior, in which the stability of the SmC and N phases is strongly dependent on the structures of both the mesogen and cross-linker. As for the mechanical behavior, the properties are strongly influenced by the nature of the cross-linker.

For the preparation of elastomers, we may use two different approaches: a two-steps method, where the monomer reacts to form polymeric chains which, after purification, are cross-linked in a second reaction to yield the network, or a one-step process, where the polymerization and the cross-linking reactions occur simultaneously. In this systematic study, where a large number of new materials must be synthesized, the second method was adopted preferably for its accessibility and versatility.[22a] Linear, rigid mesogens made of three connected aromatic groups generally present high phase transition temperatures, often near the temperature of decomposition of the molecule, preventing their future utilization in the preparation of LCPs and LCEs. A way to avoid these problems and to obtain LCPs with moderate phase transition temperatures consists in intercalating flexible spacers between the rigid units. This one-step method, which makes use of the hydrosylilation of double bonds, requires indeed the use of two monomers, one being the mesogen with two peripheral chains functionalized at both ends by double bonds, and the other one being, in our case, the disiloxane unit, namely tetramethyldisiloxane (TMDS), the required flexible subunit which will act as chain-extender as well as conferring the plastifying character to the entire system. As for the cross-linker, it can be equally functionalized by vinyl or siloxane end-groups.

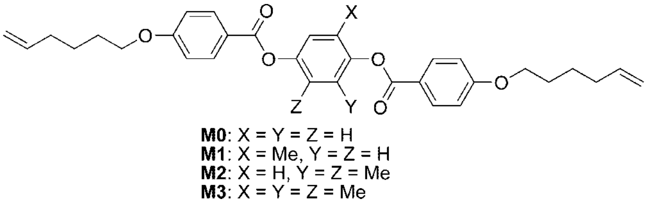
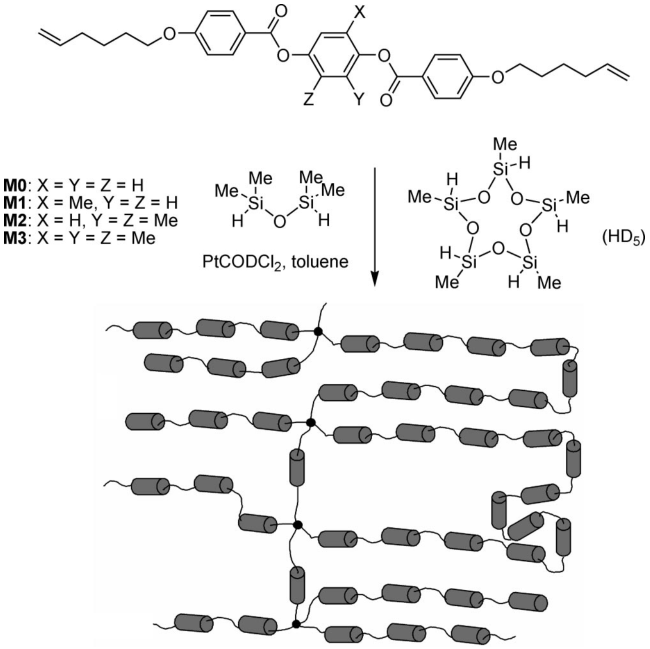


Figure 1. Molecular structures of the monomers **M0–M3**.

Scheme 1. Liquid-Crystalline Network Synthesis



Effect of the Mesogenic Monomer Structure. It is well-known that the introduction of a lateral group in the core of the mesogen or its substitution by a less symmetrical group can induce a considerable reduction of the phase transition temperatures, whatever the liquid crystalline system concerned,[22,41,42] up to a point where the mesomorphic order is totally destabilized or simply lost. However, ingenious core substitution may only destabilize the smectic order and favor preferentially the nematic phase, by a controlled reduction of the side-by-side intermolecular interactions. Thus, three methylated monomers, where the number and the position of the methyl groups were systematically changed, and their nonmethylated analogue for comparison, were prepared (Figure 1), and their thermal behavior was studied.

Synthesis and Thermal Properties of the Divinyl Monomers. The four monomers **M0**−**M3** were prepared in good yields using the same esterification procedure between 2 equiv of 4-(hex-5-enyloxy)benzoic acid and the appropriate hydroquinone derivative (Scheme S1).

All the monomers present a single nematic phase, easily identified by the optical texture developed while observing the sample under a polarized optical microscope. The texture is characterized by the existence of highly birefringent and homogeneous domains: either the sanded-threaded texture or the Schlieren texture is observed, the latter characterized by the presence of both 2- and 4-brushes disclination defects ($s = \pm \frac{1}{2}$ or ± 1, respectively, the former being the proof of the nematic ordering). The thermal stability and temperature range of the nematic phase is, as expected, strongly dependent on the nature of the core substitution. Indeed, **M0**, which is the most symmetrical and least bulky monomer with no side-group, exhibits a high-temperature nematic phase stable over a large temperature range (Table 1 and Figure 2). The behavior of the other symmetrical monomer **M2** is quasi-similar, although with a net reduction of the $T_{\mathrm{N-I}}$ by about 30 °C with respect to **M0**, which is likely linked to the relative bulkiness of the core and

Table 1. Mesomorphic Properties of the Monomers

monomer	thermal behavior[a]	ΔT (N)[b]
M0	Cr 130 (68.3) N 201 (4.1) I	71
M1	Cr 65 (45.0) N 151 (3.3) I	86
M2	Cr 124 (51.3) N 176 (3.75) I	52
M3	Cr 120 (46.0) N 122 (2.7) I	2

[a] Transition temperatures (°C) and enthalpies (ΔH in $J \cdot g^{-1}$) in parentheses. Data were measured during the second heating: Cr, crystalline phase; N, nematic phase; I, isotropic liquid; [b] ΔT (N): stability temperature domain of the nematic phase (°C).

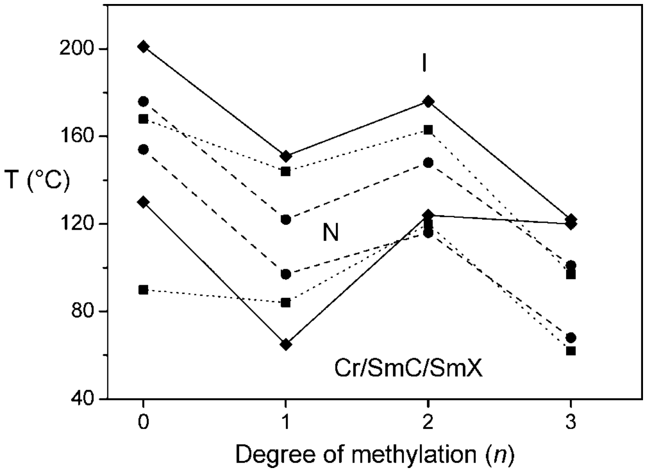


Figure 2. Temperature phase diagram of monomers **M0**, **M1**, **M2**, and **M3**, their corresponding linear polymers, and the elastomers with 10 mol % of cross-linker. $T_{\mathrm{Cr-N}}$ and $T_{\mathrm{N-I}}$: solid lines for the monomers (◆). $T_{\mathrm{SmC\text{-}N}}$ and $T_{\mathrm{N-I}}$: dashed lines for the polymers (●) and dotted lines for the elastomers (■).

the reduced intermolecular interactions. However, the broadest nematic temperature range is observed for the nonsymmetrical monomethylated monomer **M1**, mainly due to an important decrease of the melting temperature (a fall of ca. 60 °C compared to the three other monomers), but also to a substantial decrease of the clearing temperature. As for the other nonsymmetrical monomer **M3**, with the lowest molecular aspect ratio, the combination of symmetry reduction and core bulkiness (three methylene groups in the core) results in a complete destabilization of the nematic mesophase, which now exists over two degrees only; on cooling, however, the nematic phase is supercooled down to about 80 °C (Supporting Information). The variation of the crystal-to-nematic phase transition enthalpy, proportional to the strength of the intermolecular interactions, is consistent with the molecular symmetry changes: the more symmetrical the mesogens (**M0**, **M2** vs **M1**, **M3**), the larger transition enthalpy changes (Table 1).

The physical properties of the monomers (**M0**−**M3**) are thus directly connected to the number of methyl groups and to the way they are distributed in the central mesogenic core. The next step was to determine whether these trends could be preserved (and enhanced) upon the insertion of these nematogenic cores into the corresponding polymers and elastomers.

Thermal Properties of the Polymers Prepared with the Various Monomers **M0**−**M3**. The four monomers were respectively reacted with 1,1,3,3-tetramethyldisiloxane (TMDS) in stoichiometric amount, at 60 °C in toluene, to form the siloxane-based linear polymers, $[\mathbf{M}i + \mathrm{TMDS}]_n$: the hydrosylilation reaction was catalyzed by $\mathrm{PtCODCl_2}$ (Supporting Information and Table S2). Overall, the polymers were obtained with rather low degrees of polymerization (DP, n) but with acceptable polydispersity indices (PDI), ranging from 1.5 to 2.0 (PDI = M_w/M_n), in the expected range for such a polyaddition reaction according to the Carothers equation.[43] The solubility of the monomers in the solution reaction also influenced greatly the efficiency of the hydrosylilation: the least soluble monomers **M2** or **M3** led to oligomers (low DPs) rather than polymers, in contrast to the more soluble monomers **M1** and **M0**. Moreover, in order to later react under the same experimental conditions used for the preparation of the elastomers, these polymerization reactions were performed in concentrated solutions, crucial for the network formation. The good solubility of **M1** also allows performing the reaction under concentrated conditions.

