

# Hystereses of volume changes in liquid single crystal elastomers swollen with low molecular weight liquid crystal

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## Abstract

The hystereses of volume changes in liquid single crystal elastomers (LSCEs) swollen with a low molecular weight liquid crystal (LMWLC), 5CB, are studied as a function of temperature. The swollen LSCE shows significant hystereses in the volume changes at temperatures  $T_{NI}$  and  $T_A$  during the processes on heating and on cooling, where the temperature  $T_{NI}$  is the apparent nematic-isotropic transition for outside LMWLC and  $T_A$  the nematic-isotropic transition for LMWLC inside the LSCE. No significant hysteresis at  $T_B$  however can be observed which is the nematic-isotropic phase transition temperature for equilibrium shape of the swollen LSCE (networks).

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## 1. Introduction

Liquid crystal elastomers (LCEs) have attracted much attention in recent years due to one possible candidate of artificial muscles because of their thermo-mechanical and electro-mechanical effects [1–8]. LCEs consist of the cross-linked polymer chain networks and the liquid crystalline ordering of side chain mesogenic groups. They can respond to thermal change but, unlike usual low molecular weight LC (LMWLC), cannot easily respond to electric fields as well as magnetic fields. Very recently, swollen LCEs with anisotropic solvents have been studied as the most promising material for artificial muscles operated by small intensity of electric fields due to the large electro-mechanical effect [4,5]. However swollen LCEs with LMWLC show a lot of strange features such as swollen dynamics, volume

changes on temperature, various and unknown phase transitions and electric field dependences which are quite different from those in dry LCEs [4,5]. The physical mechanisms for them however have not been well understood yet.

In order to understand the swelling mechanism due to phase transitions, therefore, we have been investigating the detailed dynamics for both monodomain and polydomain LCEs swollen with LMWLCs [5,9]. Volume change dynamics of swollen LCEs as a function of temperature show a variety of different transitions [4,5] as well as birefringence measurement of swollen liquid single crystal elastomer (LSCE) [9]. We have reported then that swollen LSCE shows significant volume changes and birefringence at temperature  $T_{NI}$ ,  $T_A$  and  $T_B$  which correspond to the phase transition temperatures of the nematic-isotropic one for outside LMWLC (5CB), that for inside LMWLC of the swollen LSCEs and for swollen LSCE, respectively. In this Letter we will report the hystereses of volume changes at those transition temperatures.

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## 2. Experimental

The LCE materials studied here were originally invented and developed by Finkelmann and co-workers [10,11]. The macroscopic behavior of these materials arises from the coupling between the elastic properties of the cross-linked siloxane (8%) and liquid crystalline degrees of freedom (polymer backbones and mesogenic units, 92%). The details of the preparation for the present LCE materials are as follows [12]. They are prepared by polymer analogue reaction of polymethyl-hydrogen-siloxane with an average degree of polymerization of about 60 and the monomeric mesogen 4-butenoxy-4-methoxybenzoic acid phenylester ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{O}-\text{phenyl}-\text{COO}-\text{phenyl}-\text{OCH}_3$ ) and the cross-linking agent ( $\text{H}_2=\text{CH}-\text{O}-(\text{Si}(\text{CH}_3)_2-\text{O})_{12}-\text{CH}=\text{CH}_2$ ). The cross-linker agent is the oligomeric poly (dimethylsiloxane) with terminal vinyl groups. The concentration of the cross-linking (about 8%) is related to the reactive vinyl groups. Except for the chemistry of the cross-linking agent, the procedure of the synthesis is described in [12]. The LSCE sample is obtained by mechanical stretching after gelation (after 3 h) to obtain the director orientation,  $\hat{n}$ , parallel to the stretching direction. The cross-linking reaction is completed with the sample stretched.

