# Elongation Behavior of a Main-Chain Smectic Liquid Crystalline Elastomer

**Ryohei Ishige, Kensuke Osada, Hirotaka Tagawa, Hiroko Niwano, Masatoshi Tokita,* and Junji Watanabe**

*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan*

*Received July 23, 2008; Revised Manuscript Received August 19, 2008*

ABSTRACT: We have prepared a polydomain smectic liquid crystalline (LC) elastomer by introducing 2 mol % 1,3,5-benzenetricarboxylic acid as a cross-linker into a main-chain BB-5 polyester. The elastomer designated as BB-5/E2 forms isotropic and smectic CA (SmCA) LC phases in order of decreasing temperature similarly to the un-cross-linked BB-5 polyester. BB-5/E2 in the isotropic liquid phase shows a typical rubberlike elasticity, whereas that in the SmCA phase shows a characteristic elongation behavior accompanying a polydomain−monodomain transition: the initial strain up to 100% orients the smectic layer with its normal parallel to the elongation direction, and the further elongation does not change the layer orientation and results in permanent deformation. The corresponding stress−strain curve shows a quasi-plateau, which is a so-called "soft stress plateau", over a wide strain region from 100% to 450%. These indicate that the polymer chains folded in the oriented smectic LC elastomer at a strain of 100% are stretched on further elongation and locked by the smectic layer order. At a strain of more than 300%, the SmCA phase begins to transform into a crystal because of the entropy reduction due to direct stress to the fully extended polymer chains.

## 1. Introduction

Elastomers are built up of cross-linked polymer chains and used in a large variety of products such as elastic foams, films, bands, and tires. They possess unique mechanical properties which set them apart from all other materials. Even if the constituent polymers are liquidlike with respect to the microscopic state of order and the local molecular dynamics, cross-links suppress an irreversible flow. Thus, the sample shape is stabilized by the cross-links, while high internal flexibility of the elastomers enables this shape to change with stress much smaller than that needed for a deformation of crystalline or glassy solids. In addition to these familiar properties, elastomers also possess unique thermoelastic effects usually known as the Gough−Joule effects: (1) an elastomer held in the stretched state and under a constant load contracts reversibly on heating, and (2) an elastomer gives out heat when stretched. These unique properties are connected with a very diverse configuration of the constituent polymer chains in liquidlike order.[1]

Liquid crystals are anisotropic fluids in which a liquidlike nature exists at least in one direction of space. A typical polymer forming the liquid crystalline (LC) phase is the main-chain type of polymer, in which the mesogenic moieties forming the LC structure are included in the backbone of the semiflexible polymer chain. For the elastomer based on this main-chain LC polymer, various configurations can produce thermoelastic properties characteristic of the conventional elastomers, and then physical properties of the elastomer are expected to be connected directly to the LC structures.[2−14] If highly oriented LC elastomers are prepared, large-strain thermal actuation would be expected along the *n*-director (or polymer chain direction) with a variation of the LC temperature[10] and further at the LC-to-isotropic transition,[11−14] leading to unique mechanical properties and potential applications as mechanical actuators.[2] Together with the conventional side-chain LC elastomers,[2] the main-chain LC elastomers also present challenging problems for fundamental science, soft elasticity related to LC structures, shape memory and pattern formation on liquid crystallization, unusual formation of LC structures, and so on.

In this work, we have prepared the polydomain LC elastomer based on a main-chain liquid crystalline BB-5 polyester. The elastomer forms the smectic CA (SmCA) phase identical to that of the BB-5 polyester, in which the tilt direction of the mesogenic group with respect to the layer normal is the same in every second layer but opposite between neighboring layers.[15−18] The main-chain smectic LC elastomer presents the unique stress−strain behavior associated with the smectic layer structure including its polydomain−monodomain transition followed by a quasi-plateau, a so-called "soft stress plateau".