As for their thermal behavior, all the polymers exhibit a nematic phase, but with in addition, the induction of room-temperature, ill-defined, ordered smectic-like phases (referred to as SmX and SmY phases, as not completely characterized), and of a SmC phase, just below the nematic phase. All the polymers likely transformed into a glassy phase, although the glass transition (T_g) could hardly be detected by DSC (Supporting Information), only measured for the **M1**-containing polymer. The $T_{\mathrm{N-I}}$ was substantially reduced by about 20–30 °C when compared to that of the corresponding monomers (Table 2 and Figure 2). Interestingly, the temperature range of the nematic phase, still large but reduced with respect to the free mesogens, was found to increase concomitantly with the degree of methylation of the monomer; again, an important supercooling effect was observed for the nematic phase of the **M3**-system. The opposite behavior is observed for the SmC-temperature range, which decreases with core-substitution and is almost inseparable from the ordered smectic phase in the **M3**-containing system. It is obvious that the **M2**- and **M3**-systems are abusively referred to as polymers and cannot truly be considered as such, but despite their low DPs, their thermal behavior is drastically different to that of the monomeric precursors, showing instead the general trends observed for their **M0** and **M1** polymeric analogues (*vide supra*). This tendency for polymeric-like behavior is commonly observed in dimers and oligomers containing siloxane spacers.[44] Overall, the systematic presence of the nematic phase, despite the segmented structure of the oligomers and polymers (flexible and nonmesogenic siloxane elements[45] alternating with rigid monomeric units within the polymer backbone), is likely consequent to the reduction of the intermesogen interactions brought by the bulky siloxane units (which have a larger cross-section area than the monomers) still conferring entropic flexibility and conformational freedom to the chains,[46] and thus inhibiting, at elevated temperature, the perfect microsegregation of the different constitutive parts of the systems.[47,48]

The enthalpy values associated with the SmX−SmC phase transition point to slightly more ordered phases below the SmC phase. The presence of these two phases (SmX and SmY phases), and the strong tendency of the systems to form layered morphologies in general, can be understood by the reduction of the chains' flexibility and conformational freedom on lowering temperature, which facilitates the microsegregation of the various parts. The different orderings observed (X, Y, and C) are probably linked to various translational orders of the "tilted" mesogenic parts within the layers.

Unfortunately, the polymerization induces the formation of undesired smectic phases (SmX, SmY, SmC) due to intra and intermolecular cooperative interactions which favors the segregation of the different molecular parts. The alignment of the mesogens forces the elongation of the chain, and because the polymer is a periodic structure containing the mesogen−siloxane sequence, the preferential orientation of the mesogens favors the existence of a positional order (microsegregation), thus generating a smectic phase at low temperatures. The results also show that the molecular symmetry of the mesogen influences

Table 2. Thermal Behavior of the Polymers

polymers	thermal behavior[a]	T_{N-I}[b]	ΔT (SmC)[c]	ΔT (N)[c]
$[M0 + TMDS]_n$	SmX 107 (23.0) SmC 154 (7.2) N 176 (2.0) I[f]	25	47	22
$[M1 + TMDS]_n$	G 8 (0.08) SmX 28 (4.0) SmC 97 (4.9) N 122 (2.0) I	29	69	25
$[M2 + TMDS]_n$	SmY 66 (1.3) SmX 110 (−) SmC 116 (23.3)[c] N 148 (1.5) I[f]	28	6	32
$[M3 + TMDS]_n$	SmY 10 (1.8) SmX 68 (16.9)[d,e] N 101 (2.4) I[f]	21	0	33

[a] Transition temperatures (°C) and enthalpies (ΔH in $J \cdot g^{-1}$) in parentheses, glass transition, T_g, and heat capacity, ΔC_p ($J \cdot g^{-1} \cdot K^{-1}$) in parentheses. Data measured during the second heating: G, glass phase; SmX and SmY, ordered ill-defined smectic phases; SmC, smectic C phase; N, nematic phase; I, isotropic liquid. [b] Reduction of T_{N-I} upon polymerization of the monomer (°C). [c] ΔT (SmC) and ΔT (N): stability temperature-domain of the smectic C and nematic phases (°C), respectively. [d] Cumulated enthalpies of both transitions. [e] The SmC and the SmX are not separated enough to be distinguishable. [f] T_g not detectable and ΔC_p not measured.

the stability of the smectic mesophase against the nematic phase, as observed by Billibin.[49]

Characterization of the Elastomers Prepared with the Various Monomers **M0−M3**. As mentioned above, the synthesis of the main chain LCEs was performed according to the one-step procedure.[22a] The appropriate diolefinic mesogen forms the network by reacting via the hydrosilylation addition reaction to TMDS and the cross-linker (**HD$_5$**) as shown in Scheme 1.

All three components were dissolved in toluene, the temperature raised to 60 °C (for both the preparation of the bulk and film samples) and after adding a Pt catalyst, the hydrosilylation reaction proceeded to yield a swollen gel in toluene. For the preparation of the films, the reaction was performed in a centrifuge at 5000 rpm for about 24 to 48 h, while the bulk samples were prepared directly in a round-bottom flask. Several elastomers were prepared this way, with some of them also prepared as films, differing in the cross-linking density (the variable proportions of **HD$_5$** are 5, 10, 15, and 20 mol %, respectively; see Supporting Information) and the type of monomer. The efficiency of the synthesis and the quality of the produced elastomers were controlled by determining the soluble part content (sol. %) and the swelling behavior (α and q parameters) as a function of the proportion of the cross-linker and monomer (Tables S4 and S5) for all the elastomers: the more efficient the reaction, the less free chains inside the material, and thus the lower the sol content. When in contact with a solvent, the material swells and thus expands. This expansion is larger in principle for weakly reticulated materials than for strongly cross-linked ones.

From the analysis of these parameters (Supporting Information), one may suggest the existence of a lower and an upper limit for the ideal proportion of cross-linker to be used. As expected, the soluble content decreases upon increasing the cross-linking density, and up to a certain amount, above 15 mol % of cross-linker, it remains more or less constant. This can be explained by the fact that beyond 15 mol % of reticulation, the cross-linker mostly behaves as a chain extender (a kind of saturation effect of the reticulation process) or introduces branches and defects inevitably present with this chemistry in the network (dangling chains, loops, ...). However, with 5 mol % or less of cross-linker, a material with a high sol. % is obtained, indicating that the quantity of cross-linker used is not sufficient for obtaining a material properly cross-linked. Moreover, it can be verified that the less reticulated elastomers the higher the swelling. The swelling coefficients parallel to the direction of elongation ($\alpha_{\parallel}$) are lower than the ones in perpendicular directions ($\alpha_{\perp}$) indicating that the materials are not isotropic, but show a preferential orientation, with a maximum anisotropy for intermediate cross-linking densities (ca. 10 mol %). This observation is in good accordance with some other results published in the literature,[20,32,50,51] and it is explained by the prolate geometry of the polymer chains, which are stretched along one principal preferred direction. This is a good indication as far as the next step, the preparation of monodomains, is concerned. The global variation of volume is expressed by the degree of swelling, q. The q-values are close to those found in the literature for side-chain,[32] mixed,[32] and main-chain[51] systems and are indicative of a rather homogeneous distribution of the cross-links within the material.

Although, a too quantitative and detailed analysis of these results should be done carefully: first, the rather poor solubility of some of the monomers does not facilitate the polymerization in concentrated medium, as it was evoked for the polymers; second, due to some synthetic additional problems, that were later detected, such as the migration of the double bonds of the monomers and the volatility of the siloxane monomer, the efficiency of the hydrosilylation reaction was found to be considerably reduced.[43] In particular, the low solubility of monomers **M0** and **M2** (and to some extent the volatility of TMDS) clearly contributes to a decrease of the polymerization, hence the disappointing results reported in Table S5; these synthetic problems, specific to the chemistry used, have been since remedied and will be reported on in due course.[52] In this study, it seems however clear that the optimized system involves mainly the use of the monomer **M1** and a cross-linking density of 10 mol % as being the optimal quantity of cross-linker to be used to form a network of relatively good quality.

The mesomorphic properties of the various elastomers are compiled in Table 3 and some obvious trends can be easily observed (Figure 2). The mesomorphic behavior of the materials is not greatly affected by the method used for its preparation, and may indifferently be studied as bulk samples or film materials, a rather practical observation, since some of them could not be obtained as films, and only prepared as massif materials. Moreover, after removal of the sol content, essentially constituted of monomers and small oligomers (determined by ^{1}H NMR) from the network almost no change in transition temperature were observed, except a small increase of the glass transition. In both cases, the overall tendency consists in a slight increase of the SmC-to-N phase transition (less than 10 °C).

