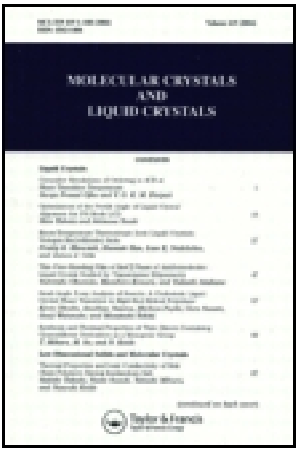

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Reviewing the Mechanisms That Affect the Critical Behaviour of Nematic Side-Chain and Main-Chain Elastomers

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Reviewing the Mechanisms That Affect the Critical Behaviour of Nematic Side-Chain and Main-Chain Elastomers

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A review of the mechanisms that influence the critical behaviour of the nematic monodomain main-chain and side-chain liquid-crystalline elastomers is presented. The crosslinking density, the applied mechanical load and the temperature at which the second crosslinking step takes place are examples of such mechanisms. This knowledge is a powerful tool when the tuning of the critical behaviour and, thus, of the thermo-mechanical response of the elastomers is needed.

Keywords Ac calorimetry; elastomers; heat capacity; latent heat; nematic

1. Introduction

Liquid-crystalline elastomers (LCEs) are materials gifted with interesting mechanical, optical and dielectric properties and they exhibit a great potential for applications [1–5]. Their properties have been extensively explored in terms of theory [6–11] and experiments [12–16]. The critical behaviour of LCEs is related to their thermo-mechanical response, i.e., most of the elongation or contraction occurs at the same temperature range where most of the transition enthalpy change is reported. A steep first order transition corresponds to an *on-off* response while a broad supercritical conversion to a rather *continuous* one.

Although initial studies considered LCEs as supercritical systems, the possibility of a critical point existence was not excluded [17–19]. Later on, experiments proved that below-critical (i.e., first order) behaviour can be also observed in nematic LCEs and that a critical point of water-vapor type exists for these materials [20]. The

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distinction and the clarification of the mechanisms that affect the LCEs critical behaviour have been achieved by recent systematic experimental thermal and structural studies [21–23]. In this paper these mechanisms are reviewed and compared, focusing on the effect of the temperature at which the second crosslinking step takes place.

2. Experimental Methods

High-resolution ac-calorimetry has been employed in order to produce accurate heat capacity temperature profiles $C_p(T)$ of the LCEs. In its principal *ac* mode of operation, an oscillating power of frequency ω is applied on the sample. This frequency is carefully chosen accounting for the elimination of temperature gradients within the sample as well as for the achievement of thermal equilibrium between the sample and the bath (i.e., the surrounding shield). Apart from the $C_p(T)$ data, the phase shift of the temperature oscillations as a function of temperature $\varphi(T)$ is also monitored. For second order (i.e., continuous) or supercritical anomalies $\varphi(T)$ evolves inversely proportional to C_p, i.e., it exhibits a dip at the temperature range where heat capacity shows a peak. On the contrary, in case of a first order (i.e., discontinuous) phase transition, the heat capacity has a non-zero imaginary part that induces an anomalous behaviour in $\varphi(T)$, typically observed in the shape of positive spikes. This is indicative of the presence of latent heat and the first order nature of the transition. Nevertheless, the *ac* mode is sensible only to the continuous changes of the enthalpy and it cannot measure the latent heat L, when the latter is present.

Our apparatus is modified in order to additionally operate in a *non-adiabatic* or *relaxation* mode. In this case the run is performed in small temperature steps, using a linearly-ramped change of the temperature. The *relaxation* mode senses both the continuous and the discontinuous change of enthalpy. By performing *ac* and *relaxation* runs and, subsequently, by comparing the $C_p(T)$ integrals of the two modes, the latent heat is quantitatively determined as follows:

$$L = \Delta H^{relaxation} - \Delta H^{ac} = \int \Delta C_{p,eff}(T)dT - \int \Delta C_p(T)dT$$

where ΔH^{ac} and $\Delta H^{relaxation}$ stand for the total enthalpy change sensed by the two modes. The use of ΔC_p (instead of C_p) defines the excess heat capacity sensitive to the continuous changes of enthalpy at the phase transition, whereas $C_{p,eff}$ stands for the artificially-high (so-called *effective*) heat capacity values that are observed for the first order transitions in the *relaxation* runs. Accordingly $\Delta C_{p,eff}$ stands for the excess heat capacity obtained by the *relaxation* runs. A more detailed description of ac calorimetry and its usefulness in the study of phase transitions and critical phenomena can be found elsewhere [24–26].