## 2. Experimental Section

**2.1. Materials.** The cross-linked BB-5 polyester (BB-5/E2) was synthesized by melt transesterification of dimethyl *p*,*p*′-bibenzoate as a mesogenic moiety, pentanediol as the spacer, and trimethyl 1,3,5-benzenetricarboxylate (TMBTC) as the cross-linker (refer to Figure 1).[10] The TMBTC fraction was set at 2 mol % because elastomers with a TMBTC content of more and less than 2 mol % showed incomplete liquid crystal formation and considerable macroscopic flow, respectively.[10]

**2.2. Methods.** Differential scanning calorimetry (DSC) measurements were carried out with a Perkin-Elmer Pyris 1 DSC instrument at a scanning rate of 10 °C min$^{-1}$ under a flow of dry nitrogen. Stress−strain curves were measured for the specimens prepared by pressing the elastomer in the isotropic liquid state into an about 0.5 mm thickness film and cutting the film into stripes with 5 mm length and 1 mm width. The stress was measured on elongating the strip set between two clumps at a 1.0 mm distance at a constant rate of 0.1 mm min$^{-1}$ with a Seiko Instruments TMA/SS 150C. Wide-angle X-ray diffraction (WAXD) measurements were performed by using a Rigaku-Denki UltraX18 X-ray generator with Ni-filtered Cu Kα radiation (40 kV, 50 mA) and a flat imaging plate. For the WAXD measurements, the sample was held in a Rigaku-Denki hot-drawing attachment. The temperature was controlled by a Rigaku-Denki PTC-20A temperature controller with an accuracy of ±1 °C. For all these measurements, the specimens were first heated to 250 °C (sufficiently higher than the isotropization temperature) to remove the effects of thermal prehistory and then slowly cooled to the desired temperatures.

* To whom correspondence should be addressed. E-mail: mtokita@polymer.titech.ac.jp.

10.1021/ma801665a CCC: $40.75 
Published on Web 10/03/2008

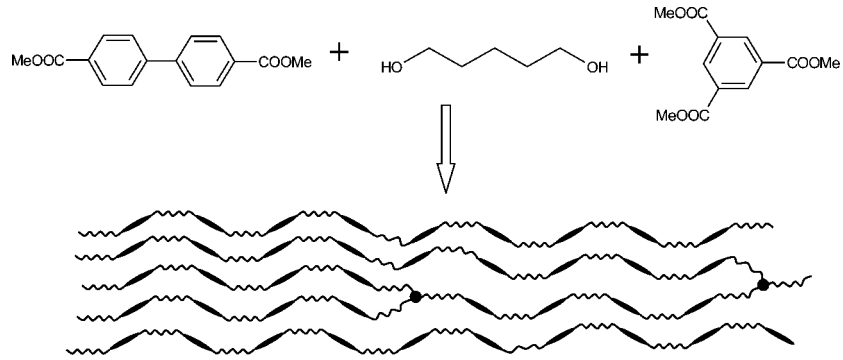


**Figure 1.** Chemical structures of reactants for polymerization and illustration of the resulting SmCA elastomer.

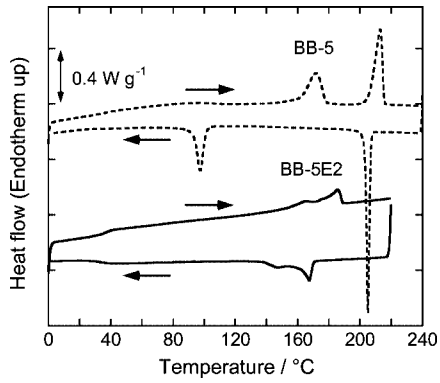


**Figure 2.** DSC thermograms of BB-5 (dashed line) and BB-5/E2 (solid line) measured at a rate of 20 °C $min^{-1}$.

**Table 1. Thermodynamic Data for the BB-5 Polyester and the BB-5/E2 Elastomer**

| | transition temperature/°C | | | transition enthalpy /kJ $mol^{-1}$ | |
|---|---|---|---|---|---|
| sample | $T_g$ | $T_m$ | $T_i$ | $\Delta H_m$ | $\Delta H_i$ |
| BB-5 | | 173 | 213 | 4.5 | 5.9 |
| BB-5E2 | 36 | | 182 | | 2.8 |

