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Abstract: Side-chain liquid crystal elastomers (SC-LCEs) have been designed by using a new smectic crosslinker. Two types of monodomain films were prepared based on polysiloxane chains, with a different relative concentration of both crosslinker and mesogenic comonomers. The mesomorphic behavior of the two SC-LCE systems was investigated by differential scanning calorimetry and polarized optical microscopy showing a different mesomorphic behavior: in one case, we obtained a nematic SC-LCE film, in the other case, a Smectic A SC-LCE film. In both systems, the mesophases were stable in a wide temperature range. Moreover, the SC-LCE films possess a relatively high orientation at room temperature. The physical-chemical properties, such as the local orientational ordering, structural organization, and dynamics of SC-LCEs' constituents were studied by means of static and dynamic ²H NMR experiments, small-angle X-ray, and wide-angle X-ray diffractions. The relevant physical properties, such as the thermo-elastic and thermo-mechanic behaviors, are reported and discussed in view of the practical applications.

Keywords: liquid crystal elastomers; nematic; smectic A; thermo-mechanic; thermos-elastic; ²H NMR; X-ray diffraction; orientational order; dynamic properties

1. Introduction

Liquid crystalline elastomers (LCEs) [1–4] represent an exciting class of soft materials with specific chemical and physical properties suitable for applications as artificial muscles, actuator systems, and sensors [5–7]. The soft and super-soft elasticity of LCEs [8] is related, on one side, to the presence of polymer networks, and, on the other side, to liquid crystalline molecules, which can be inserted as comonomers in side-chain liquid crystalline elastomers (SC-LCEs) or directly in the polymer main chain, in main-chain liquid crystalline elastomers (MC-LCEs) [9]. In addition to the deeply investigated structural and physical properties of a thermally induced actuator based on LCEs [10-20], an increasing number of papers concerns the application of external stimuli, such as UV-vis light, microwaves and infrared waves, and electric and magnetic fields, to obtain controlled and reversible shape deformations in LCE-based systems. For instance, UV-visible light can be used to induce reversible local geometric deformations in LCEs containing azo-mesogens or other photosensitive molecules, as crosslinkers, comonomers, or dopants [21–25], which are at the basis of several applications in the field of optical tunable gratings and light-driven motors. LCE-based materials responsive to infrared radiations were prepared by inserting carbon nanotubes or graphene sheets into the LCE matrix [26–28]. On the contrary, microwave irradiation was demonstrated to be effective in reaching macroscopic reversible deformations in pristine LCEs [29]. The synthesis and preparation of polymer composites based on LCEs, as a polymeric soft matrix [30–35], and electro-active or magneto-active



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). nanostructured objects is another field under great development due to the potential applications in micro-robotics. Moreover, in recent years, research efforts have been focused on the processing of LCE three-dimensional actuators [36], highly orientable soft–soft composites with the capability to obtain different geometric actuations [37], LCE-based systems with high resolution shape-memory behaviors [38–40], and new synthetic approaches [41,42] to prepare LCEs with peculiar properties, such as flexoelectricity [43] and giant lateral electrostriction [44].

The interest in new LCE-based materials related to their rich variety of applications is a great stimulus also for the development of physical models at the meso-scale [8,45–47] and for the better understanding of these systems at the molecular and supramolecular scale [15–18,48–51]. In this regard, several experimental techniques, such as Deuterium Nuclear Magnetic Resonance (²H NMR), are successfully applied to LCEs selectively labelled by deuterium in different positions (crosslinkers or comonomers) [18,33,52–56] or doped with small deuterated probes [57–60]. Static ²H NMR experiments are helpful for elucidating the nature of the isotropic (Iso) to mesophase transition [61,62], which in most of the cases is a nematic phase, while in much less of the cases is a smectic phase [11-14]. Moreover, both ²H NMR and calorimetric investigations demonstrated the presence of the paranematic phase in LCEs, characterized by a small, but detectable, local order at temperatures above the clearing point [54–57]. The possibility to prepare LCE systems selectively labelled on the crosslinker and on different comonomers allowed us to obtain an insight into a local molecular order [54–56], local heterogeneities and misalignments [57], as well as different scales of molecular dynamics of the different molecular fragments [53]. The structural and orientational properties of LCEs in the nematic and smectic phases can be obtained by NMR and X-ray diffraction [18,63], while the combination between thermomechanical and stress–strain investigations was important to fully characterize the mechanical properties of monodomain LCEs and their behavior at isotropic-nematic, isotropic–smectic A, and nematic–smectic A phase transitions [16].