Clearly, polymerization helps in stabilizing mesomorphism, with the induction of a SmC phase at the expense of crystalline phases at room temperature. This effect is enhanced after reticulation, with some small variations in the transition temperatures on the order of ±10 °C, not all significant considering the macromolecular nature of the materials.[53] Providing that the degree of reticulation is approximately of the order of 10 mol %, the mesomorphic behavior of the elastomers is comparable to that of the parent polymers for the **M2**- and **M3**-containing systems (Figure 2), while a great enhancement of the nematic temperature range is observed in the **M0**- and **M1**-containing LCEs. In contrast, increasing the proportion of the cross-links within the LCEs (>15 mol %) results in the increase of the transition temperatures as well as the extension of the SmC phase temperature domains. The cross-linker clearly imposes some rigidity to the system by decreasing the molecular freedom of the chains, contributing to the stability increase of the ordered phases, but concomitantly also shows a plastifying tendency, a counter-acting effect. The effect of the methylation degree of the mesogen is still present in the elastomer as whatever the cross-linking density (10 or 15 mol %), the stability of the SmC mesophase becomes lower as the number of methyl

Table 3. Thermal Behavior of the Elastomers Prepared with the Different Monomers and Different Proportions of Cross-Linker (HD_5)

elastomers	thermal behavior[a]	ΔT (SmC)[b]	ΔT (N)[b]
M1 + 20% HD_5	G 11 (0.2) SmC 167 (1.2) N (>200) I[c,e]	156	>33
M1 + 15% HD_5	G 10 (0.2) SmC 157 (1.9) N (>200) I[c,d,e]	147	>43
M1 + 10% HD_5	G 8 (0.3) SmC 84 (2.1) N 144 (2.4) I[d,e]	76	60
M1 + 5% HD_5	G 8 (0.3) SmC 91 (4.0) N 131 (2.0) I[d,e]	83	40
M0 + 10% HD_5	G 0 (−) SmC 90 (8.2) N 168 (3.4) I[d,f]	90	78
M0 + 15% HD_5	G −14 (0.2) SmC 73 (10.0) N 149 (1.4) I[d]	87	76
M2 + 10% HD_5	SmX 89 (6.5) SmC 120 N (2.0) 163 (1.3) I[d,f]	31	43
M2 + 15% HD_5	G 38 (0.1) SmX 77 (2.25) SmC 109 (0.7) N 161 (1.45) I[d]	32	52
M3 + 10% HD_5	G 16 (0.3) SmC 62 (0.55) N 97 (2.1) I[d,e]	46	35
M3 + 15% HD_5	G 35 (0.25) SmC 72 (1.2) N 116 (1.2) I[d]	37	44

[a] Transition temperatures (°C) and enthalpies (ΔH in $J.g^{-1}$) in parentheses, glass transition, Tg, and heat capacity, ΔCp ($J.g^{-1}.K^{-1}$) in parentheses. Data measured during the second heating; G: glass phase, SmX: ill-defined smectic phase, SmC: smectic C phase, N: nematic phase, I: isotropic state. [b] ΔT (SmC) and ΔT (N): stability temperature-domain of the smectic C and nematic phases, respectively (°C). [c] The transition for the isotropic could not be determined with accuracy because the materials started to decompose beyond 260 °C. [d] Data obtained from the bulk materials. [e] Data obtained from the films. [f] T_g not detectable and ΔC_p not measured.

groups in the central core increases. Unexpectedly, upon increasing the cross-linking density from 10 to 15 mol %, both the SmC-to-N and N-to-I phases transition temperatures increase in the case of the elastomers prepared with nonsymmetric monomers (**M1** and **M3**) while they decrease for elastomers prepared with the symmetric monomers (**M0** and **M2**), with nevertheless an attenuation of the amplitude in **M2**- and **M3**-containing elastomers.

In the graphical representation of the transition temperatures of the monomers, polymers, and elastomers as a function of the degree of methylation of the central core (Figure 2), it can be confirmed that materials prepared with the symmetric monomers, **M0** and **M2** have higher clearing points than the systems prepared with monomers **M1** and **M3**. A certain leveling effect of the methylation can be seen on going from the monomers to polymers and elastomers.

Effect of the Cross-Linker Structure. The nature of the cross-linker may also affect the thermal and mechanical properties of the elastomers.[33,54,55] In particular, as demonstrated by Greve and Finkelmann,[54a] it was shown that the orientation of the nematic director in SC-LCEs does not depend only on the nature of the mesogenic unit and the chain extender, but also on the type of cross-link used, and its concentration. We have thus decided to study the influence of the nature of the cross-linker (multiplicity, geometry, rigidity) on the thermotropic properties, with the idea to disrupt the smectic ordering, as well as to improve the mechanical properties and evaluate the maximum strain allowed of MC-LCEs prepared with a calamitic mesogen **M1**.

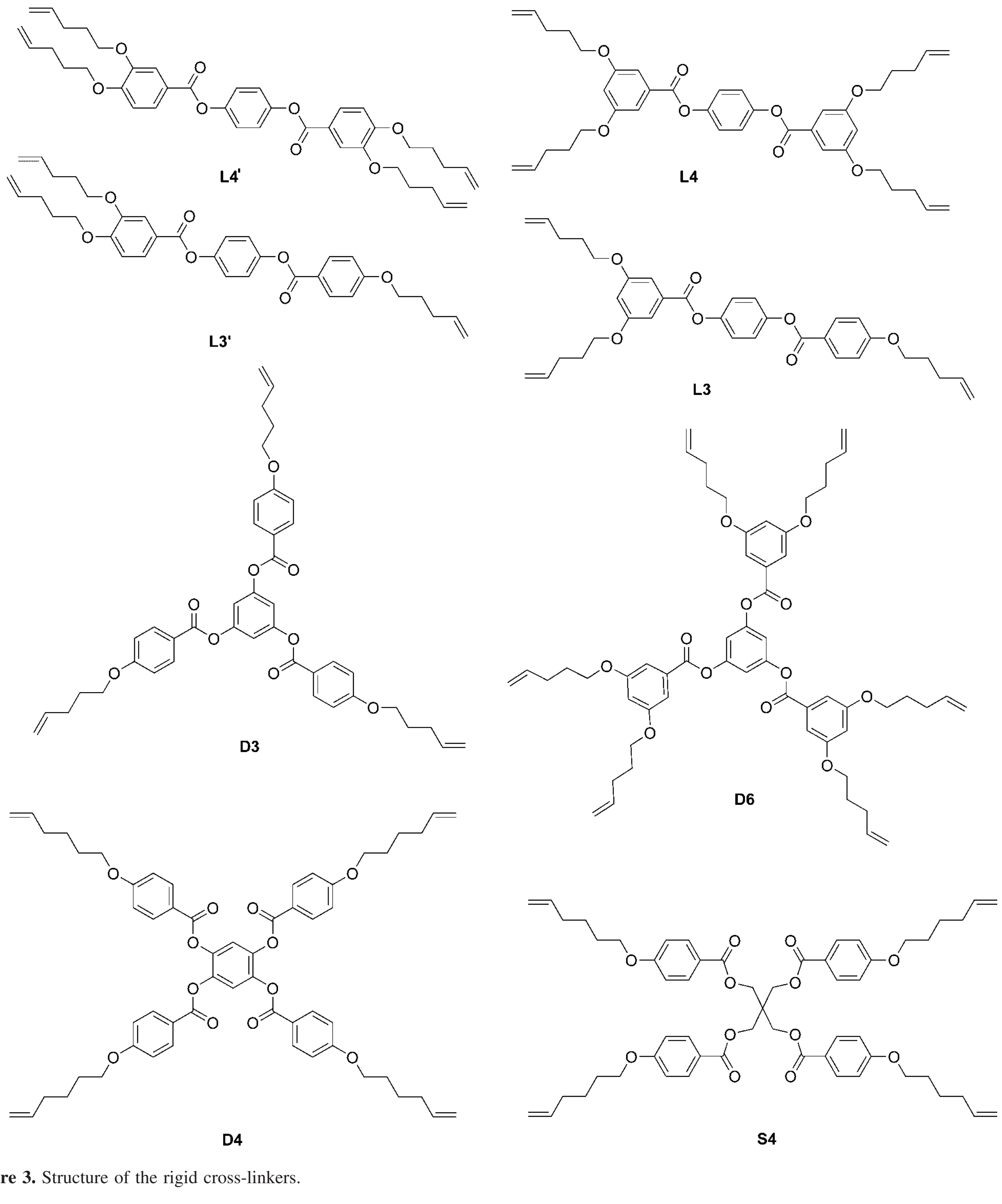
Synthesis and Characterization of the Cross-Linkers. Eight types of rigid cross-linkers were selected for this study, four having a linear structure with a functionality $\eta = 3$ (**L3**, **L3′**) and $\eta = 4$ (**L4**, **L4′**), three with a discotic shape with $\eta = 3$ (**D3**), $\eta = 4$ (**D4**) and $\eta = 6$ (**D6**), and a final one with spherical shape with $\eta = 4$ (**S4**) (Figure 3).

The linear, discotic, and spherical cross-linkers were all similarly prepared in good yields by a DCC-DMAP esterification of hydroquinone (**L4** and **L4′**), 1,3,5-trihydroxybenzene (or phlorogucinol for **D3** and **D6**), 1,2,4,5-tetrahydroxybenzene (**D4**), and pentaerythrytol (**S4**) with the correct amount of the appropriate benzoic acid 4-(pent-4-enyloxy)benzoic acid for **L3**, **L3′**, and **D3**), 4-(hex-4-enyloxy)benzoic acid (for **D4** and **S4**), 3,4-bis(pent-4-enyloxy)benzoic acid for **L3′** and **L4′**), 3,5-bis(pent-4-enyloxy)benzoic acid for **L3**, **L4**, and **D6**). The nonsymmetrical cross-linkers (**L3** and **L3′**) were prepared in two steps starting by the protection of one hydroxyl group of the hydroquinone by TBDMSCl, followed by a first esterification, the deprotection of the monosubstituted hydroquinone, and finally by a second esterification reaction. These procedures are all well detailed in the Supporting Information. Only one of them, **L3′**, is mesomorphic, showing a narrow temperature-range nematic phase (Cr 106 N 116 I), while the range of the melting points is between 43 and 112 °C.