To measure the volume changes of LSCE during the variation of temperature, we prepared two types of rectangular LSCE sample with different bulk director orientations  $\hat{n}$  (Fig. 1). One is obtained by slicing parallel to  $\hat{n}$  (*planar* sample) and the other is obtained by slicing perpendicular to  $\hat{n}$  (*homeotropic* sample). The LSCE film we prepare is  $\sim 150 \mu\text{m}$  thick and has an area of  $\sim 1.0 \text{ mm} \times 0.5 \text{ mm}$ . To observe the volume changes of the swollen LSCE, sliced LSCE samples are embedded in a well known LMWLC, 4-*n*-pentyl-4-cyanobiphenyl (5CB) between two glass plates (Fig. 1 bottom). As described in a previous communication [4,5], after

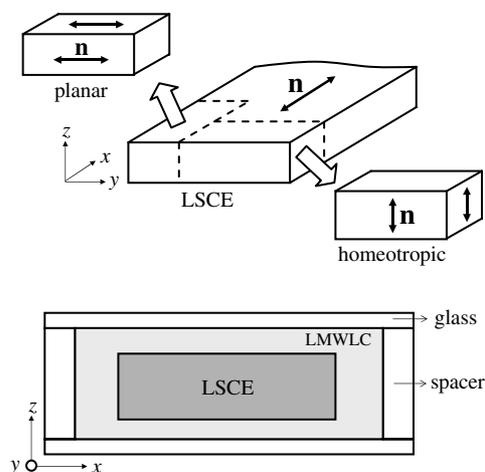


Fig. 1. Sample preparation for dry LSCE (top) and LSCE swollen with LMWLC (bottom).

swelling the LSCE (planar) sample thickness was increased with 1.8 times, i.e.  $\sim 270 \mu\text{m}$ . The anisotropy of LSCE was optically tested using crossed polarizers to confirm director orientation [5].

The sample cell was observed by a polarizing microscope (Nikon) equipped with a hot stage (Mettler Toledo FP90 Central Processor) as a temperature controller which can be simultaneously used for differential scanning calorimetry (DSC).

## 3. Results and discussion

To quantify the volume changes of dry LSCE, first we define the relative length changes parameter,  $\alpha_i$ , as the ratio of expansion/shrinkage length  $\ell_i(T)$  to the initial length  $\ell_i^0$ . Length measurements were made in the middle of each edge far from other edges.

Fig. 2 shows the relative length changes parallel ( $\hat{x}$ -direction) and perpendicular ( $\hat{y}$ - and  $\hat{z}$ -directions) to  $\hat{n}$  as a function of temperature.

Increasing temperature at the elevation rate of about 0.5 K/min, as expected, a dry LSCE monotonically shrinks parallel to  $\hat{n}$  (the  $\hat{x}$ -direction, Fig. 2a) with a somewhat faster decrease in the vicinity of  $T_c = 80^\circ\text{C}$ , the apparent nematic-isotropic phase transition temperature of the dry LSCE. It reaches its maximum shrinkage of about 67% just above  $T_c$ . According to the DSC measurement, a broad and small bump is observed at vicinity of  $T_c$ .

In contrast, the LSCE monotonically expands in direction perpendicular to  $\hat{n}$  (the  $\hat{y}$ - and  $\hat{z}$ -directions, Fig. 2b and c) on heating. Just above  $T_c$ , maximum expansions are about 120% in both the  $\hat{y}$ -direction and the  $\hat{z}$ -direction.

We note that there is a relatively small *lost* ( $\sim 2.5\%$ ) of length in  $\hat{y}$ -direction after cooling to room temperature. We can estimate that there is the *lost* of total volume changes after multiplying the length measurements. It is also important to note that no significant thermal hysteresis can be observed in the length changes of dry LSCE as well as DSC measurement.

The spontaneous change in length of LSCE along the ordered director orientation on changing the temperature has been expected by Küpfer and Finkelmann [11]. The orientational order of the mesogenic unit inside the LSCE determines the chain shape. On heating, chain shape changes that drive the shape changes of the cross-linked polymer chain network as a whole [3]. The expansion  $\parallel \hat{n}$  and the shrinkage  $\perp \hat{n}$  in lengths, as a dry LSCE sample is cooled below the nematic-isotropic transition temperature, indicate the anisotropic behavior of the cross-linked polymer chain network derived by the nematic order of the mesogenic prolate (elongated along  $\hat{n}$ ) side chains. In the nematic state, LSCE has ellipsoidal average shape of gyration of the cross-linked

