

## **Swelling behavior of liquid crystal elastomers in low molecular weight liquid crystals**

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We experimentally investigated the swelling behavior of liquid crystal elastomers (LCEs) in two anisotropic solvents such as low molecular weight liquid crystals, 5CB and MBBA. The length of LCEs by swelling expanded more than 1.8 times of its initial length which depended on the director orientation. The volume change of swollen LCEs has been investigated as function of temperature and several phase transitions were observed in both optical and a differential scanning calorimetry measurements. Electro-mechanical effects of swollen LCEs were also investigated in detail and drastic decrease of the critical field for electro-mechanical effects, 1/4000 lower than dry LCEs, was obtained.

### **Introduction**

LCEs and gels presently attract much attention due to the volume and shape changing properties caused by several environmental factors, such as solvent composition, temperature, ionic strength, pH, light, electric field, etc. [1]. LCE materials studied here is invented and developed by Heino Finkelmann and co-workers at Freiburg University, Germany. The behavior of these materials arises from a coupling between the elastic properties of the polymer chains network and the liquid-crystalline ordering of monomeric mesogen groups as the side chains. The polymer chains network is formed by added the cross-linking agents to the system of polymer chains. There are two typical domains of LCEs depending on the director orientation (the director  $\mathbf{n}$  is defined as the average direction of the liquid-crystalline ordering of side chains consisting of mesogenic groups). One is the so-called polydomain, when the mesogenic groups are macroscopically disordered in the liquid crystalline state. The other is the so-called monodomain, when the mesogenic groups are macroscopically ordered in the liquid crystalline state.

Most of the earlier studies are concentrated on the swelling effect of gels in isotropic solvent, but few studies on the swelling effect of anisotropic material (i.e. LCEs) in anisotropic solvents (low molecular weight liquid crystals; LLCs). Swelling behavior of polymer network in liquid crystal (LC) solvents has been investigated in early study by some

researchers [2, 3]. They investigated temperature dependence of the degree of equilibrium swelling and phase the behavior of LC in the system consisting of LC and polymer network. In the present study, we investigated temperature dependence of volume changes of swollen LCEs in LLCs in detail.

Additionally, spontaneous shape change of oriented side chains LCEs (monodomain) at the nematic-isotropic phase transition is firstly found by P.E. Cladis [4]. She conclude that the result gave “proof of concept” to the idea of LCEs as artificial muscles when cooperative orientation effects of the side chains (i.e. the phase transition) extended beyond a typical mesh size of the cross-linked polymer network. To check her idea, in this study, we deal with shape change of swollen LCEs with LLCs under an alternating electric field as well as its temperature dependence.

## **Experimental**

### *Samples*

LCEs, both polydomain and monodomain, were synthesized by Heino Finkelmann group at Freiburg University in Germany. The samples are prepared by polymer analogue reaction of poly(methyl-hydrogen-siloxane) with an average degree of polymerization of about 60 and the monomeric mesogen 4-butenoxy-4'-methyloxy benzoid acid phenylester ( $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{O}-\text{phenyl}-\text{COO}-\text{phenyl}-\text{CH}_3$ ) 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 the terminal vinyl groups. The concentration of the cross-linking is 8% related to the reactive vinyl groups. Except the chemistry of the cross-linking agent the procedure of the synthesis is described in [8]. The monodomain sample is mechanically loaded after gelation (after 3 hours) to obtain the director orientation. Under these conditions the cross-linking reaction is completed. These anisotropy was optically tested to confirm director orientation using cross polarizers. In order to check the anisotropic swelling behavior of these samples, we prepared three types LCE samples with different geometries against bulk director orientations  $\mathbf{n}$ . One is obtained by slicing parallel to  $\mathbf{n}$ , another by slicing perpendicular to  $\mathbf{n}$  and the last one is a polydomain film. Hereafter we call these MONO1 (i.e. planar alignment film), MONO2 (homeotropic alignment film) and POL. All samples were sliced to thin film with the dimension of about 1.0 mm in height, 0.5 mm in width and 150  $\mu\text{m}$  in thickness. We here define the  $x$  and  $y$ -directions as parallel and perpendicular to  $\mathbf{n}$  on a plane respectively, and the  $z$ -direction is perpendicular to both  $\mathbf{n}$  and the plane.

