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## Liquid Crystals

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First published on: 03 June 2009

**To cite this Article** Deng, Wei , Li, Min-Hui , Wang, Xiaogong and Keller, Patrick(2009) 'Light-responsive wires from side-on liquid crystalline azo polymers', *Liquid Crystals*, 36: 10, 1023 – 1029, First published on: 03 June 2009 (iFirst)

**To link to this Article:** DOI: 10.1080/02678290902759251

**URL:** <http://dx.doi.org/10.1080/02678290902759251>

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## INVITED ARTICLE

### Light-responsive wires from side-on liquid crystalline azo polymers

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(Received 23 December 2008; final form 19 January 2009)

The pioneering work of Professor de Gennes in the field of liquid crystalline polymers and elastomers is outlined with an emphasis on artificial muscles. To illustrate the presentation, results on light-responsive nematic liquid crystalline elastomer fibres are reported. Two kinds of light-responsive wires were fabricated from an azobenzene-containing liquid crystalline copolymer with, or without cross-linking. Cross-linked wires were obtained by the reaction between the hydroxyl groups of the liquid crystalline copolymer and the diisocyanate groups of the cross-linker. The wires showed light-responsive bending towards the direction of the incident UV light at room temperature. Uncross-linked wires, drawn from the pure azobenzene copolymer, presented the same UV light-induced bending properties.

**Keywords:** azo elastomer; photomechanical response; fibres; liquid crystalline elastomer

#### 1. Introduction

Research on smart materials is among the most dynamic fields in material science nowadays. Smart materials that respond to external stimuli by a change in shape or size, called actuators, could be used to produce forces and displacements for micro-robots, micro-pumps and sensors (1). Polymers are among the best candidates for the development of smart or responsive materials because of established advantageous properties, such as high processability, relatively low weight density, easy fabrication and low manufacturing costs (2). Many actuators based on polymer systems have been reported, such as hydrogels (3), conducting polymers (2), dielectric elastomers (4) or liquid crystalline (LC) elastomers (5–7).

In nematic LC elastomers, which are used in the present communication, the actuation uses as a motor for the contraction-expansion a reversible conformational change affecting the polymer chains at a molecular level. This conformational change occurs during a phase transition from the oriented nematic mesophase to the isotropic phase (6).

Before revealing our results on light-responsive wires actuators, we will first describe the actuation mechanism for a nematic LC elastomer artificial muscle. This will give an opportunity to recall researchers in the field, the pioneering and sometimes forgotten work of Professor de Gennes on LC polymers and elastomers.

#### 2. Actuation mechanism in nematic LC elastomers: a tribute to the pioneering work of P.-G. de Gennes

Long before the first synthesis of thermotropic main-chain and side-chain LC polymers and elastomers, de Gennes published two papers in which he developed some ideas ultimately related to 'artificial muscles'. In the paper 'Possibilités offertes par la réticulation de polymères en présence d'un cristal liquide' (Possibilities offered by the cross-linking of polymers dissolved in a liquid crystalline phase) (8), de Gennes developed the idea that macromolecular chains of a polymer dissolved in a macroscopically aligned nematic mesophase would adopt an oblate conformation. To 'freeze' the backbone anisotropy, de Gennes proposed to cross-link the polymer *in situ*, leading to a conformationally anisotropic polymer network immersed in an oriented nematic mesophase (Figure 1). In a next step, de Gennes postulated that removal of the nematic order around the anisotropic network would induce a conformational change of the macromolecular backbones, from an anisotropic (oblate) shape to an isotropic (spherical) shape. In his two last comments, de Gennes suggested that the nematic molecules could be involved in the production of the reticulation points, and that the production of the entire polymer network could be done at once by dissolving a monomer and a cross-linking agent in an oriented nematic mesophase.

In a second paper 'Réflexions sur un type de polymères nématiques' (Reflexions on a new type of

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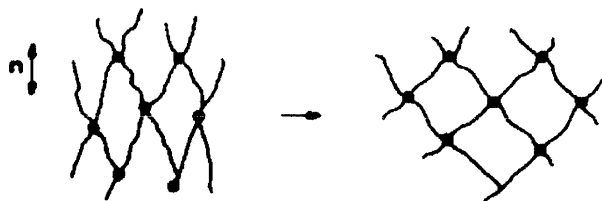


Figure 1. Schematic representation of a polymer network in an oriented nematic mesophase. In the nematic phase (left), the network adopts an anisotropic conformation elongated parallel to the nematic director. After removal of the nematic order (right), the network relaxes towards an isotropic conformation. Reprinted from (8) with permission from Elsevier.

nematic polymer) (9), de Gennes discussed the possibility of preparing what are now known as main-chain LC polymers and elastomers (Figure 2). He suggested that the introduction of flexible spacers (single component or a mixture) in between mesogenic groups could lead to nematic polymers exhibiting a fluid mesophase at reasonable temperatures. He also predicted that main-chain LC elastomers would present unusual mechanical properties, such as a strongly non-linear response to deformation of these elastomers under stress.