In this paper, we are reporting on the design and preparation of new SC-LCEs based on polysiloxane chains, containing a smectic crosslinker and two mesogenic comonomers. The two comonomers, a nematogen and a smectogen, mixed in different relative concentrations, allowed us to obtain two SC-LCE samples with a nematic phase or a smectic A phase, both stable in a reasonably broad temperature range. These new SC-LCEs were investigated and prepared in the polydomain and in the monodomain aligned forms. Differential scanning calorimetry (DSC), polarizing optical microscopy (POM), small-angle X-ray (SAXS), and wide-angle X-ray (WAXS) diffractions were performed to fully characterize the mesophase behavior and the main structural features of the two types of side-chain liquid crystalline elastomers. The thermo-mechanic and stress-strain properties of the SC-LCEs in the monodomain form were also measured. Moreover, the SC-LCE sample showing a direct transition from the isotropic to the Smectic A phase was also prepared in its deuterated form, by using a deuterium-labelled nematic comonomer, and it was studied by means of ²H NMR static and dynamic experiments. The orientational and dynamic properties of the smectic A SC-LCE sample obtained from ²H NMR are finally discussed in view of the recent advances in liquid crystalline elastomers.

2. Materials and Methods

2.1. Liquid Crystalline Crosslinker

The molecular structure of the smectic crosslinker, labelled 'C', is reported in Scheme 1.

H-C>

Scheme 1. Molecular structure of the crosslinker, labelled 'C'.

The synthesis of the smectic crosslinker is reported in ref. [64]. The mesomorphic behavior, as determined by differential scanning calorimetry (DSC), and confirmed by polarizing optical microscopy (POM), is shown in Table 1.

Table 1. Mesophase transitions determined by DSC (cooling rate of 5 K/min) of the sample labelled 'C'. Phase transition temperatures (T, °C) and phase transition enthalpy (Δ H, J/g) measured at the second DSC cycle are shown. The values of melting point (m.p.) and clearing point (c.p.) (measured on heating) are reported.

	m.p.	c.p.	Phase		Phase		Phase		Phase		Phase
T (°C)	90.0	193.2	Cr	80.9	SmJ	136.1	SmI	162.7	SmC	191.7	Iso
ΔH (J/g)	61.7	32.8		45.0		6.5		3.5		31.2	

2.2. Liquid Crystalline Elastomers

The SC-LCE samples were prepared using the well-known two-step crosslinking procedure [65], in the form of polydomains (not oriented) and monodomain (oriented) samples. The basic chemical components are shown in Figure 1 and Scheme 1. Two comonomers, namely the 4- methoxyphenyl 4-(but-3-en-1-yloxy) benzoate nematogen (denoted by M4) and the 4-methoxyphenyl 4-(undec-10-en-1-yloxy) benzoate smectogen (denoted by M11), were used, in different relative concentrations, to obtain a nematic or a smectic SC-LCE sample. The synthetic procedure and the characterization of the two comonomers is reported elsewhere [18,66,67]. For the preparation of each SC-LCE sample, 1 mmol of hydroxymethyl polysiloxane (P in Figure 1) was mixed with 'c'/2 mmol% of the smectic crosslinker 'C' (Scheme 1), 'n' mmol% of nematogen M4 (N in Figure 1), and 's' mmol% of smectogen M11 (S in Figure 1) in 2 mL of anhydrous toluene. Then, 30 μ L of 71 mmol/l Pt-catalyst solution (Dichloro (1,5-cyclooctadiene) platinum (II) from Fischer scientific, dissolved in CH₂Cl₂) was added.



Figure 1. Compounds used in the synthesis of LCE systems: (**P**) hydroxymethyl polysiloxane polymeric chain; (**S**) smectic comonomer, M11; (**N**) nematic comonomer, M4. $X = {}^{1}H$ for the not labelled SC-LCEs, while $X = {}^{2}H$ for the deuterated SC-LCEs. (The structure of the crosslinker, C, is shown in Scheme 1).