Samples are embedded in the anisotropic swelling solvents. In this study we use two kind of LLCs, 4-n-phentyl-4'-cyanobiphenyl (5CB) and 4'-methoxy-benzilidene-4-buthyl-aniline (MBBA).

### Measurements

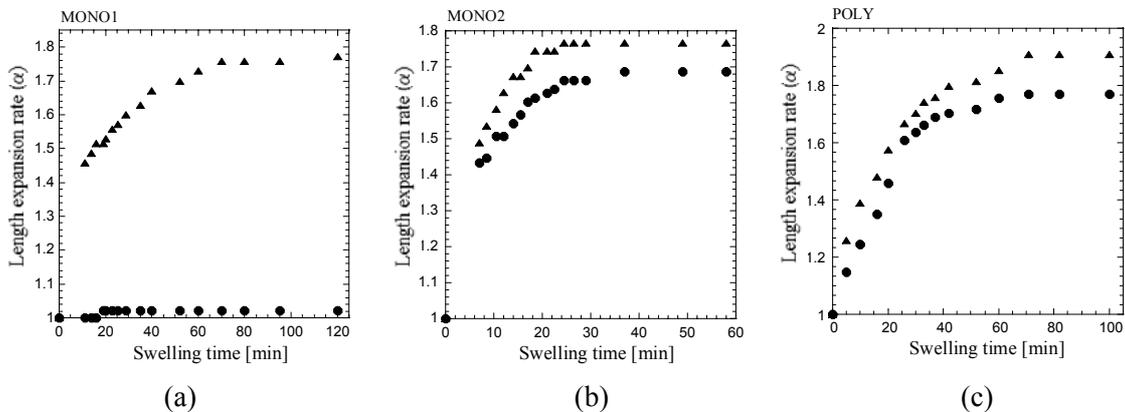
After sliced, LCE samples are embedded in anisotropic solvent between two SiO surface glass plates. The thickness was controlled by a polymer (Mylar) spacer of 350  $\mu\text{m}$ . The swelling behavior was observed in a polarizing microscope (Nikon) equipped with the hot stage (Mettler Teledo FP90 Central Processor) as temperature control which can simultaneously measure its thermal property (heat capacity) by a differential scanning calorimetry (DSC). The length expansion rate ( $\alpha_i$ ) by swelling is defined as the ratio of the swollen length  $l_i(t)$  to the initial length  $l_{i0}$  where  $i = x, y$  and  $z$ .

The electro-mechanical measurements were prepared by made an electro-optical cell consisting of two transparent ITO electrodes with very clean SiO surface that was treated to be homeotropic alignment for 5CB and MBBA and applied an alternating electric field perpendicularly to the electrodes [  $\mathbf{E} = (0,0, E_z)$  ] at fixed temperature.

### Results and discussion

#### Swelling effect

Fig. 1 shows the temporal dimension changes during swelling process of three types of slices in the low molecular weight liquid crystal 5CB. The time  $t = 0$  is a time just embedding LCE into 5CB. Fig. 1a shows variation the swelling rate of MONO1. In  $y$  direction (perpendicular to the director  $\mathbf{n}$ ) the length expansion rate  $\alpha_y$  ( $= l_y/l_{y0}$ ) increases exponentially in time and saturates with the values about 1.8 after 60 minutes. Contrast to this,  $\alpha_x$  is constant and no length change is observed. That is, in the direction parallel to the director orientation, no swelling occurs.



