Criticality Controlled by Cross-Linking Density in Liquid Single-Crystal Elastomers

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A high-resolution calorimetry and deuteron-nuclear magnetic resonance study of a paranematic-nematic phase transition was performed on liquid single-crystal elastomers. We show that density variations of both rodlike and pointlike cross-links strongly affect the mean value and the dispersion of local mechanical fields. The system exhibits an inherent weakly disordered orientational state composed of regions with the temperature profile of the nematic order parameter ranging from first order to *supercritical*. On increasing the cross-linking density the predominantly first order thermodynamic response transforms into a predominantly *supercritical* one.

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Conventional side-chain liquid single-crystal elastomers (LSCEs) are composed of a polymer backbone to which mesogenic (liquid crystalline) molecules are attached as lateral monomers, with one free end. Elastic properties are imposed by replacing a certain percentage of mesogenic monomers with either mesogenic or nonmesogenic cross-linking molecules, which interconnect the polymer segments [1]. Chemical linking of liquid crystalline units to the polymer backbone is responsible for a thermomechanical response, i.e., a large spontaneous change in geometry with temperature. Because of this property, LSCEs are widely recognized as extremely promising soft materials for actuator, sensor, and artificial muscle applications [2]. Depending on the type of application, these materials need to be functionalized so that the temperature profile of the spontaneous elongation or contraction exhibits an on-off, intermediate or continuous type response. In the language of thermodynamics, this implies that the paranematic-nematic (PN-N) evolution of the order parameter, which is responsible for the thermomechanical effect must be in analogy with liquid-vapor transition in the vicinity of the critical point, i.e., either of the first order (*subcritical*) type, continuous (critical) type, or the *supercritical* type, respectively.

The PN-N transition critical behavior in LSCEs has so far eluded both experimental control as well as theoretical understanding. Some studies reported continuous or smooth supercritical-like evolution of the order parameter [3–7] and theoretical efforts to interpret this behavior revolved around the notion of a so-called internal mechanical field conjugate to the nematic order parameter [3,4,7–10]. This field can be created and locked into the system by performing the cross-linking with a strained sample [1]. Most experiments support the interpretation with internal fields exceeding the critical value above which the transition is lost and *supercritical* evolution sets in [4]. A recent nuclear magnetic resonance (NMR) study showed that *subcritical* behavior can be promoted by doping an LSCE network with conventional nematogen [11], whereas there has been no direct observation so far of an intrinsic *subcritical* behavior in LSCEs. NMR experiments also clearly detected a significant degree of disorder in the nematic order parameter [4,11] possibly related to the quenched random disorder [12,13], which was modeled by a distribution of transition temperatures [7,11].

It was predicted [14] that the internal mechanical field G, conjugate to the nematic order parameter, could be strongly affected by the type and density of cross-links. The increasing cross-linking density was recently reported to render the temperature profile of the order parameter less steep [5], therefore affecting the phase transition criticality. For cross-linking densities large enough the PN-N transition is expected to be pushed beyond a critical point. Although the cross-links are on the average randomly functionalized into the polymer backbone, local variations in their density may lead to quenched randomness, macroscopically manifested as a random-field induced smearing of criticality described by a distribution of internal mechanical fields [13]. So far no direct thermodynamic experiments were conducted, which would explore and confirm these predictions.

In this Letter, we demonstrate for the first time that the internal stress field G and, consequently, the critical properties of the paranematic-nematic transition in LSCEs can be controlled in a systematic way by varying a single chemical parameter, i.e., the concentration of the cross-linking molecules. This was achieved by performing high-resolution ac calorimetry as well as deuteron-NMR spectroscopy on samples of different cross-linking concentrations, prepared by the two-step Finkelmann procedure [1].

Side-chain elastomers with two kinds of cross-links were chosen, the rodlike 4-(undec-10-enyloxy)phenyl-4-(undec-10-enyloxy)benzoate (V6) and the trifunctional pointlike 1,3,5-tris(undec-10-enyloxy)cyclohexane (V3). Various concentrations were measured for both cross-links, namely $x = 0.075$, 0.105, 0.125, 0.15, 0.16 for V6 and

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$x = 0.066, 0.075, 0.105, 0.125$ for V3, where x denotes the coverage of active chain groups of the polymer backbone. In all samples the polymer was based on siloxane units and 4-but-3-enyl-benzoic acid 4-methoxy-phenyl ester was used as a mesogen.

The heat capacity (C_p) data were collected using a computerized ac calorimeter capable to operate in both ac and relaxation modes. A detailed description of this method can be found elsewhere [15,16]. The comparison between the data of the two modes allows the determination of the latent heat (L) in case of a first order transition. In ac runs the data were obtained upon cooling the samples of 20–30 mg from I phase, with scanning rates of 700–850 $\mathrm{mK\,h^{-1}}$. In the relaxation runs the ramping steps were 0.7 K.