The resulting pre-polymerization mixture was then filtered into a cylindrical form for the first step of the crosslinking reaction inside a centrifuge (a rate of 5500 rpm, temperature of 343 K, and reaction time of 70 min). The resulting partially crosslinked LCE film gel was then cut into stripes to be mechanically strained. The second step of the crosslinking reaction to obtain the monodomain SC-LCEs was performed under progressive weights from 3 mg to 10 mg for each stripe. The elongated SC-LCE films were further crosslinked
 SC-LCE 1
 SC-LCE 2

 100% (P)
 20% (N)

 50% (S)
 20% (N)

 35% (C)
 10% (C)

 Image: Comparison of the second seco

at 70 °C overnight. A representation of the two SC-LCE films in the oriented and aligned phase showing the molecular components (P, N, S, and C) is reported in Scheme 2.

Scheme 2. Sketch of the two types of monodomain SC-LCEs: the aligned nematic film (SC-LCE 1) and the aligned smectic film (SC-LCE 2), with an ideal representation of the different components and their alignment with respect to the phase director, \vec{n} .

Two types of SC-LCEs, denoted as **SC-LCE 1** and **SC-LCE 2**, were prepared with the values of mmol%, namely 'c', 'n', and 's', reported in Table 2. The sample with a higher concentration of nematogen, M4, called **SC-LCE 1**, has a nematic phase stable in a wide range of temperatures, while the sample with the higher concentration of the smectogen M11, called **SC-LCE 2**, exhibits a smectic A phase, stable in a very wide temperature range. The **SC-LCE 2** was also prepared in its deuterated form (labelled '**SC-LCE 2** (**D**)') by using the deuterated mesogen, M4-d₂, deuterium labelled on the aromatic ring close to the polymerizable bond (see Figure 1) [18].

Table 2. Mesophase transitions determined by DSC (cooling rate of 5 °C/min) of the samples labelled 'SC-LCE 1', 'SC-LCE 2', and 'SC-LCE 2 (D)'. Temperature transitions (T, °C), transition enthalpy (Δ H, J/g), and thermal capacity (Cp, J/g °C) are reported. All values correspond to the second cooling run.

Sample Label:	Monomer, M4 ('n', mmol%)	Monomer M11 ('s', mmol%)	Crosslinker C ('c', mmol%)	Phase	T (°C)/[Cp (J/g °C)]	Phase	Τ (°C)/ [ΔΗ (J/g)]	Phase
SC-LCE 1	50	35	15	Glass	-11.4 [0.3]	Nematic	85.0 [2.1]	Iso
SC-LCE 2	20	70	10	Glass	-4.5 [0.40]	Smectic	121.4 [-5.3]	Iso
SC-LCE 2 (D)	20	70	10	Glass	-8.1 [0.67]	Smectic	113.3 [-5.2]	Iso

The mesomorphic behavior of the SC-LCE samples, explored by combining different experimental techniques, such as DSC and POM, are summarized in Table 2 and discussed in Section 3.

2.3. Mesomorphic Properties (DSC and POM)

The sequence of phases and phase transition temperatures were determined on heating/cooling to/from the isotropic phase by the identification of the characteristic textures and their changes observed in a polarizing optical microscope (POM NICON ECLIPSE E600POL). In the case of LCE films, they have been inserted between two glasses. The LCE film's thickness is about 150 μ m and the director is aligned along the direction of the elongation of the film (pre-determined during the preparation of the monodomain SC-LCEs). The LINKAM LTS E350 heating stage with a TMS 93 temperature programmer was used for the temperature control, which enabled the temperature stabilization within ± 0.1 °C. The phase transition temperatures and transition enthalpies were evaluated from differential scanning calorimetry (DSC Pyris Diamond, Perkin-Elmer 7) on cooling and heating the sample at a rate of 5 °C/min. The sample (10 mg) hermetically sealed in an aluminum pan was placed in a nitrogen atmosphere. The temperature was calibrated on the extrapolated onsets of the melting points of water, indium, and zinc. The enthalpy change was calibrated on the enthalpies of the melting of water, indium, and zinc. The mesomorphic behavior of the LCEs has been studied by DSC on heating and subsequent cooling (5 °C/min). Each sample was placed into a DSC sample cell holder at room temperature, cooled to -40 °C and, after 5 min, heated to 140 °C, maintained at this temperature for 1 min, cooled to -40 °C and, after 2 min, reheated once again. Several heating/cooling runs were performed, showing the perfect reproducibility of the resulting DSC curves.