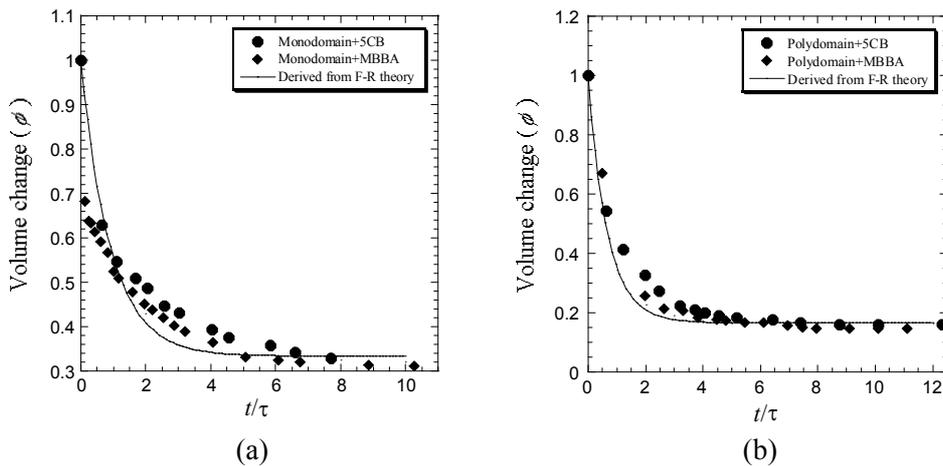
**Figure 1.** Temporal length changes during swelling process of MONO1(a), MONO2 (b) and POLY(c) in 5CB.(●) the length expansion rates in  $x$ -direction ( $\alpha_x$ ), (▲) the length expansion rates in  $y$ -directions ( $\alpha_y$ ). See text for detail.

In Fig.1b, the length changes of MONO2 by swelling are shown. Both  $\alpha_x$  and  $\alpha_y$  increase exponentially in time and saturate with the maximum value about  $1.8 \pm 0.1$ . In the film the director of LCE is homeotropic, there is no specific direction to expand in the plane. Thus it clearly shows that a volume expansion of monodomain LCE by swelling with 5CB indicates anisotropic property depending on directions to the director orientation in MONO-LCE.

Similar results to MONO2 can be observed for POLY as shown in Fig. 1c, that is, both  $\alpha_x$  and  $\alpha_y$  increase in time and saturates with about  $1.8 \pm 0.1$ . In the POLY case unlike with MONO2 the dimension  $l_z$  in  $z$  direction similarly expands in time to other direction with the rate 1.8. Thus a polydomain LCE equally expands in all directions as in isotropic gels. Similar behavior was observed for swelling MBBA replacing 5CB.

Fig. 2 shows the volume changes ( $\phi$ ) of monodomain and polydomain during swelling process in 5CB and MBBA. Where  $\phi$  is the averaged mol fraction for all directions as a first step of analysis though both LCEs and LLCs are anisotropic.  $\tau$  is the arbitrary relaxation time, experimentally obtained as, for monodomain: 15.57 min (5CB), 29.58 min (MBBA), and for polydomain: 8.10 min (5CB), 6.04 min (MBBA). The volume fraction is defined as the ratio of the LCE volumes in the swelling process  $V(t)$  and dry  $V_0$  that was calculated from the average length changes of the swollen LCE and dry LCE using a relation  $\phi = l_0^3/l(t)^3$ . The solid line in the figure is the result of theoretical calculation derived from the Flory-Rehner theory (isotropic gels) [9],

$$\tau (d\phi/dt) \cong (1/\phi^2) [\phi + \ln(1-\phi) + \chi\phi^2 + \nu\phi^{1/3}] \quad (1)$$



**Figure 2.** Volume changes during swelling process of monodomain and polydomain in 5CB and MBBA. The solid line indicates the theoretical curve (Eq. 1)