The chemical structure of the two cross-links V6 and V3 is shown in Figs. 1(a) and 1(b), respectively. In Fig. 1(a) the C_p data are presented for several concentrations of the rodlike cross-link V6. For clarity the data sets of different concentrations have been shifted along the y axis. The latent heat is quite high at low concentrations, since data of the two modes differ significantly. Note that the latent heat is released in a few K broad coexistence range indicating a broad distribution of the internal mechanical fields. The latent heat gradually decreases with increasing cross-link concentration and vanishes at $x \sim 0.15$. This demonstrates that the first order transition line is terminated in an isolated critical point. In Fig. 1(b) the C_p data are shown for the pointlike V3 cross-link. In this case a rather small amount of latent heat could only be observed at low cross-link concentrations indicating that even at small cross-link densities, the V3 samples are already close to or above the critical point. The total enthalpy $\Delta H = L + \delta H$ (ΔH is obtained from the relaxation run and continuous part of the enthalpy δH is obtained from the ac run) and the latent heat L are shown in Table I for both V6 and V3 cross-links.

Temperature profiles of the first and second moments (M_1 and M_2) of d-NMR spectra of deuterated mesogenic molecules were recently proved to reliably distinguish between *supercritical* and *subcritical* behavior in LSCEs [11]. As shown in Ref. [11] the first and the second moment, respectively, of each of the doublet lines in the d-NMR spectrum are linearly related to the average nematic order parameter $[S]_{\mathrm{av}}$ and to the average squared order parameter $[S^2]_{\mathrm{av}}$, respectively, with $[\ldots]_{\mathrm{av}}$ denoting the average over the distribution of the nematic order parameter $w_S(S)$. In order to provide for d-NMR sensitivity the V6-cross-linked LSCE networks were doped with octyl-cyanobiphenyl (8CB), deuterated at the two α-positions in the hydrocarbon chain (8CB-αd_2). The concentrations of 8CB in d-NMR experiments was low enough not to alter the intrinsic thermodynamic behavior of the systems under study. This was checked by comparing heat capacity results on pure and doped samples. The doping and measurement procedures were described in Ref. [11].

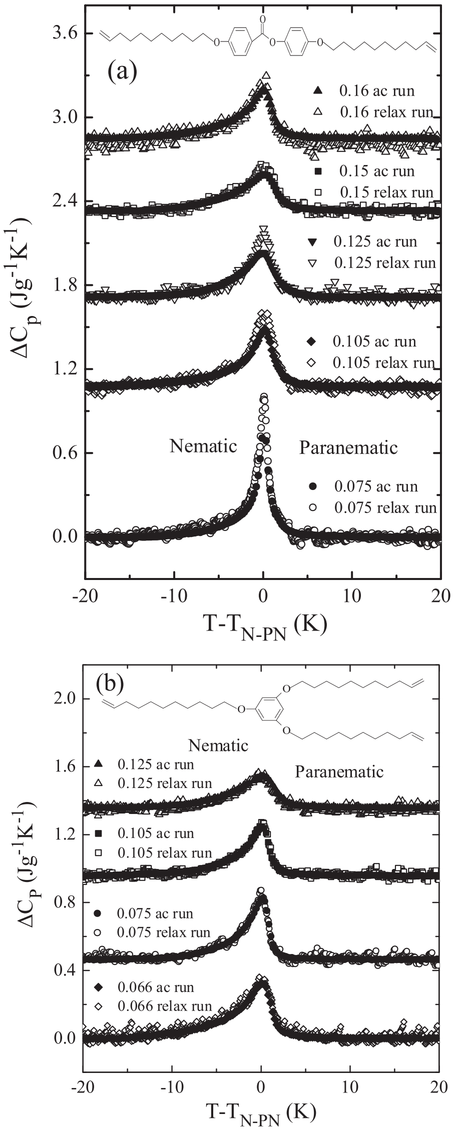

FIG. 1. (a) Temperature dependence of ac (solid symbols) and relaxation mode (open symbols) C_p data obtained for V6 concentrations. Circles stand for $x = 0.075$, rhombs for $x = 0.105$, down triangles for $x = 0.125$, squares for $x = 0.15$, and up triangles for $x = 0.16$ concentration. On the top the chemical formula of V6 cross-link is given. (b) Temperature dependence of ac (solid symbols) and relaxation mode (open symbols) C_p data obtained for V3 concentrations. Rhombs stand for $x = 0.066$, circles for $x = 0.075$, squares for $x = 0.105$, and up triangles for $x = 0.125$. On the top the chemical formula of V3 cross-link is given.