Characterization of the Elastomers Prepared with Monomer **M1** *and the Various Rigid Cross-Linkers.* The elastomers were prepared using the procedure described above and solely with monomer **M1**, with the quantities of catalysts slightly increased, and the temperature of reaction kept at 60 °C. The preparation of weakly cross-linked systems with 90 and 80 mol % of **M1** was attempted, although in the first case (90 mol % of **M1**), elastomers were not formed, likely due to the small cross-linking density (in this case, 10 mol % corresponding to 6.7, 5, and 3.3% for cross-linkers with $\eta = 3$, 4, and 6, respectively). However, doubling the cross-linking density (systems with 80 mol % of **M1**), led to another series of elastomers. The performance of the cross-linker and the efficiency of the reticulation reaction were evaluated by determining both the soluble content (sol. %) and degree of swelling (q): the more performing the cross-linker, the more efficient the reaction and the fewer free chains inside the material.

The results obtained for the elastomers prepared with monomer **M1** and different rigid cross-linkers are reported in Table S6. At identical concentrations of **M1**, the multiplicity of the cross-linker has an influence on the sol. % and the swelling behavior of the elastomers: the greater the multiplicity (functionality), the lower the soluble fractions, as expected. However, let us remember that for a fixed quantity of monomer, the quantity of cross-linker to use changes in the inverse proportion of its multiplicity. In other words, for an elevated multiplicity of the cross-linking agent, the quantity of reticulation centers is lower than that of a cross-linker with a smaller connectivity, at identical concentration (e.g., theoretically, **D6** will reticulate six linear chains, while, under identical concentration, **D3** will reticulate three chains, but is twice as concentrated). The high sol. % implies that the probability of cross-linkers with low connectivity acting as simply chain extender is rather high (since also more concentrated) than that of their homologues with a higher one. The reticulation is thus more efficient with highly multivalent systems, despite the reduced number of potential reticulation centers in the material. This is an important feature of this study, which should be an important parameter as far as the mechanical properties, and particularly the elastic behavior, are concerned. The lower the sol. % is, the less the material swells, and the better this is reticulated, as predicted by the theory,[56,57] is also verified in this series.

The nature of the mesophases was not at all affected by the insertion of the rigid cross-linkers, since both a SmC and a nematic phases are systematically observed for all the samples (Table 4). It appears that the main effect is an overall lowering of the isotropization temperatures when compared to the previous elastomers **M1** (T_{N-I} ~ 130–140 °C for 5 and 10 mol % **HD_5**), and thus an overall reduction of the mesophase


L4'

L4

L3'

L3

D3

D6

D4

S4

Figure 3. Structure of the rigid cross-linkers.

stability. The glass transition temperature is also hardly affected by the nature of the reticulation agent ($T_g \sim 4$–12 °C). Moreover, the reticulation of the linear chains by nonlinear cross-linkers (**D3**, **D6**, **S4**) contributes to a greater reduction of the smectic phase stability with respect to those cross-linked by linear ones (Table 4); **D3**, **D6**, and **S4** systems actually exhibit almost identical transition temperatures. In contrast, the stability of the nematic phase remains nearly unaltered whatever the shape of the cross-linker. The phase transition temperatures of the elastomers prepared with linear cross-linkers are generally high and not greatly dissimilar to the mesomorphic behavior of the system with 5 and 10 mol % of **HD$_5$**. The cross-linker **D4** may actually be seen as a cross rather than a disk, i.e. intermediate shape between a disk and a rod, made of two linear three-ring arms crossing at the center, thus almost not altering the smectic mesomorphism, and in this respect its influence is closer to the linear ones. Thus, using a cross-linker with a different geometry from that of the mesogen inserted in the chains produces a substantial diminution of the smectic phase temperature range without disturbing the nematic temperature range. Finally, the nematic phase accessibility was also improved.

XRD Characterization of the Elastomers. All the mesophases of the elastomers (and corresponding polymers) were systematically characterized by small angle XRD, allowing also the determination of the thickness of the smectic layers and the tilt angle of the mesogens relative to the layer normal. In this experiment, the X-ray beam is oriented in a direction normal

Table 4. Thermal Behavior of the Elastomers Prepared with M1 and Different Rigid Cross-Linkers (η is the Multiplicity)

elastomers	η	thermal behavior[a]	ΔT (SmC)[b]	ΔT (N)[b]
80% M1 + L3	3	G 4 (0.3) SmC 67 (4.0) N 102 (1.4) I	63	35
80% M1 + L3′	3	G 11 (0.3) SmC 99 (6.2) N 123 (1.9) I	88	24
80% M1 + L4	4	G 5 (0.3) SmC 42 (1.0) N 87 (1.0) I	37	45
80% M1 + L4′	4	G 8 (0.25) SmC 91 (6.0) N 114 (2.0) I	83	23
80% M1 + D3	3	G 6 (0.25) SmC 36 (0.4) N 82 (0.3) I	30	46
80% M1 + D4	4	G 4 (0.3) SmC 83 (4.55) N 118 (1.75) I	79	35
80% M1 + D6	6	G 4 (0.05) SmC 50 (0.2) N 92 (0.1) I	46	42
80% M1 + S4	4	G 6 (0.45) SmC 52 (2.4) N 86 (0.9) I	46	34

[a] Transition temperatures (°C) and enthalpies (ΔH in J·g^{-1}) in parentheses; glass transition, T_g, and heat capacity, ΔC_p (J·g^{-1}·K^{-1}) in parentheses. Data measured during the second heating: G, glass phase; SmC, smectic C phase; N, nematic phase; I, isotropic state. [b] ΔT (SmC) and ΔT (N): stability temperature-domain of the smectic C and nematic phases, respectively (°C).

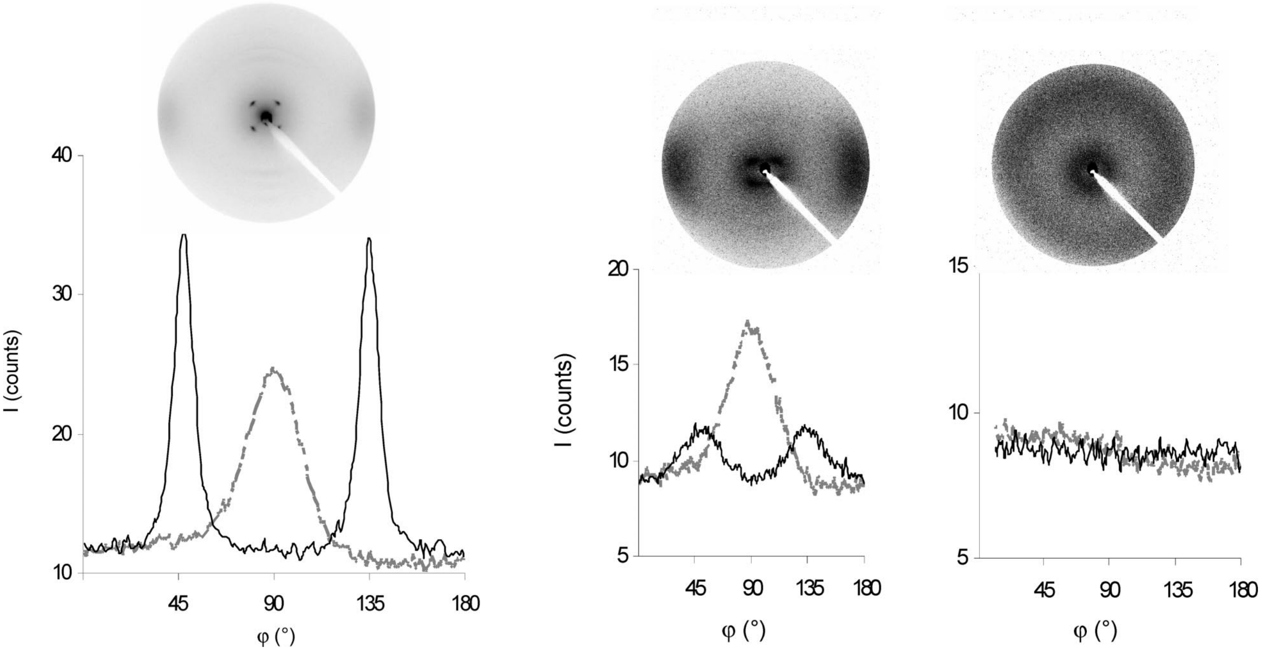


Figure 4. X-ray diffraction patterns (left to right) of the SmC (35 °C), N (115 °C), and isotropic state (155 °C) phases of the elastomer **M1** + 10% **HD$_5$**. Radial variation (angle φ) of the intensity of the small (solid line) and wide angles (dotted line) reflections corresponding to the X-ray patterns.

to the direction of elongation and normal to the surface of the elastomeric film, and well-aligned and optically clear monodomain samples with smectic layers in the film plane were obtained by uniaxial stretching.

All the studied elastomers, presenting a smectic phase, have generated oriented X-ray patterns possessing four intense Bragg spots at the small angles, symmetric with reference to the equator and to the meridian, and two crescents, diffuse, in the wide angle range, located on the equator (Figure 4). This pattern is typical of a SmC lamellar phase and is commonly observed in polymeric[58] and elastomeric systems,[22,59–61] the four spots indicate a layered structure, with the layer normal tilted relative to the mesogens orientation, and the two broad scattering halos at the wide angles are indicative that the mesogens are aligned parallel to each other and oriented in the direction of the elongation, that is in the direction perpendicular to the X-ray beam and parallel to the surface of the film. In such aligned networks, the director is macroscopically and uniformly ordered and the orientation of the smectic layer normal is conically distributed through the sample thickness, with respect to the molecular director (quasi parallel to the stretching direction).[22e,34a] The four Bragg spots slowly loose definition and become more and more diffuse as the temperature is increased, concomitantly with the overall loss of the layering of the structure (positional ordering and cybotactic groups) characteristic to the SmC-to-nematic phase transformation, while the two halos in the equatorial position remained unchanged, in agreement with the persistence of the orientational order. The halos are slightly more diffuse due to the increasing freedom of motion resulting in the partial loss of orientational order of the nematic phase. At all temperatures, a circular diffuse halo is systematically observed in the wide angles part, which corresponds to the liquid order of the siloxane groups between the mesogens. Above the nematic-to-isotropic liquid phase transformation, the diffuse spots and crescents have totally disappeared to give circular diffuse halos corresponding to the complete loss of positional and orientational orders.