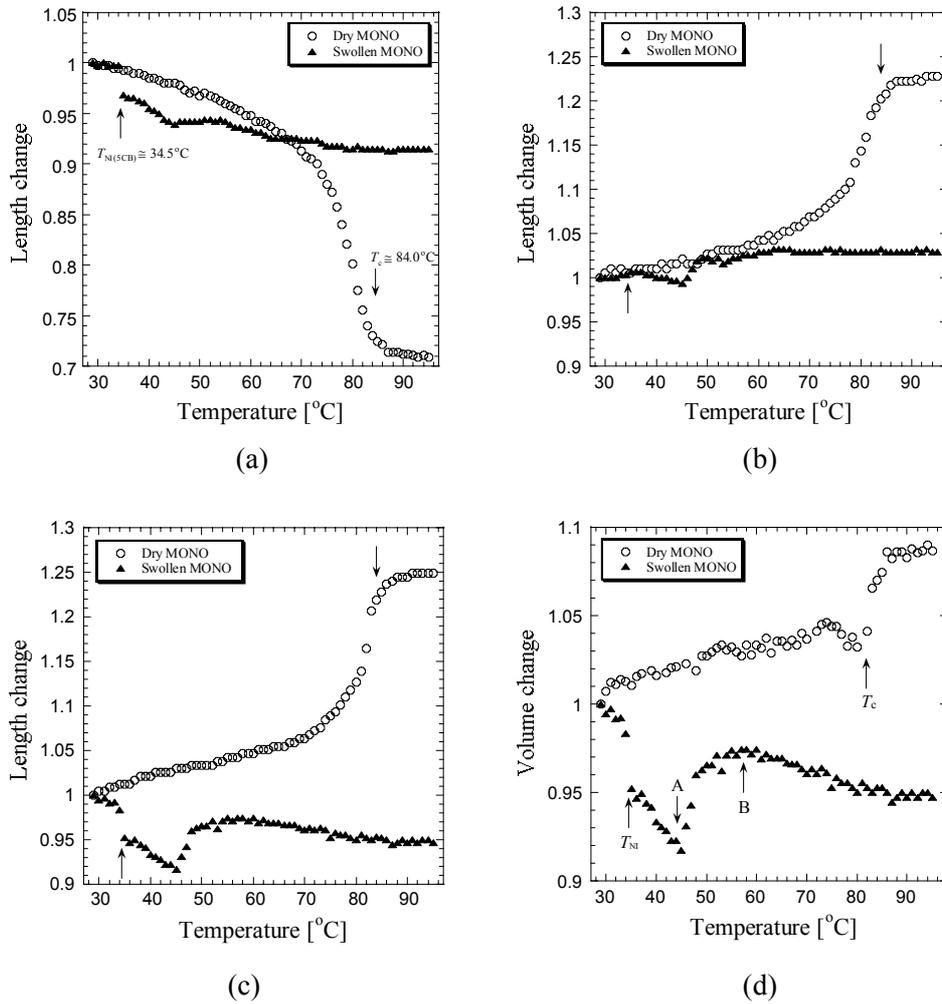
$\tau$  is a certain time constant.  $\chi$  is the Flory-Huggins interaction parameter.  $\nu = n_c v_c / V_0$ , where  $n_c$  and  $v_c$  are number of partial chain in the LCE and volume of one lattice element respectively.  $\phi$  decreases exponentially in time in both swollen monodomain LCE (Fig. 2a) and swollen polydomain LCE (Fig. 2b). The swelling process for both with 5CB and MBBA shows similar tendency. It may indicate a form for the free energy between the LCEs-5CB mixture and of the LCEs-MBBA mixture has no difference. There is some deviations of the experimental data from the theoretical curve (1) (solid line in Fig.2) based on isotropic gels. It is probably due to anisotropic properties of both LCEs and LLCs.