More recently (1982), de Gennes (10) studied the influence of the orientational nematic order on the macromolecular conformation in main-chain LC polymers. In this case, he predicted that this coupling between nematic order and macromolecular shape would lead to an elongation of the polymer backbones along the nematic director (Figure 3); at the nematic to isotropic phase transition, the polymer backbones would recover a random coil conformation, driven by entropy.

Using small angle neutron scattering, D'alless *et al.* (11) and Li *et al.* (12) presented experimental proofs of this theoretical picture.

At this time, all the 'ingredients' necessary to build a thermally stimulated 'artificial muscle' made of a nematic LC elastomer were demonstrated.

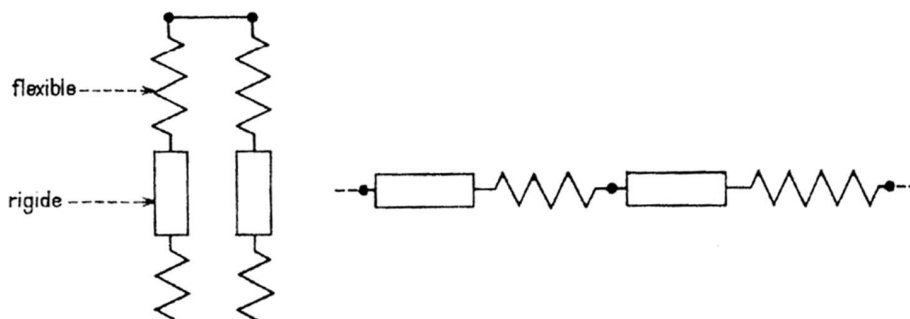


Figure 2. Schematic representation of side-chain (left) and main-chain (right) liquid crystalline polymers proposed by de Gennes. Flexible spacers and rigid rods are outlined. Adapted from (9) with permission from Elsevier.

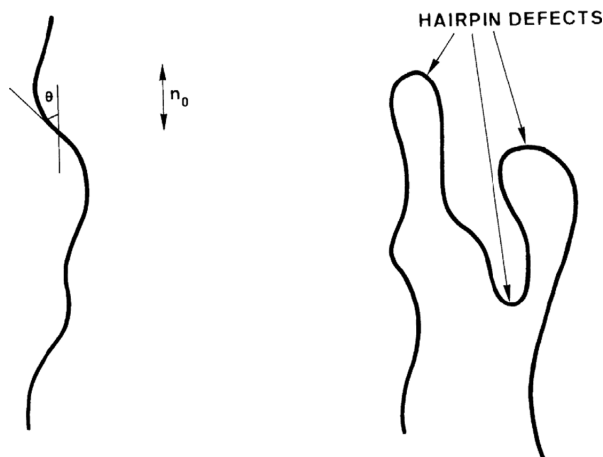


Figure 3. Schematic representation of the chain of a nematic main-chain liquid crystalline polymer (left: without a hairpin defect; right: with hairpin defects) (adapted from (10)).

What, however, was the mechanism involved in the contraction-elongation of a nematic LC elastomer 'artificial muscle'?

Consider long polymer chains with incorporated rod-like units (i.e. mesogens) within the chains, called main-chain LC polymers. Since the average macromolecular shape is coupled to the nematic orientational order, the polymer chains will elongate when their mesogens orient in the nematic phase, while in the isotropic phase, they will recover a random coil conformation (Figure 4). A change in the average macromolecular shape, from elongated to spherical, is thus introduced as the nematic-to-isotropic phase transition takes place.