2.4.²H NMR Measurements

²H NMR static experiments were carried out with a Bruker Advance III 500 MHz high resolution solid-state NMR spectrometer, equipped with an 11.74 T Bruker Ultrashield superconducting magnet. The deuterium Larmor frequency was of 76.753 MHz. The spectra were recorded as a function of the temperature, on heating and on cooling, by applying the quadrupolar echo [68] sequence with a calibrated 90 degrees pulse of 7.5 µs. The echo delay was fixed to 50 µs, the delay was 20 µs, and the delay between the consecutive acquisitions was 30 ms. The measurements of the monodomain LCE stripes was performed as described in ref. [55]. The number of scans was set between 51,200 and 102,400 at each acquired temperature depending on the sample. The temperature control was of an approximately 0.1 K of accuracy and the thermal equilibration of the sample was about 15 min at each temperature. The ²H spin–lattice relaxation times, T₁, were measured by applying the pulse sequence (90° – τ – 90° – τ ₁ – 90° – τ ₂ – ACQ) [68]. The experimental parameters are those reported in ref. [53]. The T₁ values were determined by fitting the experimental magnetization intensities as a function of τ by using the following equation:

$$I(\tau) = I_0 \left(1 - e^{-\tau/T_1} \right)$$
 (1)

The ²H spin–spin relaxation times, T₂, were measured by applying the solid-echo sequence (90° $-\tau$ – 90° $-\tau$ – ACQ) and EXORCYCLE phase cycling [69,70] with the parameters reported in ref. [53]. The T₂ values were determined by fitting the experimental magnetization intensities according to the equation:

$$I(\tau) = I_0 e^{(-2\tau/T_2)}$$
(2)

Top Spin Software for the Bruker Advance III console was used to process the ²H NMR spectra and to obtain the main spectral parameters. The calculated NMR properties and the elaboration of the spectral parameters were mostly obtained by using home-made programs written in Mathematica 5.0 software for PC (copyright 1988–2003, Wolfram Research, Inc., Champaign, IL, USA).

2.5. X-ray Diffraction

Small-angle X-ray diffraction (SAXS) studies were conducted using Bruker NanoStar system (CuK α radiation, cross-coupled Goebel mirrors, three pinhole collimation system, MRI heating stage, and Vantec-2000 area detector). Wide-angle X-ray diffraction patterns were collected with the Bruker GADDS system (CuK α radiation, Goebel mirror, point beam collimator system, adapted Linkam heating stage, Vantec-2000 area detector). The samples

of the SC-LCE stripes in the monodomain alignment were measured in transmission mode. SAXS measurements were also performed on the smectogen crosslinker, 'C' sample, in the bulk, on cooling the sample from the isotropic phase to the crystalline phase.

2.6. Thermo-Mechanic and Elastic Measurements

The thermo-mechanic measurements of the monodomain SC-LCEs have been performed on a home-built computer-controlled setup comprising a temperature-controlled cell, a strain gauge, and a linear actuator for the stretching of the samples, which allowed for the simultaneous measurement of the temperature, force, and sample length, L(T). The variations of the SC-LCE length were recorded as a function of the temperature at different heating–cooling rates by using a constant-force feedback loop with a minimal force of about 1 mN. The same apparatus has been used to measure the elastic modulus by stretching the LCE film and simultaneously recording the applied stress.

3. Results and Discussion

3.1. Mesophase Properties of the Crosslinker 'C'

The new SC-LCEs were prepared by using a crosslinker, labelled 'C' (see Scheme 1 and Table 1), which shows a series of tilted smectic phases, as evidenced by the formation of schlieren-type optical textures in samples with one free surface (Figure 2). Similar POM images were observed in other smectic LCs [71].



Figure 2. Optical textures observed in liquid crystalline phases of crosslinker 'C' for sample with one free surface: (**A**) SmC at 185 °C, (**B**) SmI at 145 °C, and (**C**) SmJ at 130 °C. The width of the pictures is about 100 μ m.

Small-angle X-ray diffraction measurements allowed for the determination of the temperature dependence of the layer spacing, *d*, (Figure 3). Consistent with the tilted arrangement of the molecules within smectic layers, the *d* values were found to be considerably smaller than the estimated molecular length, $L \sim 52$ Å (Gaussian 98 with b3lyp/3–21 g) [72]. The observed increase in the layer spacing during the cooling might be attributed to the increase in the orientational order of the molecules, causing the growth of the effective molecular length in the mesophases. The phase sequence 'SmC–SmI–SmJ' has been observed in other smectic LCs and it corresponds to an increase in the ordering from a short range (SmC) to a long-range order (SmJ), which is also associated with the appearance of a 2D structure, typically a hexatic one, in the smectic phase [73].