Temperature dependence of the dimension changes of dry and swollen monodomain samples are shown in Fig. 3. Here, the volume change  $V(T)$  is normalized by the LCE volumes in the equilibrium swollen state  $V_s$  at room temperature. The typical of length changes in  $x$ ,  $y$  and  $z$  directions are shown in Fig. 4a, b and c respectively. Increasing temperature, with rating of about  $0.7^\circ\text{C}/\text{sec}$ , dry monodomain gradually shrinks in  $x$ -direction (parallel to the director) by around  $T_c = 84^\circ\text{C}$  which is the nematic-isotropic phase transition temperature of dry LCE. In contrast, LCE stretches in  $y$  and  $z$ -directions (both are perpendicular to the director) when it is heated up. Close to  $T_c$ , drastic changes of lengths for all direction are observed owing to phase transition. The length change at  $T_c$  however in all direction disappeared for swollen LCE and no change is obtained as seen in Figs. 3a, b and c. Instead, for example with 5CB, a big change for all direction is observed at nematic-isotropic transition of 5CB ( $T_{\text{NI}} \cong 34.5^\circ\text{C}$ ).

In Fig. 3d, temperature dependence of the volume changes of monodomain LCE is shown. Increasing temperature, the volume changes in dry sample slightly increase almost linearly till  $80^\circ\text{C}$ . Close to  $T_c$ , a big expansion of the volume occurs owing to its nematic-isotropic transition and then saturates with the value about 1.08. It is known that the isotropic gels show no volume changes with increasing temperature. This result clearly indicates that the phase transition of LCE plays an important role in the temperature dependence of the volume changes in the monodomain sample.

On the other hand, drastic difference for swollen LCEs from dry samples can be observed. There exists almost no change of the length in  $x$ -direction in swollen LCE except a jump indicating its shrink at  $T_{\text{NI}}$  of 5CB and a very small dip at  $T_A \cong 45^\circ\text{C}$ . In  $y$ -direction, however, the length change is also small but different from in  $x$ -direction. There is no change at  $T_{\text{NI}}$  at all but small jump indicating elongation at  $T_A$ .

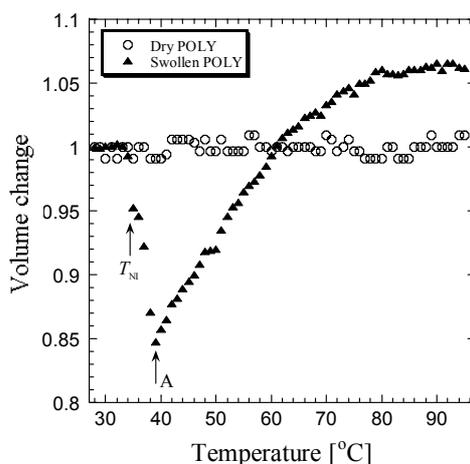
However, the length change of  $z$ -direction has a variety. There is a big jump in the change indicating shrink at  $T_{\text{NI}}$ , in temperature between  $T_{\text{NI}}$  and  $T_A$  considerable decrease, and around  $T_B$  again a jump indicating elongation. We do not yet understand these mechanisms for shrinking and elongating. Due to these anomalous changes in  $x$ ,  $y$  and  $z$ -directions, the volume change shows complicate temperature dependence as sown in Fig.3d. According to the DSC



**Figure 3.** Dependence of volume changes of dry and swollen monodomain LCEs on temperature (d). (a) typical length change in  $x$ -direction, (b) in  $y$ -direction, (c) in  $z$ -direction. See text for detail.

measurement, a sharp peak is observed at  $T_{NI}$  and two broad and small bumps are obtained at  $T_A$  and  $T_B$ . It therefore suggests that some phase transition may occur. At this moment, however, we do not determine what those phases are. To determine these unknown states more investigation is necessary.