The graphics for the radial variation of the intensities of the small- and wide-angle reflections for the smectic, nematic and isotropic phases are shown in Figure 4. They were obtained after normalization of the intensity for the small and wide angles. For the smectic phase, the intensity at the small angles is higher than the intensity at the wide angles (predominance of positional order). For the nematic phase, what prevails is the intensity at the wide angles, in agreement with the partial loss of positional order. In the isotropic state, there is no long distance order. The results are consistent with those obtained for related systems.[22]

The thickness of the smectic lamellae is almost invariant in the temperature range of the SmC stability of all the elastomers (Supporting Information). For the **M1** + 10% **HD$_5$** system and up to 84 °C, the periodicity is ca. 25 Å. This is smaller than the smectic periodicity measured by Rousseau et al.[22b] for a very closely related system (d = 33.7 Å) but in the same range than those found for the polymers and elastomers reported in this

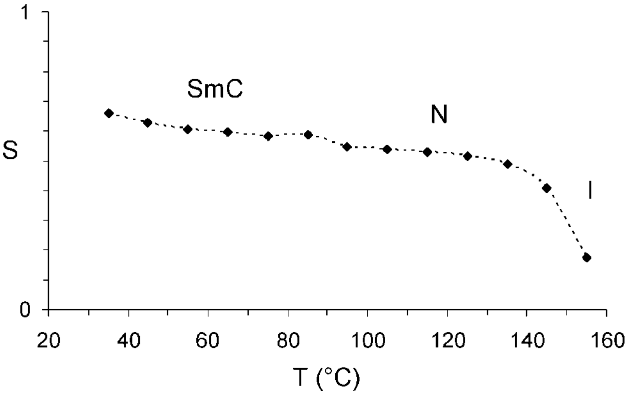


Figure 5. Variation of the order parameter *S* as a function of temperature (SmC, N, I: smectic, nematic phases, and isotropic liquid; elastomer **M1** + 10% **HD$_5$**).

study (d = 24−27 Å) and previously.[22a] The periodicity is substantially smaller than the total length of the segment comprising both the monomers (**M*i*** and TMDS, ca. 34 Å) in the stretched conformation in agreement with the tilt of the rigid unit in the smectic layer by about 45°. Above 84 °C, the phase is nematic, but it is still possible to measure the periodicity within the cybotactic groups, with some uncertainty due to the relative broadness of the diffusion peaks (Figure S4).

The tilt angle θ (angle between the layer normal and mesogen) can be deduced from the X-ray pattern with respect to the direction of stretching. It decreases slowly with increasing temperature, in agreement with the increase of the mesogen cross-section area (d is almost constant), which increases concomitantly with the temperature due to chain volume expansion (Figure S5).

The order parameter, S, was estimated using the modified Debye−Scherer equation at various temperatures. As shown in Figure 5, S decreases with increasing temperature, expected due to thermal fluctuations which contribute to the augmentation of the mean deviation with the director. In the smectic phase, up to 85 °C, the order parameter is quasi-constant, with a value of 0.65. Then, it starts to diminish regularly in the nematic phase down to 0.55 and then falls abruptly close to the isotropic phase down to nearly 0 (this value does not reach 0 because of the reticulation points). This value of S is comparable to that found for other systems with side-end and side-on topologies (0.68,[61] 0.7350 and 0.8,[62] 0.6[63]), with mixed (0.8[32]) and with main-chain (0.8,[22a] 0.7–0.8[51]). These values seem to be independent of the type of monomer insertion within the elastomer or on the nature of the mesophase (SmA, SmC, or N), but are evidently influenced by the facility to orient the sample, and thus by the structure of the system (lateral chains vs main chains).

Thermoelastic Behavior of the Elastomers. In this part, instead of presenting the data for all the elastomers, we decided to have a comparative discussion between two elastomers, one bearing the soft cross-linker (**HD$_5$**), the other made with **D6**, the only elastomer with a rigid cross-linker for which it was possible to prepare an oriented film. Regarding the structural similarities between these two elastomers, with almost identical functionality (with multiplicities of five and six, respectively) of the cross-linking moieties and degree of cross-linking, elastic properties may be compared, and the effect of the rigid cross-linker evaluated.

As for SC-LCEs, the smectic state is characterized by a two-dimensional rubber elasticity, with a strong anisotropy of Young's modulus, greater in the normal to the lamellae than the parallel direction.[64] Consequently, the orientation of the elastomers in the smectic state is difficult to achieve. A good orientation would thus necessitate the utilization of heavier load, with the risk to damage and even break the film. To avoid the rupture of the films during this process, the elastomeric films were loaded with a smaller weight. The elastomer prepared with **D6** was aligned at room temperature, due to its mechanical fragility. The sol content and swelling anisotropies obtained for both systems (vide supra) are similar in the bulk, but slightly differ as films (Supporting Information). Thus, not only the elastomers with **HD$_5$** are better cross-linked than those prepared with **D6**, they are also easier to align than those with the rigid cross-linker (higher Δq). For the same reasons as those invoked for SC-LCEs, the material swells preferentially in the directions perpendicular to the stretching one.

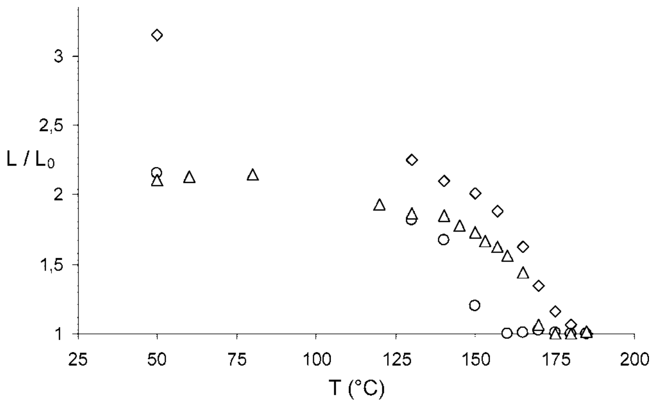


Figure 6. Elongation of elastomer **M1** + 10% **HD$_5$** as a function of temperature, with a load equivalent to 2.30 kPa. Measurements performed during first (squares) and second heating (triangle), and first cooling (circles). L_0, the minimal length, was determined in the isotropic liquid (T_{NI} = 144 °C).

The elastic behavior can be evaluated, in a first approximation, by the estimation of the length of the monodomain as a function of temperature and load (Figure 6). The maximum length of the elongation is about 2.15 times that of the length of the film in the isotropic state and remains stable and reversible after several cycles (Figure 6). The shift of the elongation observed during the first heat and with subsequent heating–cooling cycles is a common situation to all elastomers and is due to both the elastic and plastic components of the material: the elastic one is reversible since it is fixed by the cross-links, while the plastic is simply due to physical interactions between polymer chains. Therefore, the importance in measuring from the isotropic phase and to wait that the system has reached a new equilibrium for the viscous component to vanish must be stressed. Indeed, when submitted to a stress, a material may relax very slowly, and it is convenient to wait between consecutive measurements to guaranty a new equilibrium for the system (about 1000 s after stimuli, i.e., temperature change). The fact that the measurements are fully reproducible (perfectly superimposed lines) shows that the system can reach equilibrium and relax rapidly (within a few hours, for ΔT = 150 °C).

The amplitude of the elongation as a function of the load allows evaluating the limit of the mechanical resistance of the material. Since the elongation ratio L/L_0 does not vary, in general, over a certain range of applied loads, we can deduce the maximum of constraints to apply to keep the complete reversibility of the contraction−elongation cycle, which is independent of small variations. Loads of 2.30−48.0 kPa were put onto the elastomer **M1** + **HD$_5$** (Figure 7). It was observed that the profile remains unchanged and that the maximum length variation of the sample is constant with temperature, on the order of 135%. Almost no change is observed either on cooling or heating; only a small hysteresis is observed in the vicinity of the nematic-to-isotropic liquid transformation due to the load

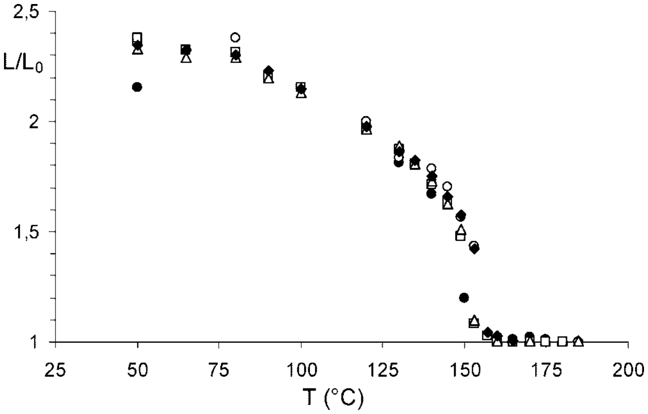


Figure 7. Variation of the elongation of the elastomer **M1** + 10% **HD**$_5$ as a function of temperature and of the applied load in the director direction, on cooling [(●) 2.30 kPa; (◆) 11.7 kPa; (△) 24.0 kPa; (○) 36.0 kPa; (□) 48.0 kPa] ($T_{\mathrm{SmC\text{-}N}}$ = 84 °C, T_{NI} = 144 °C).