Figure 3. Temperature dependence of the layer distance, d (Å), of the smectogen 'C'. In the inset, a scheme showing relation between the molecular length, L, of the most extended conformer and the layer spacing, d, for tilted smectic.

3.2. Mesophase and Structural Properties of the New SC LCEs

In this work, the smectogen 'C' was used as a crosslinker to prepare the new SC-LCEs in the polydomain and in the monodomain forms. The relative concentration of the crosslinker was chosen from 10% to 15%, according to the literature [18,52], with the aim of preparing mechanically robust LCEs. Relative concentrations of all chemical components of the new SC-LCEs are reported in Table 2. Despite the flexibility of the smectogen (see also its molecular structure in Figure 3), to guarantee the soft and elastic properties of the new SC-LCEs, a mixture of two standard mesogens, namely M4 and M11, was chosen. These two comonomers were widely studied by means of different techniques [16,18,53–55,74] and they were used to prepare a series of SC-LCEs showing the nematic and the Smectic A phases [16,18]. Based on previous studies [16,18,53,74], the relative concentration of the two co-monomers, M4 and M11, was selected to obtain a nematic SC-LCE (M4:M11 of 50/35) and a smectic A SC-LCE (M4:M11 of 20/70). As expected, these two different relative concentrations of the nematogen M4 and the smectogen M11 are optimal to obtain SC-LCEs with a single phase (nematic or smectic A) stable in a very wide temperature range. The mesomorphic behavior of the two samples, SC-LCE 1 and SC-LCE 2, as determined by DSC, are reported in Table 2. For each SC-LCEs, several samples were prepared in the form of polydomain and oriented monodomain stripes. A selection of the representative microphotographs obtained during POM observations on the monodomain smectic SC-LCE 2 sample is shown in Figure 4.



Figure 4. Microphotographs of the textures for **SC-LCE 2** elastomer: (**A**) texture at room temperature (27 °C); (**B**) texture of the SmA phase (60 °C); (**C**) texture of the SmA phase (110 °C); (**D**) texture of the Iso-SmA phase transition (118 °C). The width of the pictures is about 200 μ m.

The birefringence phenomenon due to the aligned smectic domains of the thin film is clearly observed by decreasing the temperature from the isotropic phase, confirming the occurrence of an ordered phase. It should be noted that the smectic A liquid crystalline elastomer in the form of monodomain stripes shows no defects in the morphology at a macroscopic level; in fact, the film appears completely transparent, thus confirming the very good homogeneous alignment.

The two SC-LCE monodomain stripes were investigated by X-ray diffraction. An X-ray diffraction pattern of an aligned **SC-LCE 1** (Figure 5A) taken at room temperature is typical for the nematic phase, where only broad diffuse signals are observed in small-angle and in the wide-angle regions. In the pattern of the **SC-LCE 2** (Figure 5B), a series of sharp commensurate signals is seen in small-angle range, while the high-angle signal, positioned at the orthogonal azimuthal direction with respect to small-angle signals, is similar to that observed for **SC-LCE 1**. Such a pattern is characteristic for a well-aligned lamellar structure showing no long-range positional correlations within the layers; thus, it is fully consistent with the smectic A phase assignment.



Figure 5. Typical X-ray diffraction patterns: (**A**) monodomain **SC-LCE 1** in the nematic phase at 25 °C; (**B**) monodomain **SC-LCE 2** in the Smectic A phase at 25 °C.

Figure 6 reports the evolution of small-angle XRD patterns as a function of the temperature for the monodomain SC-LCE 2 sample. In the smectic A phase, a small increase in the layer's thickness is observed (from 31.8 Å to 32.8 Å, with a positive thermal expansion coefficient of the order of 0.01 Å/K). It should be noted that the smectic layer periodicity is slightly larger than the length of the smectogen comonomer, M11, which is about 28.8 Å (see Figure 6). This feature can be explained by taking into account that the polymer backbone and the crosslinker 'C' also contributes to the average thickness of the smectic layers and influences the structure of the smectic domains. Moreover, the values of *d* of the SC-LCE 2 sample within the smectic A phase are similar to those obtained in similar LCE systems showing an SmA phase and containing high concentrations of M11, as a comonomer [18]. The transition from the SmA phase to the isotropic liquid, which is not usual in LCEs but is widely investigated in low-molecular weight liquid crystals [75,76], is not abrupt; instead, a smooth decrease in the diffraction signal's intensity is observed which is associated with its gradual broadening due to the continuous decrease in the correlation length of the positional order of the molecules in the isotropic liquid. As shown from the ²H NMR results, the SmA-Iso phase transition in liquid crystalline elastomers is of a weak first order, as observed in other similar systems [10-14]. The behavior of the



studied elastomer just above the SmA-Iso transition is similar to that observed in other LCEs with a direct transition from the isotropic to the smectic-A phase [10,12,16] and it is also coherent with the thermo-mechanic trend reported in the following paragraph.