Temperature dependence of the volume changes in polydomain LCE is shown in Fig.5. Unlike the case of dry monodomain sample, the volume change of a dry sample does not show any big change at  $T_c$  and the volume is constant over whole temperature range. It is similar to isotropic gels and therefore polydomain LCE could be an isotropic elastomer. A big volume change occurs however for swollen polydomain. Two big shrinks are observed at  $T_{NI}$  (5CB) ( $\cong 34.5^\circ\text{C}$ ) and  $T_A \cong 39.0^\circ\text{C}$ , heating further the volume increases by near  $T_c$



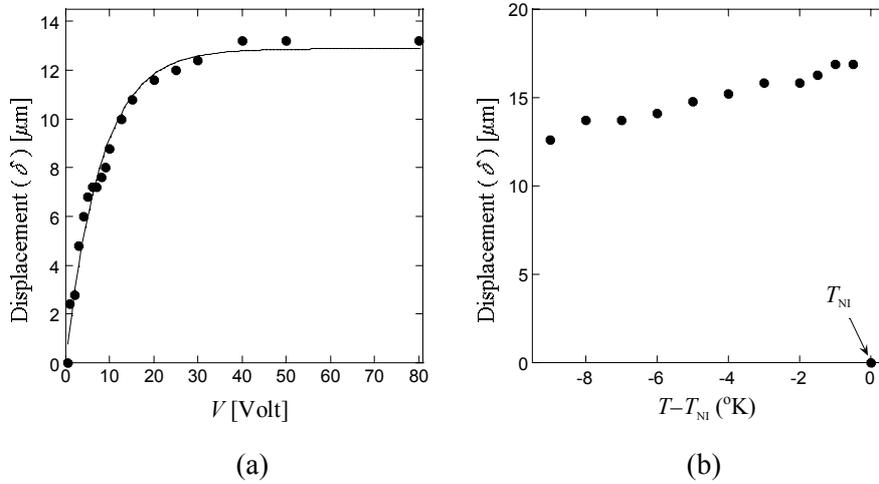
**Figure 4.** Dependence of volume changes of dry and swollen polydomain LCEs on temperature.

(nematic-isotropic transition temperature of LCE). According to DSC measurements, similar peak and bump are observed but more investigation will be required.

#### *Electro-mechanical effects*

Applying an electric field to the swollen LCEs with LLCs, LLC molecules will easily rearrange their orientation parallel to the fields. This electro-mechanical effect is mediated by mobile LLCs free to move in and out of the LCEs, the LC side chains could communicate with each other on length scales extending beyond a typical mesh size of the cross-linked polymer network, then a weak electric field, rather than temperature changes, could also trigger a spontaneous shape change. The investigations in shape changes of liquid-crystalline polymers by electric fields were reported by some researchers. In 1986, Zentel [6] reported his observation on shape variation of cross-linked liquid-crystalline polymers, which are swollen with nematic LLCs, by electric fields. Subsequently, Barnes et al. [6] reported their largest shape change of about 20% contraction of an elastomer swollen in 6CB (cyanohexyl-biphenyl) when both elastomer and 6CB were isotropic. Later, in 1994 Kishi et al. [7] reported the quantitative results of shape changes of swollen polydomain LCEs under acting a dc electric field,  $E = 0.3\text{MV/m}$ . Below we will described our resent results on this subject.

A sliced polydomain film (the thickness is  $20\ \mu\text{m}$ ) was embedded in 5CB (after swelling sample expands to about  $\sim 40\ \mu\text{m}$ ) to observe the electro-mechanical effects. Spontaneous shape changes were observed when an alternating electric field applied perpendicularly to the electrodes. In Fig. 5a, the variation of shape changes (determined by



**Figure 5.** Electro-mechanical effect of swollen polydomain LCE. Displacement  $\delta$  versus applied voltage ( $V$ ) at  $T = 26^\circ\text{C}$  is expressed in (a). (b) temperature dependence of  $\delta$  in field ( $f = 50\text{Hz}$ ,  $V = 50\text{V}$ ). See text for detail.