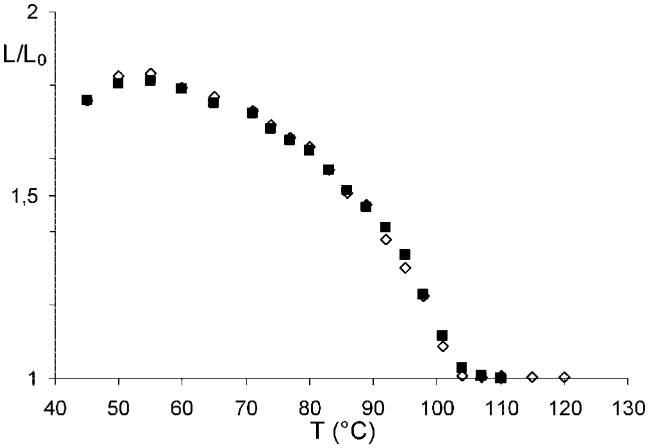


Figure 8. Variation of the elongation of the elastomer 80% **M1** + **D6** as a function of temperature, with two different applied forces in the direction of the director [(■) 9.70 and (◇) 15.0 kPa]. Measurements performed on cooling ($T_{\mathrm{SmC\text{-}N}}$ = 48 °C, T_{NI} = 87 °C).

(which affects moderately the transition temperatures), since this is observable only above load greater than 11.7 kPa (Supporting Information).[51]

As for the elastomer 80% **M1** + **D6**, the elastic behavior is unchanged after several heating–cooling cycles (no hysteresis either at the nematic-to-isotropic liquid transformation) with the complete superposition of the curves obtained with two different loads (Figure 8). However, this system shows a much smaller rate of elongation than the system with **HD**$_5$ (85% versus 135%) or of other MC-LCEs systems.[32,51,65] In this case, the elongation ratio is of the order to that observed for SC-LCEs (only about 15–20% of elongation greater).[50,62] In order to increase the amplitude of the elongation, it seems clear that reducing the volume fraction of cross-linker used is necessary, which should be possible, providing a great improvement of the reticulation reaction.

The Young modulus, E, was evaluated from the stress–strain experiment, at 110 °C in the isotropic liquid phase (Figure 9). For the elastomer 80% **M1** + **D6**, the stress–strain curve consists of two parts. At deformations below 30–35%, the linear stress–strain variation gives an estimate of the elastic modulus E, equal to 5.6×10^4 N·m^{-2}, a value of the order to that found with some mixed main-/side-chain systems; E in this case was found to increase with the increasing amount of main-chain constituent ($E = 2.1 \times 10^4$ to 25.2×10^4 N·m^{-2}).[32,51] A smooth change of stress–strain slope occurs at a threshold deformation greater than 35%, when the elastic modulus takes a slightly lower value, $E = 3.7 \times 10^4$ N·m^{-2}, indicative that some residual anisotropy remains. The Young modulus of the elastomer **M1** + **HD**$_5$ could not be measured due to the elevated transition temperatures, in particular, the isotropization temperature.

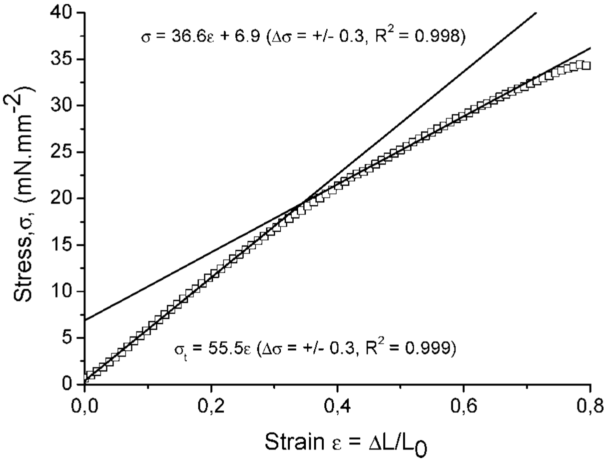


Figure 9. Stress–strain experiment for elastomer 80% **M1** + **D6** at 110 °C in the isotropic liquid phase (σ_t = true uniaxial stress).

It is known that increasing the temperature (of the experiment) may diminish the possibility to detect the soft elasticity plateau, and clearly the latter has never been detected in the isotropic phase.[1,32,51] However, the absence of ”hard behavior” can be due to other parameters, such as the curing process (or the second reticulation) to stabilize the monodomain at room temperature in the smectic phase or by the anisotropy introduced by a discotic rigid cross-linker, both inhibiting or at least discouraging a soft behavior. It is suggested that the elastic behavior of a LCE is linked to its preparation. Indeed, a material cross-linked in the nematic phase should present a behavior harder than if reticulated in the isotropic liquid.[1,17,66,67] Thus, the elastomer 80% **M1** + **D6**, which was cross-linked in the smectic phase, will always retain a residual anisotropy, even in the isotropic liquid phase that prevents this soft behavior before breaking.

The other systems prepared with the rigid cross-linkers could not form stable monodomains. The elastomers prepared in the bulk were thus all aligned in the isotropic state, by applying traction with a load. The materials were cooled to room temperature, the charge was removed, and the length of the aligned material could be measured. The film was then heated again to the isotropic state, and its length (L_0) was measured. This process permitted the evaluation of the capacity of the material to contract during the transition to the isotropic state, after having been stretched to its maximum length. The graphic shown in Figure 10 represents the maximum ratio L/L_0 for the different elastomers, as function of the cross-linkers geometry and multiplicity and compared to a film obtained with the system **M1** + 10% **HD**$_5$, having a value of about ~135%. This value, obtained for a flexible punctual cross-linker, is higher than the values obtained for any of the materials prepared with the rigid and bulky cross-linkers.

These results suggest that, for a similar geometry of the cross-linker, the maximum strain is lower as the multiplicity is increased. This observation agrees with the theoretical predictions of Tsige and Stevens,[67] who have simulated the influence of the multiplicity of the cross-linker (η = 3, 4, and 6) of a reticulated polymeric system. They concluded that elastomers prepared with cross-linkers of low multiplicity allow larger strains than the elastomers prepared with cross-linkers of high multiplicity. They present two main explanations for this behavior. The first one is the stoichiometry: for materials

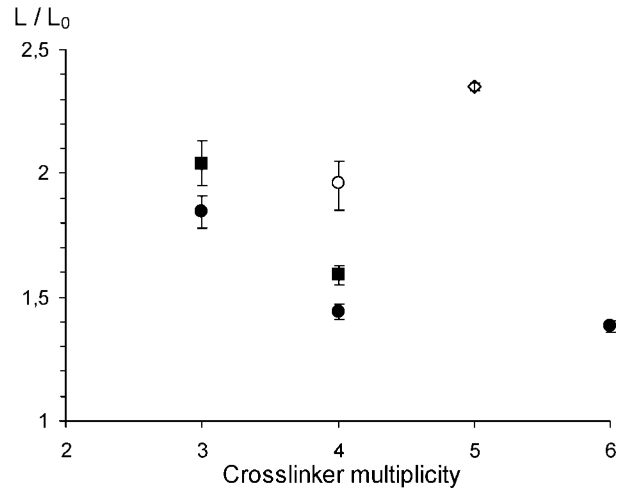


Figure 10. Graphic showing the maximum strain (L/L_0) for the elastomers prepared with rigid cross-linkers in the bulk. Elastomers 80% **M1** + cross-linker and **M1** + 10% **HD$_5$**. Solid symbols, rigid cross-linkers: (■) linear (**L3**, **L4**); (●) discotic (**D3**, **D4**, **D6**); Open symbols, flexible cross-linkers: (○) spherical (**S4**); (□) maximum strain obtained for an elastomeric film of **M1** + 10% **HD$_5$**.

prepared with higher multiplicity cross-linkers; the concentration of reticulation points lowers as the multiplicity increases, resulting in increasing separation of neighboring reticulation centers. The second reason is connected to the excluded volume around the reticulation point, particularly important for the cross-linkers with a high multiplicity. Indeed, the high number of chains around the reticulation point prevents the existence of another reticulation point in its vicinity, meaning that the chains are locally more packed in the case of an elastomer prepared with a cross-linker of low multiplicity, thus allowing larger elongations for these materials. In this work, the authors concluded that the use of highly covalent cross-linkers produces more resistant materials, allowing the use of larger load before breaking, but with a smaller strain capacity. These considerations may also help to explain the behavior of the elastomers prepared with cross-linkers of equal multiplicity but with different geometry.

Thus, a flexible cross-linker allows a better arrangement of the chains around the reticulation point, favoring larger elongations than the ones allowed for materials prepared with less flexible cross-linkers. The use of linear cross-linkers allows larger strains than the ones found when using discotic cross-linkers. This is in agreement with the predictions of Terentjev[56] and Warner,[68] who suggested that the anisotropy of the cross-linking points may couple with the anisotropy of the mesogens, in the mesophase. The more similar are the cross-linker and the mesogen structures, the stronger the coupling. We found that, in contrast, the incorporation of discotic cross-linkers reduces the stability of the smectic phase due to the stronger perturbations near the reticulation points, and the difficulties of the chains to remain locally perfectly parallel.