Figure 6. Temperature evolution of small-angle XRD pattern for the monodomain **SC-LCE 2** sample. Diffracted intensity is coded with color (red to yellow to blue). On the right-top side, the optimized molecular structure of M11 (smectogen) showing its average length. On the right-bottom, layer spacing (d—black points) and diffraction signal width at its half-maximum (fwhm—red points) are reported as a function of temperature.

3.3. Thermo-Mechanic and Elastic Properties of New SC LCEs

The thermo-mechanic properties of the two SC-LCE samples are reported in Figure 7. Here, the normalized elongation L/L_0 of the SC-LCE 1 and SC-LCE 2 are reported as a function of the temperature. The temperature dependences of L/L_0 in the case of SC-LCE 1 is typical of side-chain LCEs with a nematic phase [16]. In this sample, the maximum elongation is about 43% at room temperature with respect to the length in the isotropic phase (L_0) , obtained with a load of 1 mN/mm^2 . In the case of the SC-LCE monodomain sample with the higher concentration of M11, namely the SC-LCE 2, the hermos-mechanic temperature trend shows a much smaller elongation with respect to nematic SC-LCE 1. Lowering the temperature from the isotropic phase, the elastomer film elongates in the direction of the local SmA phase director until it reaches ~15%. The maximum elongation is reached at about 118 °C, which is close to the temperature transition iso-SmA. Within the temperature range of the stability of the SmA phase, the elongation of the SC-LCE 2 slowly decreases, reaching the value of ~10% at room temperature. This behavior has been observed in several SC-LCE samples with a concentration of M11 higher than 50% [16], and in other LCEs with a smectic phase [11–14,17,77–80]. This thermo-mechanic behavior can be explained with the formation of layered local structures, whose layer spacing is gradually reduced by decreasing the temperature. The higher molecular packing lowers the mechanical response of the LCEs in the smectic phase, and the LCE stripes appear to be stiff [16]. Similarly to what was observed in other SmA LCEs [12], this shrinkage process is related to an increasing perfection of the smectic structure rearrangement of the network with a consequent realignment of both comonomers and polymer chains.



Figure 7. Thermo-mechanic measurements on the two monodomain SC-LCE samples: **SC-LCE 1** (black) and **SC-LCE 2** (red). Temperature transitions are indicated with dotted lines.

The elastic properties of the two SC-LCE samples were investigated at room temperature, as reported in Figure 8. The elastic modulus, E, was measured by applying a uniaxial mechanical stress parallel to the phase director, \vec{n} . In the case of the nematic **SC-LCE 1**, the typical rubber elastic response of nematic networks is observed and the value of 234 kPa is comparable to that measured in similar LCEs with the nematic phase [16]. In the **SC-LCE 2** sample, with a smectic A phase stable at room temperature, the value of the elastic modulus is about 2 MPa, which confirms the presence of a smectic structure and the typical enthalpy-elastic behavior ascribable to the long-range 1D order of the smectic layered structures [81]. If we compare the results obtained for these two SC-LCEs with those reported in the detailed investigation [16] of the thermo-mechanic and elastic properties of strongly crosslinked bimesogenic monodomain LCEs, with the controlled relative composition of nematogenic and smectogenic constituents, it is possible to conclude that they represent the two limiting cases of a typical soft nematic LCE (i.e., **SC-LCE 1** sample) and typical smectic A LCE (i.e., **SC-LCE 2** sample).



Figure 8. Elastic modulus of monodomain **SC-LCE 1** (**A**) and **SC-LCE 2** (**B**) samples measured at room temperature. Stretching and compression were applied at a controlled value of the force. Black curve corresponds to experimental data while red curves are linear fitting functions, y = Ex + b.