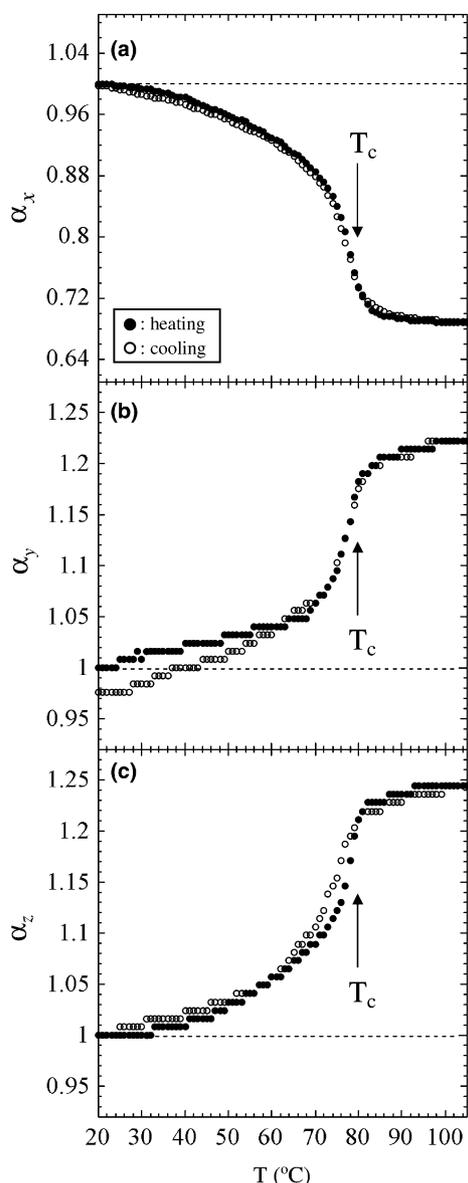


Fig. 2. Temperature dependence of the relative length changes,  $\alpha_i$ , for dry LSCE, (●) heating and (○) cooling. (a)  $\alpha_x \parallel \hat{n}$ , (b)  $\alpha_y \perp \hat{n}$  and (c)  $\alpha_z \perp \hat{n}$ . The drastic length changes are observed at  $T_c$  ( $\sim 80^\circ\text{C}$ ), the apparent nematic-isotropic phase transition temperature of the dry LSCE. No significant thermal hysteresis can be observed on cooling and heating. However, there was a small *lost* of the length in  $\hat{y}$ -direction after cooling process.

polymer chain aligned with the director, which radius of gyration  $R_{\parallel}$  along the director becomes larger than that perpendicular to the director,  $R_{\perp}$ . Just above the  $T_c$ , the nematic order becomes lost then the cross-linked polymer chains change to the isotropic spherical shape. In birefringence measurement [9], above  $T_c$ , LSCE was not perfectly isotropic because it still birefringence that is known as a typical feature of LSCE as being a consequence of ‘frozen-in’ nematic order in LSCE [13].

Fig. 3 presents the shape changes of dry LSCE during the heating and the cooling process for planar and ho-

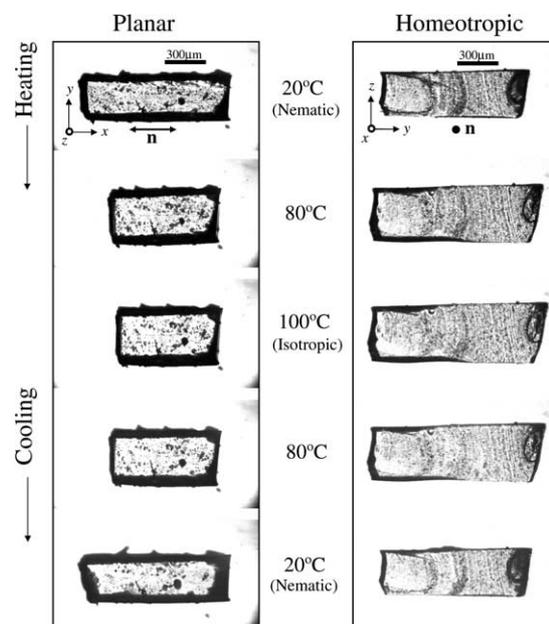


Fig. 3. Reversible process of dry LSCEs (*planar* and *homeotropic* samples) as a function of temperature. Temperature rate is  $\sim 0.5\text{ K/min}$ . As expected that the dimension of LSCE  $\parallel \hat{n}$  shrinks on heating and again expands on cooling. In contrast, the dimensions  $\perp \hat{n}$  expand on heating.

meotropic samples. As described above, *planar* sample shrinks  $\parallel \hat{n}$  ( $\hat{x}$ ) and expands  $\perp \hat{n}$  ( $\hat{y}$ ) on heating. In the *homeotropic* sample, where  $\hat{n}$  are perpendicular to the surfaces, its shapes expand on heating. After cooling, all dimensions show a reversible process.