Figure 2(a) shows an example of a simultaneous fit of M_1 and M_2 values, extracted from the measured spectra of the $x = 0.105$ V6-cross-link sample, using Landau-de Gennes (LdG) modeling of free energy, $F = F_0 + A(T - T^*)S^2 + BS^3 + CS^4 - GS$, with distributed parameters T^* and G [11]. The main feature of the M_2

TABLE I. The total enthalpy ΔH and the latent heat L of the PN-N transition for all measured concentrations x of V6 and V3-cross-link elastomers. The errors for both ΔH and L, including the C_p data scattering and the error in the noncritical background estimation, are between 0.05–0.10 J g^{-1}.

x	ΔH_{V6} (Jg^{-1})	L_{V6} (Jg^{-1})	ΔH_{V3} (Jg^{-1})	L_{V3} (Jg^{-1})
0.066	-	-	1.70	0.10
0.075	2.65	0.45	1.50	0.05
0.105	2.45	0.30	1.40	0.0
0.125	1.70	0.20	1.20	0.0
0.15	1.65	0.05	···	···
0.16	1.60	0.00	···	···

temperature profile is the pronounced peak at temperatures where the slope of $M_1(T)$ is maximal. This is indicative of a distribution of the nematic order parameter, $w_S(S)$, which can be modeled by assuming Gaussian-distributions $w_T^*(T^*)$ and $w_G(G)$.

We observe that $w_G(G)$ plays a dominant role since it reproduces the temperature dependencies of M_1 and M_2 more accurately than the distribution of any other parameter in the LdG expansion, particularly at high temperatures in the paranematic phase, i.e., for small S, where the experimental error is relatively small [Fig. 2(b)].

The latent heat L can be alternatively determined via d-NMR, using the equation $L = \frac{1}{2\rho} a \int T_{\text{N-PN}}(S_+^2 - S_-^2) w_G(G) dG$, where S_+ and S_- are the order parameters of the nematic (N) and paranematic (PN) phase at $T_{\text{N-PN}} = T^* + 2B^2/(9AC) - 3CG/(AB)$, and ρ is the density of the LSCE. The above expression for the latent heat L is a generalization for inhomogeneous systems of the standard I-N latent heat expression [17]. The LdG parameters A, B, C, T^*, and G, can be determined from the M_1 and M_2 T dependencies. Very little variation of the mesogen-related fit parameters A, B, and C was detected across the set of investigated samples. The model with homogeneous $G = G_0$ and inhomogeneous T^* yields $G_0/G_C > 1$, i.e., a *supercritical* transition with $L = 0$, for $x = 0.105$ and $x = 0.125$. Here $G_C = -B^3/(27C^2)$ is the critical internal mechanical field. In contrast, the model with inhomogeneous G and homogeneous T^* gives rise to $L > 0$, in agreement with calorimetric results (see Table I). In addition to a better description of $M_2(T)$ profiles, the scenario of inhomogeneous G rather than T^* thus also yields a better match between the calorimetric data and the NMR results. Hence, we regard LSCEs as systems with coexisting *subcritical* and *supercritical* regions. Their ratio is set by parameters of the $w_G(G)$ distribution: the mean internal field value G_0 and its distribution width σ_G.

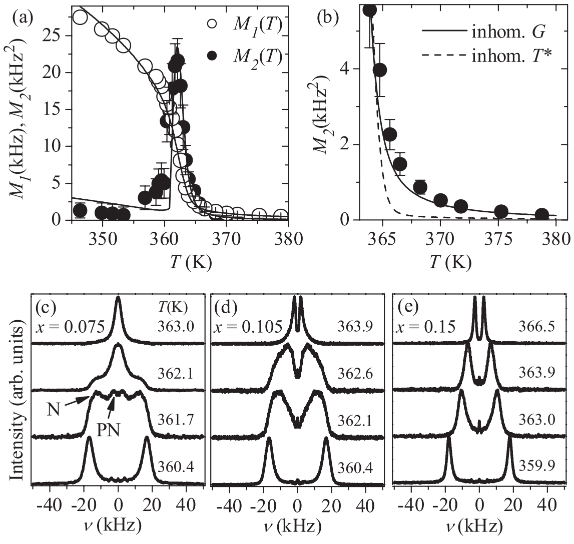

FIG. 2. Above: (a) Simultaneous fit of $M_1(T)$ and $M_2(T)$ values extracted from the measured spectra of the $x = 0.105$ V6-cross-link sample. (b) High-temperature close up of the $M_2(T)$ data from (a) fitted either with a distribution of G (solid line) or of T^* (dashed line). Below: A selection of NMR spectra for $x = 0.075$ (c), 0.105 (d) and 0.15 (e). Arrows denote spectral features attributed to paranematic (PN) and nematic (N) phases.