3.4. ²H NMR Studies of the Smectic SC LCE Sample

A further investigation was performed on the SC-LCE showing the smectic A phase, by means of ${}^{2}H$ NMR spectroscopy. To this aim, a monodomain SC-LCE 2 sample was prepared by following the same procedure described in Section 2.2, by using the nematic comonomer deuterium-labelled on the phenyl moiety, namely the nematogen M4-d₂ shown in Figure 2A. The deuterated sample, called SC-LCE 2 (D), was characterized by POM and DSC (see Table 2). As it can be noted, the temperature transition from the isotropic to the SmA phase was shifted to lower temperatures with respect to the not-labelled sample. This can be attributed to the deuteration substitution or to small differences in the loads applied during the second crosslinking step of the SC-LCE synthesis. A 'sandwichlike' sample formed by the square pieces of monodomain SC-LCE 2 (D) was prepared following the procedure reported in refs [53,74] to perform static ²H NMR measurements, as described in Section 2.4. A selection of the ${}^{2}H$ NMR spectra recorded on the cooling of the SC-LCE 2 (D) sample from 120 °C to 30 °C are reported in Figure 9. The ²H NMR spectra in the oriented phase are characterized by a well-defined doublet ascribable to the deuterons present on the phenyl ring of the nematogen M4, indicating the good alignment of the monodomain sample in its SmA phase. At temperatures above the isotropic-SmA transition temperature, the ²H NMR spectra are characterized by a single peak, which is typical of disordered (liquid-like) phases. In the vicinity of the mesophase transition, a very small quadrupolar splitting can be measured, which is the proof of a partial local orientation of the mesogens. In the case of SC-LCE showing the isotropic to nematic transition, this phenomenon was interpreted as the evidence of a critical phase transition [53–57] (or subcritical/critical/supercritical phase transition, depending on the crosslinker density). In the present SC-LCE system, the direct transition from the isotropic to SmA phase shows the typical features of a weak first order phase transition. This feature has been theoretically explained by a phenomenological model based on the modified Landau-de Gennes theory [79] and the existence of a weak first order transition is correlated with the relatively high crosslinker density (i.e., 10% in the presence case). The temperaturedependence of the quadrupolar splitting, obtained by fitting the spectral doublets with two Lorentzian functions, is shown in Figure 9.



Figure 9. On the left and on the right: selection of ²H NMR spectra of the deuterated **SC-LCE 2** (**D**) sample recorded on cooling from the isotropic phase to room temperature. Vertical lines on the two spectral stackplots (from 103 °C to 68 °C and from 65 °C to 32 °C) are eye guidelines. In the center: temperature dependence of the quadrupolar splitting, Δv_{quad} . The vertical dotted line indicates the temperature transition as observed by ²H NMR spectroscopy.

As observed on structurally similar liquid crystalline elastomers [53,74], the quantitative analysis of the temperature-dependence of ²H NMR quadrupolar splitting (Δv_{quad}) can be done by using Equation (3) [82,83], which expresses the relationship between the measured quadrupolar splitting of the deuterons on the aromatic fragment and the orientational order parameters, S_{zz} and Δ_{biax} (=S_{xx} – S_{yy}), referred to the biphenyl axes frame (with z parallel to the para axis):

$$\Delta\nu_q = \frac{3}{2}q_{aa}\left\{S_{zz}\left(\cos^2\varphi - \frac{1}{2}\sin^2\varphi - \frac{\eta}{6}\cos^2\varphi + \frac{\eta}{6} + \frac{\eta}{3}\sin^2\varphi\right) + \Delta_{biax}\left(\frac{1}{2}\sin^2\varphi + \frac{\eta}{6}\cos^2\varphi + \frac{\eta}{6}\right)\right\}$$
(3)

Here, η is 0.04 and q_{aa} is 185 kHz, according to the literature for aromatic deuterons [84]. The angle ϕ between the C-D bond and the *para* axis of the biphenyl fragment is fixed equal to 60°. The application of Equation (3), by assuming a fragment biaxiality of 0.05, as in analogous LCEs prepared with the comonomer M4-d₂ [75], gives rise to a local order parameter, S_{zz}, which ranges from 0 (far above the temperature transition) to ~0.52 at room temperature. It should be noticed that at temperatures lower than 55 °C, the spectra become much broader (see Figure 9), as it can also be observed from the trend of the half-height line-broadening (Δv_{fwhm}) reported in Figure 10B.



(A)

(B)

Figure 10. (A) ²H NMR spin–lattice relaxation times (T₁, ms) and spin–spin relaxation times (T₂, μ s) as a function of 1000/T(K) of the **SC LCE 2** (**D**) sample, deuterium labelled on the nematic comonomer, M4-d₂. (**B**) ²H NMR spectral line width ($\Delta \nu$, kHz), namely $\Delta \nu_{fwhm}$, as a function of temperature T (°C) of the **SC LCE 2** (**D**), deuterium labelled on the nematic comonomer, M4-d₂. Dashed vertical lines indicate the phase transition temperature.