Monodomain nematic main-chain LCEs were prepared using the *two-step* procedure described in [27]. Sample quantities of 30–40 mg were placed in home-made cells made of high-purity silver. A very thin layer of teflon (~0.1 mm) was placed between the sample and the cell walls in order to prevent any unwanted stress, that could affect the phase transition behaviour. Sufficient free space was accounted for an unhampered change of the sample's dimensions. The heat capacity of the empty cell was subtracted in order to obtain the net C_p of the LCE.

3. Results and Discussion

As it has been demonstrated for monodomain side-chain and main-chain LCEs crosslinked in the nematic phase, the crosslinking density affects the critical behaviour along the paranematic (PN) to nematic (N) phase transition [21,22]. A critical point of water-vapour type is observed in the phase diagram as a function of the crosslinking density. Note that the term PN is used due to the non-zero order parameter that has been observed in nuclear magnetic resonance measurements for elastomers [21]. The evolution of the latent heat as a function of crosslinking density follows a rather linear dependence. The effect stands for side-chain LCEs with different types of crosslinkers, rod-like and tri-functional, as well as for main-chain LCEs with penta-functional crosslinkers. Hence, it emanates that this parameter holds universally for LCEs.

Recent experiments on monodomain main-chain LCEs explored the impact of the mechanical load for samples. An experimental study was performed on samples crosslinked under different mechanical loads, still both of them strong enough to orient the sample and produce a monodomain structure. High-resolution calorimetric data demonstrated that by increasing the load the critical behaviour of the PN-N phase transition shifts towards the supercritical regime [23].

In the *two-step* crosslinking method [27], the first crosslinking step is always performed by swelling all the components in toluene at high temperatures, corresponding to the isotropic phase. The second crosslinking step is used to lock-in the applied mechanical load. In our initial studies on the crosslinking density dependence of criticality, the second crosslinking step for all the samples was performed in the N phase [21,22]. Hence, the effect of the crosslinking temperature itself was still unknown. In order to discern the impact of this mechanism on the critical behaviour, the influence of the other mechanisms should be minimised. Hence, main-chain elastomer samples of identical crosslinking density (4% mol) and of the same applied mechanical load (91 kPa) were chosen for the investigation of this issue. The chemical formulae of the components for such main-chain elastomers can be found elsewhere [23].

Both *ac* and *relaxation* runs have been performed for samples that differ solely in the temperature of the second crosslinking step. The features of these samples are as follows: the LCE1 has been crosslinked at a significantly higher temperature where no nematic order exists, the LCE2 at the onset of the N phase, while the LCE3 at a temperature where the N phase is well-established. The heat capacity temperature profiles obtained by the two modes of operation can be seen for the three LCEs in Figure 1. A dramatic effect has been observed concerning the sharpness and the broadness of the C_p anomalies among the three samples. The deeper in the N phase the crosslinking is performed, the sharper and narrower the anomaly appears. The latent heat L for the LCE1 is slightly above the experimental resolution, it progressively increases for the LCE2 and then it jumps to markedly higher values for LCE3. It follows that a very different critical behaviour and, thus, thermomechanical response can be achieved by changing the temperature of the second crosslinking step for samples of identical composition. This dramatic difference is related to the fact that when one performs the crosslinking in lower temperature there is already some nematic order present. Hence, the remaining free chains orient along the N director and then become frozen-in the elastomer structure, something that cannot be achieved when the crosslinking takes place in the absence of nematic order.

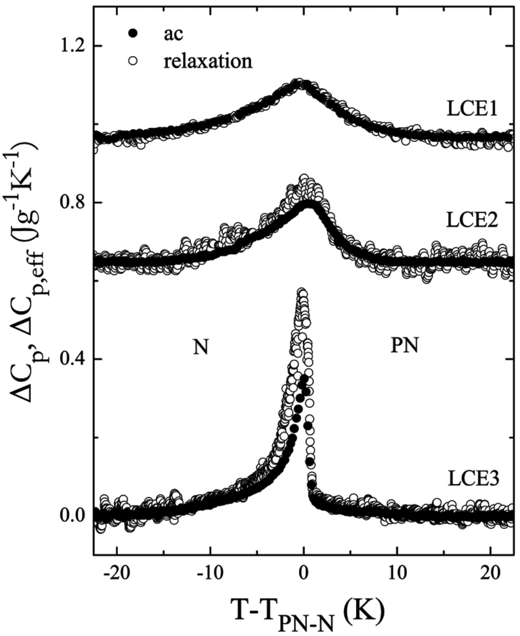

Figure 1. The heat capacity temperature profiles for main-chain elastomer samples crosslinked in different temperatures are presented, named as LCE1, LCE2 and LCE3 in the order of decreasing the crosslinking temperature. The data of *ac* runs are represented by solid symbols and the data of *relaxation* runs by open symbols. T_{PN-N} stands for the transition temperature defined from the *ac* runs and the datasets have been shifted along the y-axis for display reasons.