Fig. 4 shows the relative length changes for LSCE swollen with LMWLC as a function of temperature. Here  $\alpha_i$  is defined as the ratio of expanded/shrunk length  $\ell_i(T)$  to the length of LSCE in the equilibrium swollen state. On heating, relatively small length changes of swollen LSCE are observed predominantly around  $T_{NI}$  of the LMWLC ( $T_{NI} \sim 34^\circ\text{C}$  for 5CB) and no remarkable changes at  $T_c$ . A sharp ( $\sim 2\%$ ) decrease in lengths is observed in the LSCE length parallel  $\hat{n}$  ( $\hat{x}$ ) at  $T_{NI}$  as well as perpendicular to  $\hat{n}$  ( $\sim 3\%$  and  $\sim 2\%$  in  $\hat{y}$ - and  $\hat{z}$ -direction respectively). A significant length variation is observed at  $T_A$ . Above  $T_B$ , the swollen LSCE shrinks ( $\sim 7\%$ ) in direction parallel to the director  $\hat{n}$  (the  $\hat{x}$ -direction, Fig. 4a) and expands ( $\sim 3\text{--}4\%$ ) in direction perpendicular to the director  $\hat{n}$  (the  $\hat{y}$ - and  $\hat{z}$ -directions, Fig. 4b and c).

In the previous communication [5], we have introduced a ‘guest-host’ scenario for explain the temperature dependence of the swollen LSCE. The effect of isotropic LMWLC solute (guests) is to shrink the network solvent (hosts) parallel to the director  $\hat{n}$  (Fig. 4a) and expand it slightly perpendicular to the director  $\hat{n}$  (Fig. 4b and c). When the guests are isotropic but the host is nematic ( $T_{NI}$ ), free LMWLCs are ejected from the host LSCE. At  $T_{NI} < T < T_A$ , the

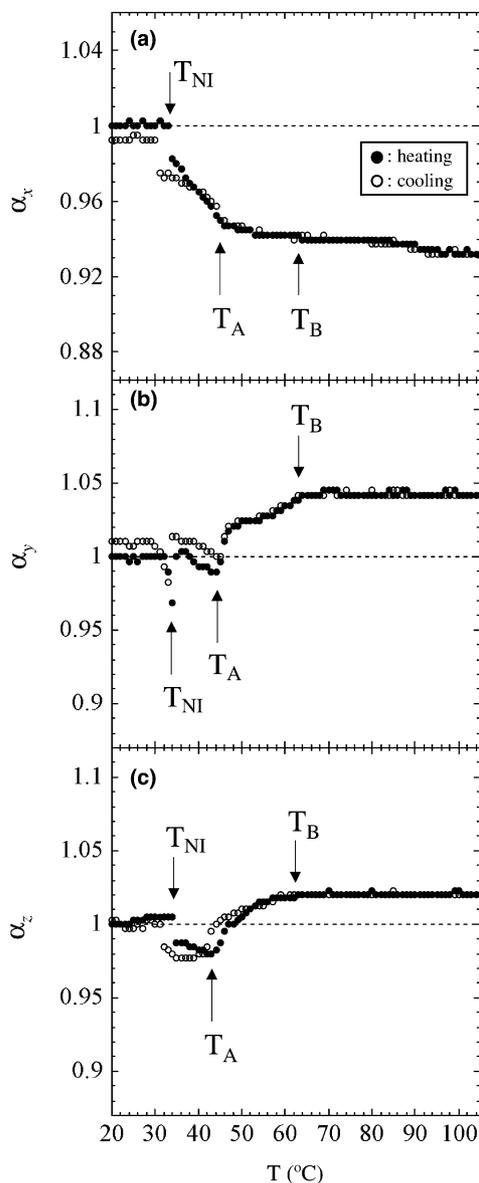


Fig. 4. Temperature dependence of the relative length changes of LSCE swollen with 5CB, (●) heating and (○) cooling. (a)  $\alpha_x \parallel \hat{n}$ , (b)  $\alpha_y \perp \hat{n}$  and (c)  $\alpha_z \perp \hat{n}$ . The length changes show the jumps at  $T_{NI}$  (the nematic-isotropic transition temperature of the LMWLCs) and relatively small length variations at  $T_A$ .