## 3. Results

**3.1. Transition Behavior of the Elastomer.** The DSC thermogram of the BB-5/E2 elastomer is shown in Figure 2. It includes the glass transition of the SmCA phase at around 40 °C and an SmCA−isotropic phase transition at around 182 and 167 °C, respectively, in heating and cooling cycles. No crystallization takes place at any condition. In Table 1, the thermodynamic data for BB-5/E2 are listed and compared with those of BB-5. The SmCA−isotropic transition temperature ($T_i$) is slightly lower than that observed for BB-5, and the isotropization enthalpy is approximately half that of BB-5. These observations suggest a smaller degree of liquid crystallinity and/or a less ordered smectic structure possibly due to random distribution cross-links in the elastomer[19] although the smectic layer spacing of 15.2 Å is the same as that of BB-5.[16,17]

**3.2. Elongation Behavior of the Elastomer in the Isotropic State.** First, we refer to the stress−strain behavior of the isotropic BB-5/E2 elastomer. Figure 3a shows a typical stress−strain curve observed at 205 °C on loading and unloading processes. The elastomer undergoes large and reversible rubberlike deformation as expected for the conventional elastomer.

When the isotropic elastomer is highly elongated, the isotropic phase transforms into the SmCA phase. This strain-induced phase transformation is detected clearly by the X-ray diffraction pattern. Figure 4a shows the X-ray pattern taken for unstrained BB-5/E2 at 205 °C. It includes only a broad halo ring characteristic of the isotropic melt. On the other hand, the same

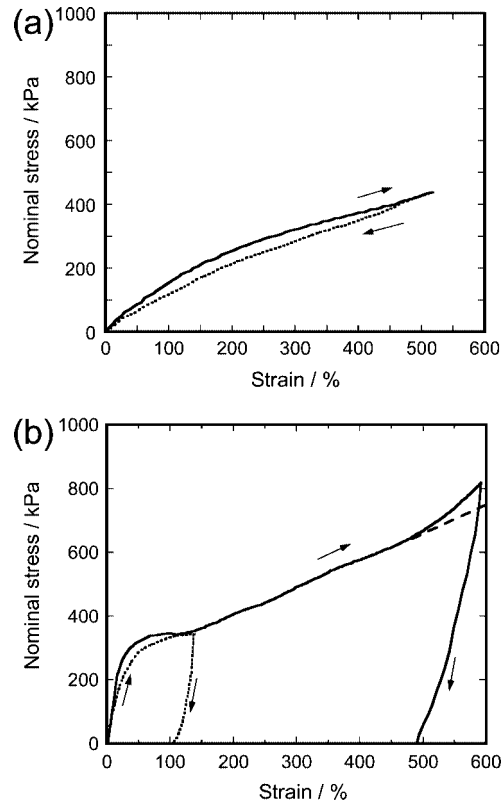


**Figure 3.** Stress−strain curves of BB-5/E2 on loading (solid line) and unloading (dotted line) (a) in the isotropic state at 205 °C and (b) in the SmCA state at 140 °C. In (b), stress−strain curves on unloading from the strains of 130% and 580% are also shown.

sample elongated up to a strain ($\varepsilon$) of 175% at the same temperature shows the pattern typical for the SmCA structure in Figure 4b. On heating, this diffraction pattern changes to the original one; i.e., the strain-induced SmCA phase transforms to the isotropic liquid. Figure 5 shows $T_i$ thus corrected on heating at a constant strain. $T_i$, which is 182 °C for the unstrained initial sample, increases linearly with the applied strain.