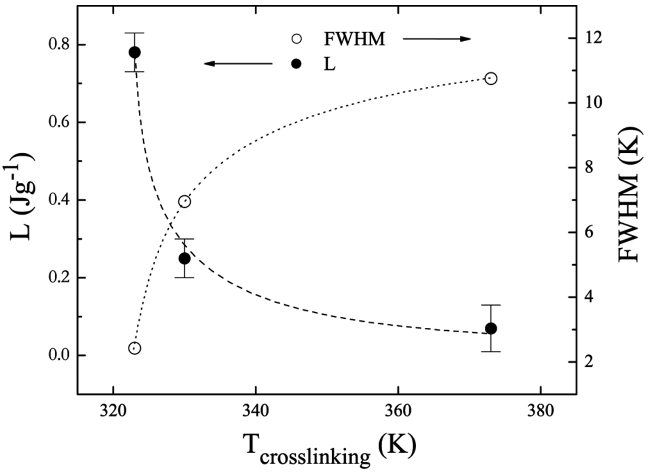

Figure 2. The dependence of L (solid symbols) and of FWHM (open symbols) as a function of $T_{crosslinking}$ is presented. A strong dependence (upon the crosslinking temperature) is realised for both parameters. The dashed and dotted lines serve as guides to the eye.

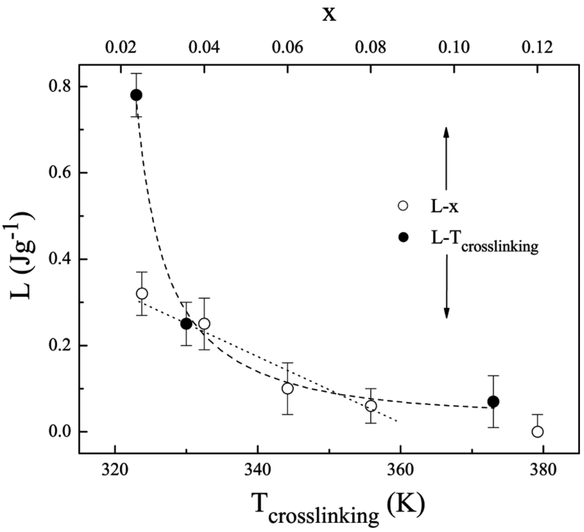

Figure 3. The latent heat L dependence on T$_{crosslinking}$ (solid symbols) and on crosslinking density × (open symbols) is displayed in a common plot. The stronger L-T$_{crosslinking}$ dependence with respect to the weaker L-x one can be visualised. The dashed and dotted lines serve as guides to the eye.

The impact of the crosslinking temperature can be pictured also in Figure 2 where the full-width at half-maximum (FWHM) of the heat capacity anomalies as well as the released latent heat are graphically represented as a function of crosslinking temperature. The dependence of both parameters upon the crosslinking temperature is strong. On the contrary, the latent heat dependence on the other mechanisms, such us the crosslinking density (exhibiting a rather linear dependence) and the applied mechanical load, is rather mild. This can be nicely visualised in Figure 3, where the dependence of latent heat versus crosslinking density as well as versus crosslinking temperature is plotted for monodomain nematic main-chain LCEs. Hence, the temperature of the second crosslinking step exhibits the most striking effect on the critical behaviour of main-chain liquid-crystalline elastomers. The reported similarities between side-chain and main-chain systems [22] suggest that the strong impact of the crosslinking temperature should also hold in side-chain liquid-crystalline elastomers.

4. Conclusions and Perspectives

A review of the mechanisms that affect the critical behaviour in the vicinity of PN-N phase transition of side-chain and main-chain liquid-crystalline elastomers has been presented, based on high-resolution calorimetric measurements. Although the crosslinking density and the applied mechanical load mildly affect the criticality, the temperature of performing the second crosslinking has a remarkably stronger effect. The understanding of the distinct role of these mechanisms serves as a guide for the synthesis of liquid-crystalline elastomers tuned towards *on-off* or *continuous* thermomechanical response according to the needs of applications.

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