outside LMWLC guests are isotropic but the inside bound ones are still nematic, similarly to free-bound water relation in conventional gels [14]. This results in partial order of nematic for the inside LMWLC even above  $T_{NI}$ . When both guests and host are isotropic ( $T_A$ ), the previously expelled guests reenter the host LSCE. At  $T_B$ , the host has reached its equilibrium shape in the nematic state (just below  $T_{NI}$ ) and does not expand (in fact it shrinks with increasing temperature) more in LSCE.

According to the birefringence measurements [9] of swollen LSCE as a function of temperature, the evident intensity changes are observed at temperature  $T_c$  for dry

LSCE and  $T_{NI}$ ,  $T_A$  and  $T_B$  for swollen LSCE as well as in DSC measurements.

Fig. 5 shows the volume changes,  $V(T)/V_0 = \alpha_x \alpha_y \alpha_z$ , for dry (Fig. 5a) and swollen LSCEs (Fig. 5b) as a function of temperature.

In Fig. 5b, we note that there is a small but clear hysteresis in the transition temperature  $T_{NI}$  during the processes on heating and cooling. That is,  $T_{NI\uparrow}$  is about 34 °C on heating and about  $T_{NI\downarrow}$  is 32 °C on cooling. The difference  $\Delta T_{NI}$  is  $\sim 2$  °C, which was driven by thermal hysteresis of LMWLC solutes (5CB). According to DSC measurement, the thermal diagram for heating and cooling of 5CB shows the hysteresis where the freezing point is lower ( $\sim 2$ – $4$  °C) than its melting point. Similarly there is also a small hysteresis in the

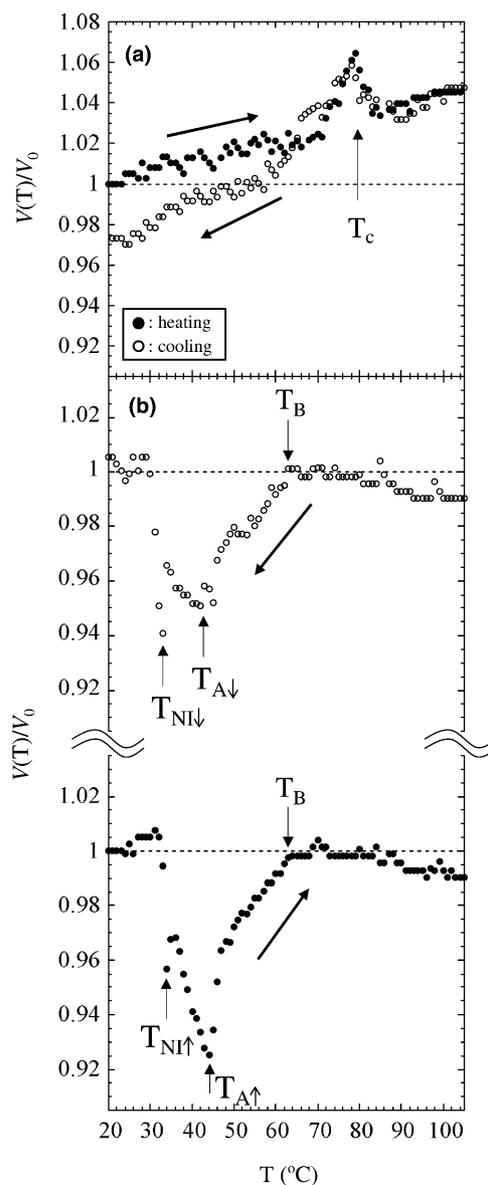


Fig. 5. Temperature dependence of the volume changes for dry LSCE (a) and swollen LSCE (b), (●) heating and (○) cooling.

transition temperature  $T_A$ , such as about  $T_{A\uparrow} = 44$  °C on heating and  $T_{N\downarrow} = 42$  °C on cooling, i.e.  $\Delta T_A = (T_{A\uparrow} - T_{A\downarrow}) \sim 2$  °C. On the contrary, no significant hysteresis can be observed at  $T_B$ . Depending on these hystereses, hystereses of volume changes can be clearly observed.