**3.3. Elongation Behavior of the Elastomer in the SmCA State.** In the SmCA phase, the elongation behavior completely differs from that of the isotropic phase. A typical stress−strain curve observed at 140 °C is shown in Figure 3b. A linear stress−strain relation at the initial stage up to $\varepsilon = 30\%$ is followed by a sudden decrease in the slope of the curve in the strain region of $\varepsilon = 30-100\%$. Then the slope becomes constant over the strain region up to $\varepsilon = 450\%$. After passage through this wide quasi-plateau region, the stress increases again with an increase of the strain before breaking at $\varepsilon = 500-600\%$. Consequently, the stress−strain relation can be divided into the

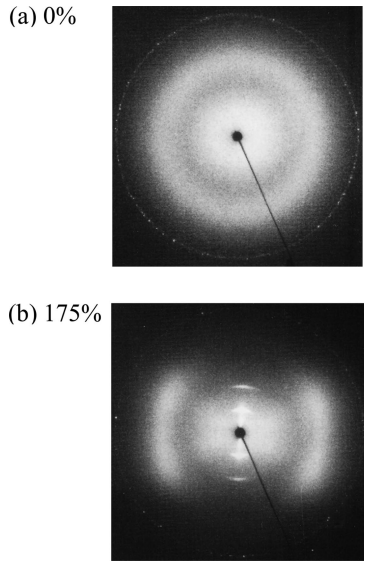


**Figure 4.** WAXD patterns of BB-5/E2 elongated in the isotropic liquid state at 205 °C at strains of (a) 0% (original) and (b) 175%. The elongation is in the vertical direction.

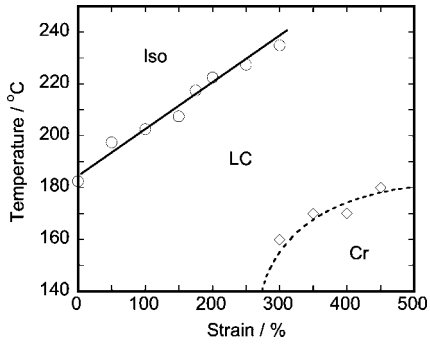


**Figure 5.** Isotropic to SmCA (open circles) and SmCA to crystal (closed circles) transition temperatures of BB-5/E2 plotted as a function of strain. Lines are to guides to the eye.

following four parts: regions I ($\varepsilon = 0-30\%$), II ($\varepsilon = 30-100\%$), III ($\varepsilon = 100-450\%$), and IV ($\varepsilon = 450\%$ and above). On unloading especially from the quasi-plateau region III, almost all of the strain remains. This deformed elastomer can recover its original shape only when it is heated to the isotropic liquid state.

Through these four strain regions, the SmCA structure is highly oriented. Parts a−d of Figure 6 show typical X-ray diffraction patterns taken for the samples elongated at various strains at 140 °C. Here, the sample was elongated successively to $\varepsilon = 450\%$ at 20% intervals and kept at each strain for 10 min to measure the X-ray patterns. The unstrained sample ($\varepsilon = 0\%$) shows two ring-shaped reflections, the inner sharp ring attributable to the smectic layer ordering and the outer diffuse halo to liquidlike association of the mesogens within a layer (see Figure 6a). On stretching the sample, the intensity of the inner layer reflection grows near the meridian (the elongation direction), and at $\varepsilon = 50\%$ the reflection maximum locates definitely on the meridian (see Figure 6b), showing the orientation of smectic layers with its layer normal parallel to the stretching direction. Such an orientation of the SmCA structure is completed at $\varepsilon = 100\%$, as found in Figure 6c where the layer reflection lies on the meridional line and the outer halo shows four maxima above and below the equator.[16,17] On further elongation up to $\varepsilon = 500\%$ before breaking, the X-ray pattern is not altered essentially (see Figure 6d). This orientation behavior of the smectic layer is totally surveyed from Figure 7,