Usually, the analysis of the temperature dependence of the ²H NMR spectra of LCEs requires quite sophisticated models [57], since they are inherently heterogeneous systems at the micro-scale level. The eventual local misalignment of the phase directors in the micro-domains, as well as the presence of a distribution of the local orientational order, cannot be excluded [53–57]. In the present case, additional information about the eventual heterogeneities can be obtained from the analysis of the temperature dependence of the half-height linewidths and both relaxation times, T_1 and T_2 .

Focusing on the spin–lattice relaxation times (T₁ versus 1000/T) reported in Figure 10A, we can observe an almost continuous trend at the isotropic to SmA transition and the occurrence of a minimum in the SmA phase, around T = 50–56 °C.

A similar temperature-dependence of the ²H NMR spin–lattice relaxation times has been observed in other side-chain LCEs containing deuterated comonomers linked to the polymer chain [53,75]. In particular, the values of T_1 in the mesophase formed by liquid

crystalline elastomers are in the range of 6–12 ms, as observed in other LCEs [53,75], and the presence of a minimum indicates that the characteristic correlation time, $\tau_{\rm C}$, associated with the dynamic processes active in the high frequency range of 10–100 MHz, passes from a fast to slow regime. This phenomenon is not observed in low-molecular weight LCs and this is due to the fact that once the mesogens are connected to the polymer chains, their overall reorientational motions, namely the spinning and tumbling processes, are much slower (i.e., the relative diffusion coefficients are two or three orders of magnitude smaller) than in the case that they are completely free to move [53].

The trend of the spin-spin relaxation times (T_2) versus the temperature, reported in Figure 10A, indicates a linear temperature-dependence in the isotropic phase, associated with a drop of the T_2 from 6.5 ms to ~300 µs at the transition between the isotropic and SmA phase. A sudden change in the slope of the T-dependence of T_2 is observed at the phase transition. Within the SmA phase, the values of T₂ decrease much more slowly, reaching the value of \sim 100 μ s at room temperature. A similar behavior and similar values of T₂ were obtained on the SC-LCEs prepared with deuterated M4 (and M11) [53,75]. Another interesting feature is related to the nature of the ²H NMR spectral linewidth (Figure 10B). In fact, the homogeneous contribution to the linewidth, Δv_{fwhm} , which can be calculated from the measured T₂, as $fwhm_{homo} = 1/(\pi T_2)$ [85–87], coincides with the ²H NMR spectral linewidth, evaluated from the half-height of the Lorentzian peaks. This finding can be interpreted in terms of the motional processes responsible for the measured ²H NMR spectral linewidth: the motions affecting the ²H NMR linewidth are in the extreme motional narrowing regime, as observed in other cases in LCEs prepared with deuterated comonomers [53,75]. Different phenomena have been found in LCEs deuterium-labelled on the crosslinker, whose molecular motions are usually much hindered due to the two links to the polymer chains [53,75].

4. Conclusions

In this paper, we are reporting a complete study of new side-chain liquid crystalline elastomers in the form of monodomain films, containing a new smectic crosslinker and two comonomers, a nematogen and a smectogen, in different relative concentrations. Two types of SC-LCE films were designed and characterized, showing a nematic or a smectic A phase stable in a wide temperature range. The mesomorphic and structural studies based on X-ray diffraction confirmed the good alignment and uniaxial orientation of the two SC-LCE systems, while the thermo-mechanic and thermo-elastic characterizations indicate that the two SC-LCE films have good properties to act as shape-memory materials for an application in the field of soft actuators. Detailed investigations were performed on the SC-LCE film showing a direct transition between the isotropic and the smectic A phase. All the experimental measurements confirm the nature of the weak first-order transition in agreement with the theoretical models describing the Iso-SmA transition in LCEs. The observed thermo-mechanic behavior could be interpreted as due to the formation of layered local structures, whose layer spacing is gradually reduced by decreasing the temperature, while the increasing perfection of the smectic structure lowers the mechanical response of the LCEs within the smectic phase. This process is associated with an increase in the orientational order within the SmA phase, as confirmed from ²H NMR spectroscopy. Both static and dynamic investigations based on the ²H NMR measurements indicate a relatively high orientational order of the nematic comonomer and the presence of dynamic motions passing from a fast to a slow regime within the SmA phase.

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