With increasing temperature, the volume of dry LSCE slightly increases almost linearly up to 80 °C with about a  $\sim 2\%$  increase at  $T_c$ . Just above  $T_c$ , about 2% volume decrease occurs when the tethered mesogenic side-chains become isotropic at the LSCE apparent nematic-isotropic transition and the volume change  $V(T)/V_0$  saturates at about 1.05. The net volume change between room temperature and  $\sim 105$  °C of the LSCE is only about 5% (Fig. 5a). In the present study, the volume of dry LSCE is the *lost* of about  $\sim 3\%$  after cooling to  $\sim 20$  °C. No significant trace of a net volume changes hysteresis can be observed in the dry LSCE.

In the swollen LSCE (Fig. 5b), a net volume decrease of  $\sim 4\%$  at  $T_{NI}$  on heating,  $\sim 4\%$  LMWLC is pushed out of the LSCE. The volume change of the swollen LSCE is opposite to that of bulk LMWLCs which shows the jump of the volume increase at  $T_{NI}$  [15]. Between  $T_{NI}$  and  $T_A$ , the volume sharply decreases an additional  $\sim 4\%$ , then rises back to its volume just below  $T_{NI}$ . For  $T > T_B$ , the volume decreases monotonically ( $\sim 1\%$ ) up to 105 °C. There are relatively small hystereses around  $T_{NI}$  and  $T_A$  ( $\sim 2$  °C), but no significant hysteresis at  $T_B$  as describe above. Due to these hystereses of transition temperatures, volume changes show rather big differences  $\sim 6\%$  at  $T_{N\downarrow}$  and  $\sim 3\%$  at  $T_{A\downarrow}$ . That is, for example, 6% more shrunk at  $T_{N\downarrow}$  and 3% more expanded at  $T_{A\downarrow}$  on cooling than on heating. Therefore it can be said that absorbing-in and pouring-out dynamics for LMWLC molecules at  $T_{NI}$  and  $T_A$  are quite different. This is probably due to the anisotropic interactions between polymer networks and LMWLC molecules.

#### 4. Conclusion

We discussed the volume changes of dry and swollen LSCE (in LMWLC, 5CB) as a function of temperature and found many interesting results.

- (1) The drastic net volume changes are observed at  $T_c$  ( $\sim 80$  °C), i. e. the apparent nematic-isotropic phase transition temperature of the dry LSCE. In the present experiment, we found a relatively small volume *lost* ( $\sim 3\%$ ) after the cooling process.
- (2) The dry LSCE shows no remarkable hysteresis of the volume changes. We suggest this is because the concentration of the cross-linker agent in the LSCE system studied here is rather small. The strong cross-linking may lead to hard elasticity, that is closer properties to solids. It is therefore expected that the clear hysteresis of volume changes hystereses may be observed for larger concentration of the cross-linker agent in the LSCE system.
- (3) In the swollen LSCE, the volume changes are observed at different temperature that indicated a variety of different transition. We explained these volume transitions by a ‘guest-host’ scenario in [5]. According to this idea we could interpret it as follows. When the guests (LMWLCs solute) are isotropic but the host is nematic ( $T_{NI} \sim 34$  °C), LMWLCs are ejected from the host LSCE. When both guests and host are isotropic ( $T_A$ ), the previously expelled guests reenter the host LSCE. At  $T_B$ , the host has reached its equilibrium shape.
- (4) A rather small hysteresis of the volume changes is observed around  $T_{NI}$ . We predicted that this hysteresis is due to the thermal hysteresis occurred in LMWLC (5CB) solute. No significant hysteresis at  $T_B$  can be observed.
- (5) There observe the heating and cooling dependences of the hystereses in the volume changes in the swollen LSCE. The dependence at  $T_A$  is different from that at  $T_{NI}$  which may suggest the anisotropic interactions between LMWLC molecules and LSCE networks.

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