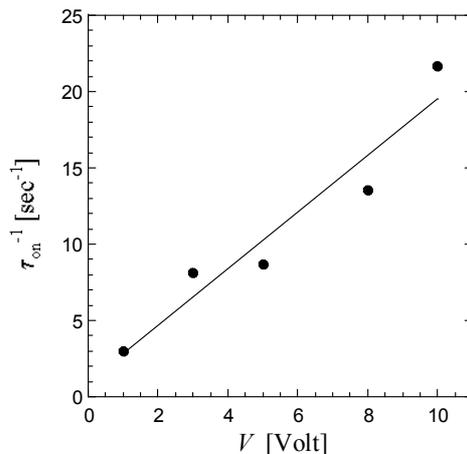
displacement  $\delta$  of sample shape from its equilibrium swollen state) from zero volts position is shown. Temperature is controlled at  $26^\circ\text{C}$ . The solid line is a fit to:

$$\delta(V) = 12.88 [1 - \exp(-V/7.97)] \quad (2)$$

Increasing voltage, with fixed frequency ( $f = 50\text{Hz}$ ), the shape change increases and saturates with the maximum value about  $13 \mu\text{m}$ . According to the fitting, saturation is about  $20\text{V}$ . The threshold voltage is about  $1.0\text{V}$ ,  $1/4000$  times smaller than that of dry LCE.

Fig. 5b shows temperature dependence of shape change in field ( $f = 50\text{Hz}$  and  $V = 50\text{V}$ ). As temperature is increased, shape change increases slightly. Maximum contraction is achieved at temperature just before the nematic-isotropic phase transition. In the isotropic phase, no displacements were observed.

The spontaneous shape changes of swollen LCEs are induced by the reorientation of anisotropic solvent molecules inside the LCE. This reorientation influences many mesogenic side chains cooperatively which in turn reorient to change the network shape making it thicker along  $\mathbf{E}$  and thinner perpendicular to  $\mathbf{E}$ . Since in the isotropic phase the reorientation of solvent molecules could not occur, it does not drive the shape change. Though 5CB is isotropic, the mesogenic side chains are still in nematic phase until about  $84^\circ\text{C}$  that it is still possible to contract but should be applied in high voltage ( $\sim 4000\text{V}$ ).



**Figure 6.** Voltage dependence of inverse relaxation time of swollen polydomain LCE when the field is switched “on”.

Fig. 6 shows applied voltage dependence of the relaxation times when the field is switched “on”. Increasing the voltage, the inverse of relaxation time increase monotonically (linear or probably square). Above 10 V, the image analysis could not be done, because of the limitation of our image software (NIH-Image). The response of spontaneous shape changes speed less than a second when the field is switched off.

### Summary and Conclusions

We have presented in this study the swelling behavior of LCEs with LLCs and found the following facts.

- (1) The swelling process may be described by the Flory-Rehner theory.
- (2) The complex volume changes of swollen LCEs are observed, which may indicate a variety of different phase transitions. However to determine them more detailed studies are necessary.
- (3) The threshold field for electro-mechanical effects has been lowered by swollen LCEs of which value becomes 1/4000 times smaller than that of dry LCEs.

Finally we would like to mention about the mechanism of the volume changes by temperature. Due to rubber elasticity of LCEs, elevating temperature dry LCEs may shrink with strong elasticity. Therefore if there are no other effects like phase transitions of solvents and LCEs, the volume of dry LCEs is basically either constant or monotonically shrinking. The experimental facts such as jumps of the volume change are due to the interaction changes between LCE networks and solvents LLCs by phase transitions. Also increasing elastic

constants, LCEs exclude absorbing LLCs. The detailed mechanisms are left in future works. We would like to thank Profs. P. Cladis, H. Finkelmann and H. R. Brand for supplying LCEs, many valuable suggestions and discussions.

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