The selection of spectra for V6-cross-link compositions $x = 0.075$, 0.105 and 0.15 is shown in Figs. 2(c)–2(e), whereas the optimal $M_1(T)$ and $M_2(T)$ fitting parameters are collected in Table II. The trend towards supercriticality on increasing the cross-linking density, as observed in calorimetric measurements, is clearly confirmed. This is so since we identify clear coexistence of PN (inner doublet) and N (outer doublet) phase in the low cross-linking density limit ($x = 0.075$), whereas in the high cross-linking density limit ($x = 0.15$) a smooth evolution of S, characteristic for *supercritical* behavior, is observed. The intermediate $x = 0.105$ sample exhibits a significant linewidth broadening at the transition, which is again a demonstration of a phase coexistence, although without well resolved *PN* and *N* doublets. In general the $x = 0.075$ sample exhibits prevalently *subcritical* behavior, whereas in the $x = 0.15$ sample the behavior is prevalently *supercritical*, in agreement with calorimetry results, which within experimental error detects zero latent heat in the $x = 0.15$ sample. The ratio G_0/G_C of 1.15 in the $x = 0.105$ sample suggests that, on average, this system should be characterized as *supercritical*. Nevertheless, the popu-

TABLE II. Mean value G_0 and standard deviation σ_G of the distribution w_G and latent heat L as obtained from the optimal fits to NMR data for all measured concentrations x of the V6-cross-linked LSCEs.

x	G_0/G_c	σ_G/G_c	L_{NMR} (Jg^{-1})
0.075	0.4 ± 0.1	0.6 ± 0.3	0.51 ± 0.16
0.105	1.15 ± 0.15	0.7 ± 0.2	0.16 ± 0.06
0.125	1.45 ± 0.3	0.6 ± 0.2	0.105 ± 0.04
0.15	2.0 ± 0.2	0.8 ± 0.2	<0.01

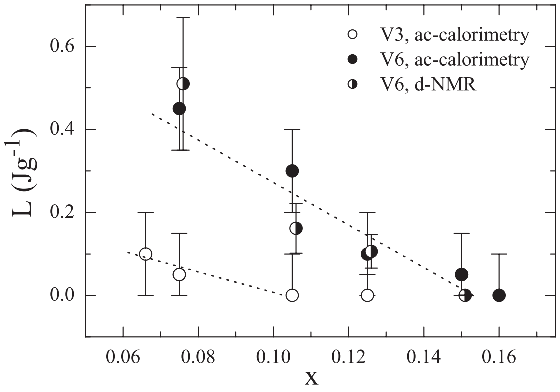

FIG. 3. The latent heat of PN-N transition for all the concentrations of the two cross-links V6 (solid circles) and V3 (open circles). Half-solid circles represent calculated latent heat based on the *d*-NMR data (see related text below).

lation of *subcritical* regions is substantial and gives rise to a nonzero latent heat detected by ac calorimetry.

The results of *d*-NMR and calorimetry measurements are summarized in the $L(x)$-plot of Fig. 3. The calorimetry and *d*-NMR points are obtained in completely independent experiments. In spite of the relatively large error bars that take into account the data scattering in heat capacity experiment and the cumulative errors in all LdG free fitting parameters in *d*-NMR experiments, the trend towards supercriticality is clearly evident, particularly so for the V6 sample. It is noteworthy that the two independent experimental methods yield consistent results. The observed trend is in accordance with the recent theoretical prediction which relates the magnitude of the internal field to the cross-linking density in homogeneous LSCEs [14]. The internal field G is a linear to quadratic function of the cross-linking density, depending on the value of parameters such as the ratio of the order parameters of the cross-linker and the mesogen, cross-linking history, and the shape of the cross-linker. Specifically, for rodlike shaped cross-linkers (V6) and the cross-linking history typical for the LSCE samples investigated in this study, the theoretically predicted [14] critical value of the internal mechanical field G_C is estimated at about $x = 0.105$. This value is in a good agreement with our calorimetric and NMR experimental data.

In conclusion, we demonstrate experimentally that the critical properties of the paranematic-nematic transition in LSCEs can be manipulated by varying the concentration of the cross-linking molecules. NMR and heat capacity experimental results reveal the existence of a random-field induced smearing of criticality, manifested in the coexistence of regions with transition behavior spanning from *subcritical* to *supercritical*. This heterogeneity manifests itself in a nonzero latent heat even if the system on the average can be categorized as supercritical. This behavior can be described by distributed internal mechanical fields. It is only the average thermodynamic response of an LSCE that can be characterized as *subcritical* or *supercritical*. The transition from the former to the latter could be induced by increasing the cross-linking density. This provides for a simple route to predetermine critical properties of LSCEs by controlling a single parameter during the synthesis of the network.

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