Conclusions

In this work, we have shown that small changes in the symmetry of the mesogens have a considerable impact on the phase transition temperatures and on the stability of the mesophases. The symmetrical monomers present the highest clearing temperatures, in contrast to the nonsymmetrical ones, which present a low-melting behavior. Regardless of the molecular symmetry, the presence of lateral methyl groups clearly destabilizes the smectic phase at the expense of the nematic phase, facilitating therefore its accessibility. Similarly, the insertion of rigid cross-linkers results in the overall destabilization of the mesomorphism, rendering the isotropic state more accessible, permitting the study, and thus the evaluation of the mechanical properties of the systems.

Interestingly, increasing the cross-linking density of the elastomers favors the stability of the smectic phase (probably because the cross-linking reaction takes place at a temperature where the corresponding polymer is in the smectic phase).

While the core methylation has little effect on the mechanical properties, the increase of the cross-linking connectivity on the one hand and the discotic shape on the other hand diminish the ability of the elastomers to elongate (Figure 10), and the more rigid the cross-linker, the more fragile the corresponding elastomer.

The results obtained in this work allowed us to evaluate the effects that could be expected on the properties of an elastomer by tuning the cross-linker (multiplicity, geometry, rigidity, density): cross-linkers with high multiplicity allow one to obtain better reticulated materials (lower sol. % and lower swelling degrees), while those with a smaller multiplicity allow one to obtain elastomers capable of larger strains. It becomes clear that the choice of the cross-linker can be made according to the behavior expected for the material: mechanically resistant materials or very elastic/high-strain capable materials.

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Supporting Information Available: Text giving materials and methods, synthesis of the monomers and cross-linkers, preparation of the polymers, preparation of the elastomers, thermal and liquid crystal behavior of the monomers, polymers, and elastomers, characterization of the mesomorphic properties by X-ray diffraction, and thermo-elastic behavior, schemes showing the syntheses of the compounds, tables of thermal behavior data, characterization data, reaction conditions, variation of soluble content, and applied charges, and figures showing the sequence of preparation, X-ray patterns of the elastomers, variations of the periodicity and tilt angles as a function of temperature, and the elongation of the elastomer as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Warner, M.; Terentjev, E. *Prog. Polym. Sci.* **1996**, *21*, 853–891. (b) Terentjev, E. *J. Phys.: Condens. Matter* **1999**, *11*, R239–R257. (c) Terentjev, E. *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 101–107. (d) Warner, M.; Terentjev, E. *Liquid Crystal Elastomers, International Series of Monographs on Physics 120*; Oxford Science Publications: Oxford, U.K., 2003.
(2) Brand, H. R.; Pleiner, H.; Martinoty, P. *Soft Mater.* **2006**, *2*, 182–189.
(3) de Gennes, P.-G. *C. R. Sci. Acad. Sci. Ser. B* **1975**, *281*, 101–103.
(4) Kuhn, W.; Hargilay, B.; Katchalsky, A.; Eisenberg, H. *Nature* **1950**, *165*, 514–516.
(5) Auroy, P. *Pour Sci.* **2002**, *294*, 88–93.
(6) Mark, J. E. *Prog. Polym. Sci.* **2003**, *28*, 1205–1221.
(7) (a) Zentel, R. *Liq. Cryst.* **1986**, *1*, 589–592. (b) Barnes, N. R.; Davis, J. F.; Mitchell, G. R. *Mol. Cryst. Liq. Cryst.* **1989**, *168*, 13–25. (c) Lehmann, W.; Skupin, H.; Tolksdorf, C.; Gebhard, E.; Zentel, R.; Kruger, P.; Losche, M.; Kremer, F. *Nature* **2001**, *410*, 447–450. (d) Köhler, R.; Stannarius, R.; Zentel, R. *Appl. Phys. A: Mater. Sci. Process.* **2005**, *80*, 381–388. (e) Yusuf, Y.; Huh, J.-H.; Cladis, P. E.; Brand, H. R.; Finkelmann, H.; Kai, S. *Phys. Rev. E* **2005**, *71*, 061702. (f) Spillmann, C. M.; Ratna, B. R.; Nacirib, J. *Appl. Phys. Lett.* **2007**, *90*, 021911. (g) Yusuf, Y.; Hashimoto, S.; Cho, D.-U.; Brand, H. R.; Finkelmann, H.; Kai, S. *Mol. Cryst. Liq. Cryst.* **2007**, *477*, 127–135.
(8) (a) Finkelmann, H.; Nishikawa, E.; Pereira, G. G.; Warner, M. *Phys. Rev. Lett.* **2001**, *87*, 015501. (b) Cviklinski, J.; Tajbakhsh, A. R.; Terentjev, E. M. *Eur. Phys. J. E* **2002**, *9*, 427–434. (c) Hogan, P. M.;

Tajbakhsh, A. R.; Terentjev, E. M. *Phys Rev. E* **2002**, *65*, 041720. (d) Warner, M.; Terentjev, E. *Macromol. Symp.* **2003**, *200*, 81–92. (e) Li, M. H.; Keller, P.; Li, B.; Wang, X.; Brunet, M. *Adv. Mater.* **2003**, *15*, 569–572. (f) Camacho-Lopez, M.; Finkelmann, H.; Palfy-Muhoray, P.; Shelley, M. *Nat. Mater.* **2004**, *3*, 307–310. (g) Beyer, P.; Zentel, R. *Macromol. Rapid Commun.* **2005**, *26*, 874–879. (h) Kondo, M.; Yu, Y.; Ikeda, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1378–1382. (i) Ikeda, T.; Mamiya, J.; Yu, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 506–528.

(9) de Gennes, P.-G. *C. R. Acad. Sci. Paris, Ser. IIb* **1997**, *324*, 343–348.

(10) (a) Finkelmann, H.; Kaufhold, W.; Noirez, L.; Tenbosch, A.; Sixou, P. *J. Phys. II* **1994**, *4*, 1363–1373. (b) Knight, D. P.; Vollrath, F. *Philos. Trans. R. Soc. London, B* **2002**, *357*, 155–163.

(11) (a) Li, M.-H.; Keller, P. *Philos. Trans. R. Soc. London, A* **2006**, 1–15. (b) Buguin, A.; Li, M.-H.; Silberzan, P.; Ladoux, B.; Keller, P. *J. Am. Chem. Soc.* **2006**, *128*, 1088–1089. (c) Spillmann, C. M.; Naciri, J.; Martin, B. D.; Farahat, W.; Herr, H.; Ratna, B. R. *Sens. Act. A* **2007**, *133*, 500–505.

(12) (a) Kim, S. T.; Finkelmann, H. *Macromol. Rapid Commun.* **2001**, *22*, 429–433. (b) Finkelmann, H.; Kim, S. T.; Munoz, A.; Palffy-Muhoray, P.; Taheri, B. *Adv. Mater.* **2001**, *13*, 1069–1072. (c) Schmidtke, J.; Kniesel, S.; Finkelmann, H. *Macromolecules* **2005**, *38*, 1357–1363.

(13) (a) Finkelmann, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 816–824. (b) Schätzle, J.; Finkelmann, H. *Mol. Cryst. Liq. Cryst.* **1987**, *142*, 85–100. (c) Brand, H. R.; Finkelmann, H. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, J. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. *3*,Chapter V, pp 277–302.

(14) (a) Zentel, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1407–1415. (b) Mayer, S.; Zentel, R. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 545–551.

(15) Kelly, S. *J. Mater. Chem.* **1995**, *5*, 2047–2061.

(16) Xie, P.; Zhang, R. *J. Mater. Chem.* **2005**, *15*, 2529–2550.

(17) Urayama, K. *Macromolecules* **2007**, *40*, 2277–2288.

(18) Talroze, R. V.; Zubarev, E. R.; Kuptsov, S. A.; Merekalov, A. S.; Yuranova, T. I.; Plate, N. A.; Finkelmann, H. *React. Funct. Polym.* **1999**, *41*, 1–11.

(19) Hanus, K.-H.; Pechhold, W.; Soergel, F.; Stoll, B.; Zentel, R. *Colloid Polym. Sci.* **1990**, *268*, 222–229.

(20) Bergmann, G.; Finkelmann, H.; Percec, V.; Zhao, M. *Macromol. Rapid Commun.* **1997**, *18*, 353–360.

(21) Ortiz, C.; Wagner, M.; Bhargava, N.; Ober, C.; Kramer, E. *Macromolecules* **1998**, *31*, 8531–8539.

(22) (a) Donnio, B.; Wermter, H.; Finkelmann, H. *Macromolecules* **2000**, *33*, 7724–7729. (b) Rousseau, I.; Mather, P *J. Am. Chem. Soc.* **2003**, *125*, 15300–15301. (c) Rousseau, I.; Qin, H.; Mather, P. *Macromolecules* **2005**, *38*, 4103–4113. (d) Rogez, D.; Brandt, H.; Finkelmann, H.; Martinoty, P. *Macromol. Chem. Phys.* **2006**, *207*, 735–745. (e) Sanchez-Ferrer, A.; Finkelmann, H. *Macromolecules* **2008**, *41*, 970–980.

(23) Marta Giamberini, M.; Ambrogi, V.; Cerruti, P.; Carfagna, C *Polymer* **2006**, *47*, 4490–4496.

(24) (a) Beyer, P.; Terentjev, E. M.; Zentel, R. *Macromol. Rapid Commun.* **2007**, *28*, 1485–1490. (b) Beyer, P.; Braun, L.; Zentel, R. *Macromol. Chem. Phys.* **2007**, *208*, 2439–2448.