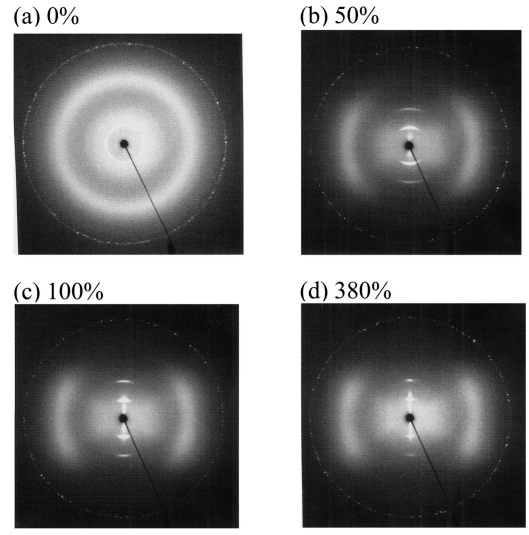


**Figure 6.** WAXD patterns of BB-5/E2 elongated at 140 °C at strains of (a) 0% (original), (b) 50%, (c) 100%, and (d) 380%. The elongation is in the vertical direction.

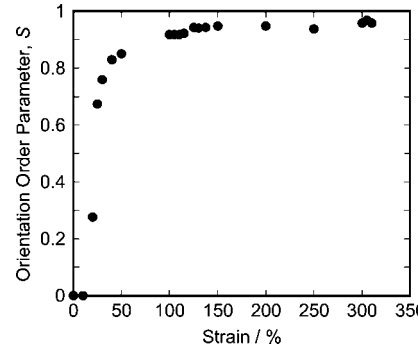


**Figure 7.** Dependence of the layer orientation parameter of the SmCA liquid crystal upon the applied strain for BB-5/E2. The data were collected from the X-ray patterns taken for the elastomer elongated at 140 °C.

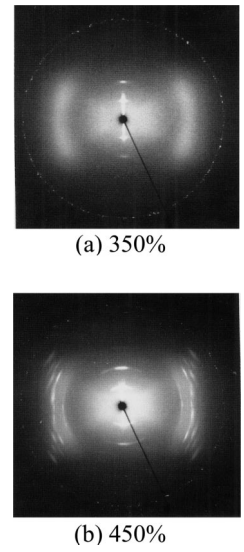


**Figure 8.** WAXD patterns of BB-5/E2 elongated at 180 °C with strains of (a) 350% and (b) 450%. The elongation is in the vertical direction.

where the orientational order parameter of the smectic layer, $S$, which is calculated from azimuthal scans on the layer reflections by the Hermans method,[20,21] is plotted against the applied strain.

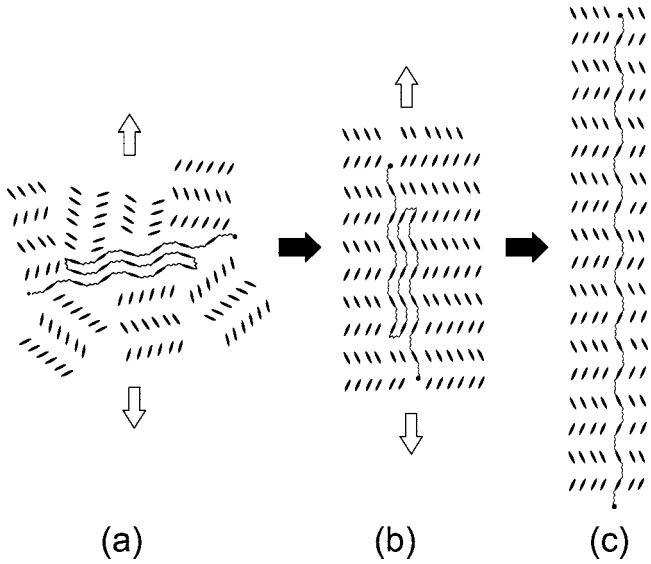


**Figure 9.** Schematic illustration of the structural change on elongation of BB-5/E2 in the SmCA phase. The smectic layers randomly placed in (a) are well oriented by the initial elongation stage at strains up to 100% (see (b)) although the chains are folded. Subsequent elongation up to 380% unfolds the folded polymer chains without changing the layer orientation as in (c).