(25) (a) Schuring, H.; Stannarius, R.; Tolksdorf, C.; Zentel, R. *Macromolecules* **2001**, *34*, 3962–3972. (b) Stannarius, R.; Kohler, R.; Dietrich, U.; Losche, M.; Tolksdorf, C.; Zentel, R. *Phys. Rev. E* **2002**, *65*, 041707.

(26) Bourgerette, C.; Chen, B.; Finkelmann, H.; Mitov, M.; Schmidtke, J.; Stille, W. *Macromolecules* **2006**, *39*, 8163–8170.

(27) Zhang, B.-Y.; Meng, F.-B.; Zang, B.-L.; Hu, J. *Macromolecules* **2003**, *36*, 3320–3326.

(28) Zanna, J. J.; Stein, P.; Marty, J. D.; Mauzac, M.; Martinoty, P. *Macromolecules* **2002**, *35*, 5459–5465.

(29) Hotta, A.; Terentjev, E. M. *J. Phys.: Condens. Matter* **2001**, *13*, 11453–11464.

(30) Brown, D. H.; Dasa, V.; Allen, R. W. K.; Styring, P. *Mater. Chem. Phys.* **2007**, *104*, 488–496.

(31) (a) Zentel, R. *Angew. Chem. Adv. Mater.* **1989**, *101*, 1437–1445. (b) Zentel, R.; Brehmer, M. *Acta Polym.* **1996**, *47*, 141–149.

(32) Wermter, H.; Finkelmann, H. *e-Polym.* **2001**, 000. no. 13.

(33) (a) Tajbakhsh, A. R.; Terentjev, E. M. *Eur. Phys. J. E* **2001**, *6*, 181–188. (b) Clarke, S. M.; Hotta, A.; Tajbakhsh, A. R.; Terentjev, E. M. *Phys. Rev. E* **2001**, *64*, 061702. (c) Clarke, S. M.; Hotta, A.; Tajbakhsh, A. R.; Terentjev, E. M. *Phys. Rev. E* **2002**, *65*, 021804.

(34) (a) Merekalov, A. S.; Kuptsov, S. A.; Shandryuk, G. A.; Talroze, R. V.; Bezborodov, V. S.; Terentjev, E. M. *Liq. Cryst.* **2001**, *28*, 495–502. (b) Shandryuk, G. A.; Kuptsov, S. A.; Shatalova, A. M.; Plate, N. A.; Talroze, R. V. *Macromolecules* **2003**, *36*, 3417–3423.

(35) (a) Finkelmann, H.; Gleim, W.; Kock, H. J.; Oppermann, W.; Rehage, G. *Proc. IUPAC, I.U.P.A.C., Macromol. Symp.* **1982**, *28*, 556. (b) Kock, H. J.; Finkelmann, H.; Gleim, W.; Rehage, G. *Polym. Sci. Technol.* 1985, *28*, 275–293.

(36) Kupfer, J.; Finkelmann, H. *Macromol. Chem. Rapid Commun.* **1991**, *12*, 717–726.

(37) (a) Thomsen, D. L., III; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B. R. *Macromolecules* **2001**, *34*, 5868–5875. (b) Naciri, J.; Srinivasan, A.; Jeon, H.; Nikolov, N.; Keller, P.; Ratna, B. R. *Macromolecules* **2003**, *36*, 8499–8505. (c) Shenoy, D. K.; Thomsen, D. L.; Keller, P.; Ratna, B. R. *J. Phys. Chem. B* **2003**, *107*, 13755–13757.

(38) Spilmann, C. M.; Naciri, J.; Chen, M.-S. A.; Srinivasan, B. R. Ratna *Liq. Cryst.* **2006**, *33*, 373–380.

(39) Komp, A.; Finkelmann, H. *Macromol. Rapid Commun.* **2007**, *28*, 55–62.

(40) (a) Di Maio, L.; Iannelli, P.; Pragliola, S.; Roviello, A.; Sirigu, A. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 433–438. (b) Caruso, U.; Hatfull, L.; Roviello, A.; Sirigu, A. *Polymer* **1999**, *40*, 6753–6760.

(41) Demus, D. *Liq. Cryst.* **1989**, *5*, 75–110.

(42) Caruso, U.; Pragliola, S.; Roviello, A.; Sirigu, A.; Iannelli, P. *Macromolecules* **1995**, *28*, 6089–6094.

(43) Carothers discusses these problems in: Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953. The Carothers equation limits PDI to values of 2 and below, and is defined as PDI $= M_\mathrm{w}/M_\mathrm{n} = 1 + p$, where M_w is the weight average molecular weight, M_n, the number average molecular weight, and p the conversion ($p = 1$ for total conversion).

(44) (a) Ganicz, T.; Stanczyk, W. A.; Białecka-Florjanczyk, E.; Sledzinska, I. *Polymer* **1999**, *40*, 4733–4739. (b) Imrie, C. T.; Henderson, P. A. *Chem. Soc. Rev.* **2007**, *36*, 2096–2124.

(45) Akiyama, E.; Matsui, N.; Nagase, Y. *Liq. Cryst.* **1997**, *23*, 425–438.

(46) Aguilera, C.; Bartulin, J.; Hisgen, B.; Ringsdorf, H. *Makromol. Chem.* **1983**, *184*, 253–262.

(47) Zhang, B.; Liu, L.-M.; Feng, Z.-L.; Jia, Y.-G. *Liq. Cryst.* **2003**, *30*, 1015–1019.

(48) Mitchell, G.; Davis, F.; Ashman, A. *Polymer* **1987**, *28*, 639–647.

(49) Billibin, A.; Solovjeva, J.; Girbasova, N.; Schwarz, G. *Macromol. Chem. Phys.* **2000**, *201*, 1088–1100.

(50) Nishikawa, E.; Finkelmann, H. *Macromol. Chem. Phys.* **1999**, *200*, 312–322.

(51) (a) Wermter, H. Flüssigkristalline Co-Elastomere: Synthese, Untersuchungen der mecanischen Eigenschaften, Direktororientierung und thermoelastisches Verhalten. Ph.D. Thesis, Albert-Ludwigs-Universität, Freiburg i. B., Germany, **2001**. (b) Brandt, H. Statisch- und dynamisch-mecanische Untersuchungen an neuen flüssigkristallinenHauptketten-Netzwerken. Ph.D. Thesis, Albert-Ludwigs-Universität, Freiburg i. B., Germany, **2004**.

(52) The results of these investigations will be reported in due course. Bispo, M. Synthèse et caractérisation d′élastomères à chaînes principales. Propriétés mésomorphes et thermoélastiques. Ph.D. Thesis, Université Louis Pasteur, Strasbourg, France, **2006** (http://eprints-scd-ulp.u-strasbg.fr:8080/672/01/These_tot_160107.pdf).

(53) Davis, F. *J. Mater. Chem.* **1993**, *3*, 551–562.

(54) (a) Greve, A.; Finkelmann, H. *Macromol. Chem. Phys.* **2001**, *202*, 2926–2946. (b) Hiraoka, K.; Sagano, W.; Nose, T.; Finkelmann, H. *Macromolecules* **2005**, *38*, 7352–7357. (c) Kundler, I.; Finkelmann, H. *Macromol. Chem. Phys.* **1998**, *199*, 677–686.

(55) (a) Zhang, B.-Y.; Hu, J.-S.; Jia, Y.-G.; Du, B.-G. *Macromol. Chem. Phys.* **2003**, *204*, 2123–2129. (b) Hu, J.-S.; Zhang, B.-Y.; Jia, Y.-G.; Chen, S. *Macromolecules* **2003**, *36*, 9060–9066. (c) Zhang, B.-Y.; Liu, L.-M.; Yao, D.-S.; Zhang, L.-F. *Colloid Polym. Sci.* **2005**, *283*, 1143–1148.

(56) Fridrikh, S.; Terentjev, E. *Phys. Rev. E* **1999**, *60*, 1847–1857.

(57) Zhang, B.-Y.; Jia, Y.-G.; Yao, D.-S.; Dong, X.-W. *Liq. Cryst.* **2004**, *31*, 339–345.

(58) Davidson, P. *Struct. Bonding (Berlin)* **1999**, *95*, 1–39.

(59) Read, D.; Duckett, R.; Sweeney, J.; McLeish, T. *J. Phys. D: Appl. Phys.* **1999**, *32*, 2087–2089.

(60) Zubarev, E.; Kuptsov, S.; Yuranova, T.; Talroze, R.; Finkelmann, H. *Liq. Cryst.* **1999**, *26*, 1531–1540.

(61) Hiraoka, K.; Uematsu, Y.; Stein, P.; Finkelmann, H. *Macromol. Chem. Phys.* **2002**, *203*, 2205–2210.

(62) Assfalg, N.; Finkelmann, H. *Macromol. Chem. Phys.* **2001**, *202*, 794–800.

(63) Li, M.-H.; Keller, P.; Yang, J.; Albouy, P.-A. *Adv. Mater.* **2004**, *16*, 1922–1925.

(64) Nishikawa, E.; Finkelmann, H.; Brandt, H. *Macromol. Rapid Commun.* **1997**, *18*, 65–71.

(65) Tajbakhsh, A.; Terentjev, E. *Eur. Phys. J. E* **2001**, *6*, 181–188.

(66) Küpfer, J.; Finkelmann, H. *Macromol. Chem. Phys.* **1994**, *195*, 1353–1367.

(67) Tsige, M.; Stevens, M. *Macromolecules* **2004**, *37*, 630–637.

(68) Verwey, G. C.; Warner, M. *Macromolecules* **1997**, *30*, 4196–4204.

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