The high orientation of the smectic layers with $S = 0.96$ has already been achieved at $\varepsilon = 100\%$, and its orientation is sustained with a further increase in strain.

Strain-induced crystallization of the SmCA elastomer has been observed at high strains by the X-ray diffraction patterns including several sharp reflections instead of the outer halos characteristic of the SmCA liquid crystal (see Figure 8). This crystallization seems to relate to the significant increase of the slope in the final region IV in the stress−strain curve, which may be attributed to stress starting to work directly on the extended chains, which can induce the crystallization. On heating the crystallized sample at the strain, the sharp reflections turn into the halos. By this change in the X-ray diffraction pattern, we determined the melting temperature of the crystal ($T_m$) and plotted it against the applied strain in Figure 5. $T_m$ decreases with decreasing strain, and no crystallization takes place with strains less than 300% and at temperatures lower than 160 °C within the experimental time scale in this work (1 h). For example, the elastomer elongated at $\varepsilon = 250\%$ and at 155 °C takes 1 day to show the diffraction pattern characteristic of the crystal phase.

## 4. Discussion

Overall structural changes on elongation of the SmCA elastomer are schematically illustrated in Figure 9. Two distinct features should be noted.

The first feature relates to the smectic layer orientation. As observed in the X-ray pattern in Figure 6b, the layer normal, i.e., the polymer chain axis, is aligned parallel to the elongation direction. Such a parallel orientation looks like ordinal, but differs completely from the perpendicular orientation in the uncross-linked SmCA phase, which has been explained both by mutual slips of chain-folded lamellae and by liquidlike flow of the polymers within a smectic layer.[21,22] In the cross-linked SmCA, the ends of the polymer are fixed at the cross-linking points. The elongation force on the SmCA elastomer, hence, works directly on the polymer chains so as to stretch the polymer chain between cross-linking points, leading to the parallel orientation rather than the perpendicular one. It should be noted here that the side-chain-type smectic LC elastomers prefer the perpendicular orientation on elongation.[23,24] This indicates the essential difference in the mesogens' orientation on stretching the backbone between these two classes of LC polymers.

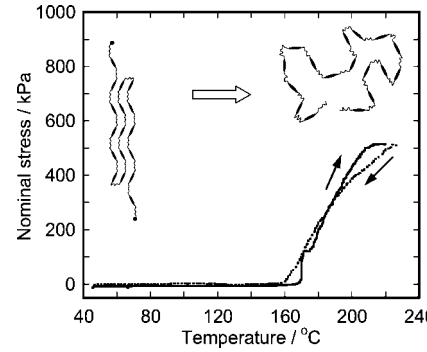


**Figure 10.** Temperature dependence of the contradiction force of BB-5/E2 elongated at a constant strain of 150%. Heating and cooling processes are indicated by the arrows. The contraction force appears on the transformation of the SmCA state to the isotropic state as schematically illustrated in the inset.

The second feature is that the SmCA elastomer can be elongated up to a strain of ~500% more than 5 times larger than the strain of 100% at which the layer orientation is completed (refer to Figure 7). This means that at the initial stage of 100% the polymers are apparently oriented, but not fully extended. Only the unfolding of the folded polymer chain gives a reasonable explanation for this behavior as illustrated in Figure 9b,c.[21,25−28] The elongation of the elastomer after the completion of the layer orientation should unfold the folded polymer chains, increase the distance between neighboring cross-linking points, and draw mesogens within a polymer backbone to the different smectic layers in neighbors (see Figure 9). Although the entropy of the polymer chain is reduced by the unfolding, the extended polymer configuration can be locked in newly formed smectic layers. The strain in the region of 100−550% is hence retained completely at zero stress, resulting in a quasi-plateau (so-called soft stress plateau) in the stress−strain curve and the permanent deformation of the stretched sample.

The permanent deformation of the stretched SmCA elastomer is in contrast with the entropy elasticity observed in the same elastomer in the isotopic liquid state. This contrast is directly detected from the contraction force generated through the SmCA−isotropic transition in the constantly strained elastomer. Figure 10 shows the temperature dependence of the contraction force measured for the elongated elastomer with a constant strain of 150%. Before the measurement, the smectic elastomer was elongated and relaxed at 140 °C so that the stress became zero. Then the temperature was scanned between the SmCA and isotropic phases while the strain was kept constant. On entrance into the transition temperature zone, the contraction force arises and approaches a constant value (compare Figure 10 with Figure 2). On cooling, it decreases to zero around the liquid crystallization temperature. This stress variation on heating and cooling cycles is reversibly observed. Thus, one knows that the elongated configuration of the polymer is locked on the smectic layer formation and that the contraction of the elastomer takes place only when the layer structure disappears in the isotropic liquid state.

It can thus be concluded that the high elongation after the complete orientation of the smectic structure is attributable to unfolding of the folded polymer chains accompanied by the aberration of the cross-linking points and that the permanent deformation is caused by locking of the chain conformation due to the one-dimensional layer order of the mesogens included in the polymer backbone. In this aspect, our recent paper[10] on the main-chain nematic elastomer is interesting. The nematic

elastomer showed entropy elasticity similarly to the isotropic elastomer: the elongation caused unfolding of the hairpin folding similarly to that in the present smectic elastomer, but folding re-formed to gain entropy immediately after the applied stress was released. This behavior distinct from that of the smectic elastomer is attributed to the absence of a layer structure.

After the completion of the chain extension, the strain or stress will work directly on the chain to increase the stress significantly. In the stress−strain curve shown in Figure 3b, this stress increment is observed at strain beyond 500%. The direct strain to the elongated polymer chain decreases the conformational chain entropy in the SmCA state and then causes the crystallization. The elastomers elongated at temperatures lower than 160 °C show similar stress−strain curves, but the reflections characteristic of the crystal have not been observed in the X-ray diffraction pattern (see Figure 6d). This may be due to a kinetic reason: a decrease in temperature slows the crystallization rate so that the crystat does not grow in size large enough to give diffraction peaks within the experimental time scale in this work.

## 5. Conclusion

The main-chain liquid crystalline BB-5 polyester was cross-linked by introducing 2 mol % TMBTC as the cross-linker. The resultant BB-5/E2 elastomer shows a clear phase transition of SmCA to an isotropic liquid. BB-5/E2 in the isotropic state shows a reversible stress−strain relationship which is very similar to that of the conventional rubbers and transforms to the SmCA phase on high strain elongation. This SmCA phase returns to the isotropic phase with decreasing strain.

Elongation of BB-5/E2 in the SmCA state orients the smectic layers with their layer normal parallel to the elongation direction. The perfect orientation of the smectic structure is achieved at $\varepsilon = 100\%$, but the elastomer can be elongated further up to 500% without changing the structure and the orientation of the smectic LC and shows a soft stress plateau in the stress−strain curve. This suggests that the chains are folded in the elastomer at $\varepsilon = 100\%$ and unfolded during further elongation. The more stretched chain conformation is locked in the smectic layer structure composed by the mesogens included in the chain backbone, resulting in permanent deformation of the elastomer. After the completion of chain extension, the stress works directly on the polymer chain so that the smectic liquid crystal is transformed to the crystal. Thus, the main-chain smectic LC elastomer presents an elongation behavior completely different from those of isotropic and nematic elastomers. Various structures of smectic phases and associated interactions with external fields will allow us to produce smectic elastomers possessing distinct mechanical features.[29,30]

## References and Notes


(1) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon Press: Oxford, U.K., 1975.
(2) Warner, M.; Terentjev, E. M *Liquid Crystal Elastomers*; Oxford University Press: Oxford, U.K., 2003.
(3) Hanus, K.-H.; Pechhold, W.; Soergel, F.; Stoll, B.; Zentel, R. *Colloid Polym. Sci.* **1990**, *268*, 222.
(4) Wilbert, G.; Zentel, R. *Macromol. Chem. Phys.* **1996**, *197*, 3258.
(5) Bergmann, G. H. F.; Finkelmann, H. *Macromol. Rapid Commun.* **1997**, *18*, 353.
(6) Ortiz, C.; Wagner, M.; Bhargava, N.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1998**, *31*, 8531.
(7) Donnio, B.; Wermter, H.; Finkelmann, H. *Macromolecules* **2000**, *33*, 7724.
(8) Rousseau, A.; Mather, P. T. *J. Am. Chem. Soc.* **2003**, *125*, 15300.
(9) Li, M.-H.; Keller, P.; Yang, J.; Albouy, P.-A. *Adv. Mater.* **2004**, *16*, 1922.
(10) Tokita, M.; Tagawa, H.; Funaoka, S.; Niwano, H.; Osada, K.; Watanabe, J. *Jpn. J. Appl. Phys.* **2006**, *45*, 1729.
(11) Ahir, S. V.; Tajbakhsh, A. R.; Terentjev, E. M. *Adv. Funct. Mater.* **2006**, *16*, 556.
(12) Beyer, P.; Terentjev, E. M.; Zentel, R. *Macromol. Rapid Commun.* **2007**, *28*, 1485.
(13) Beyer, P.; Braun, L.; Zentel, R. *Macromol. Chem. Phys.* **2007**, *208*, 2439.
(14) Ishige, R.; Tokita, M.; Naito, Y.; Zhang, C. Y.; Watanabe, J. *Macromolecules* **2008**, *41*, 2671.
(15) Watanabe, J.; Hayashi, M. *Macromolecules* **1988**, *21*, 278.
(16) Watanabe, J.; Hayashi, M. *Macromolecules* **1989**, *22*, 4083.
(17) Watanabe, J.; Kinoshita, S. *J. Phys. II* **1992**, *2*, 597.
(18) Watanabe, J.; Hayashi, M.; Nakata, Y.; Niori, T.; Tokita, M. *Prog. Polym. Sci.* **1997**, *22*, 1053.
(19) Olmsted, P. D.; Terentjev, E. M. *Phys. Rev. E* **1996**, *55*, 2444.
(20) Mitchell, G. R.; Windle, A. H. In *Developments in Crystalline Polymers*; Bassett, D. C., Ed.; Elsevier: London, 1988; Vol. *2*.
(21) Tokita, M.; Tokunaga, K.; Funaoka, S.; Osada, K.; Watanabe, J. *Macromolecules* **2004**, *37*, 2527.
(22) Osada, K.; Koike, M.; Tagawa, H.; Funaoka, S.; Tokita, M.; Watanabe, J. *Macromolecules* **2005**, *38*, 7337.
(23) Nisikawa, E.; Finkelmann, E. *Macromol. Chem. Phys.* **1997**, *198*, 2531.
(24) Nisikawa, E.; Finkelmann, E. *Macromol. Rapid Commun.* **1997**, *18*, 65.
(25) Tokita, M.; Watanabe, J. *Polym. J.* **2006**, *38*, 611.
(26) Tokita, M.; Osada, K.; Yamada, M.; Watanabe, J. *Macromolecules* **1998**, *31*, 8590.
(27) Adams, J. M.; Warner, M. *Eur. Phys. J. E* **2005**, *16*, 97.
(28) Beyer, P.; Terentjev, E. M.; Zentel, R. *Macromol. Rapid Commun.* **2007**, *28*, 1485.
(29) Goodby J. W.; Coates, D. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. *2A*, Chapter 5.
(30) Adams, J. M.; Warner, M. *Phys. Rev. E* **2005**, *71*, 021708.


MA801665A