If these long polymer chains are now cross-linked, a new kind of rubber, called a nematic LC elastomer, is obtained. If the nematic LC elastomer is judiciously prepared, so that all the nematic polymer chains are, on average, oriented uniformly in the whole sample, the microscopic, molecular level shape change will be translated to a collective macroscopic shape change of the elastomer sample

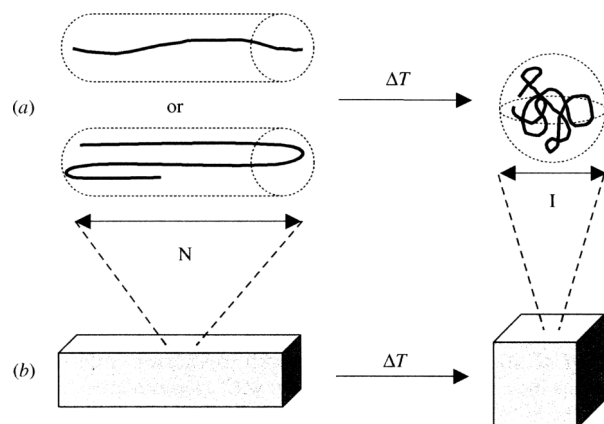


Figure 4. (a) Conformation of a main-chain liquid crystalline polymer in the nematic (N) and isotropic (I) phases. (b) Macroscopic shape change of the monodomain sample of a main-chain liquid crystalline elastomer at the nematic-isotropic transition. Reproduced with permission from (6).

(Figure 4). The cross-links will ensure a memory of the supramolecular organisation present in the nematic phase; so, when the LC elastomer is cooled back below TNI, the macroscopic sample will return to its initial shape (Figure 4). Several groups developed thermally stimulated LC elastomer actuators based on this concept (7, 13, 14), but most of them were not aware that they used the ‘ahead of time’ ideas developed by Professor de Gennes!

In the last paper de Gennes wrote on this subject, ‘Un muscle artificiel semi-rapide’ (A semi-fast artificial muscle) (15), he proposed building a striated artificial muscle composed of a triblock copolymer (Figure 5). This triblock copolymer-based lamellar artificial muscle was realised experimentally some years later (16). In the concluding remarks of this paper, de Gennes suggested that other stimuli could be used besides a temperature jump and in particular light.

As a matter of fact, it is common knowledge in the LC community that in azobenzene-containing mesogenic molecules, a LC-to-isotropic phase transition can be induced by irradiation with light of suitable

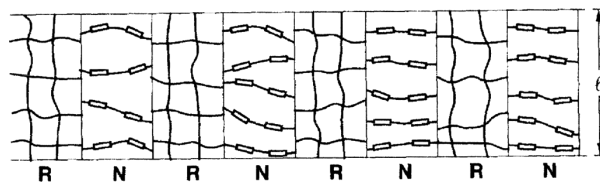


Figure 5. A striated artificial muscle based on a triblock copolymer RNR in a lamellar phase with cross-links in the R part. Reproduced from (15) with permission from Elsevier.

wavelength (17, 18). The light-induced phase transition is provoked by the trans-cis photoisomerisation of the azo groups, inducing a large change in the shape of the molecules, from a LC rod-like shape for the trans isomer to a kinked non-mesogenic shape for the cis isomer.

Years after this suggestion, making use of the reversible photo-induced trans-cis isomerisation of the azobenzene group, many papers reported the photo-responsive behaviour of azo-containing LC elastomers (19–25).

In the following section, we present our latest results on light-responsive wires made of side-on LC azo polymers.

### 3. Light-responsive wires from side-on LC azo polymers

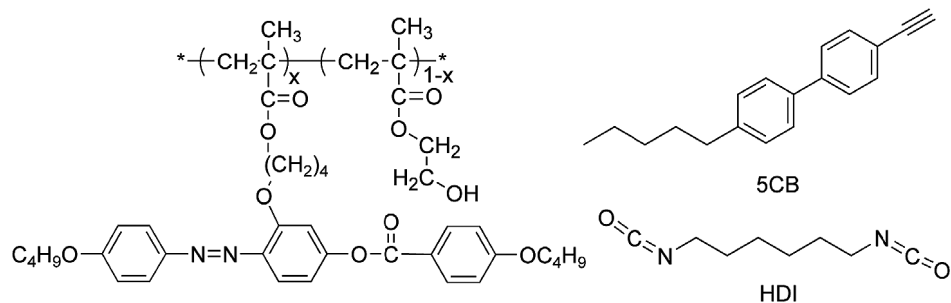
As stated previously, in order to visualise at a macroscopic level the conformational change occurring at a molecular level, all the macromolecules in the material have to be oriented parallel to each other to form a nematic ‘liquid single crystal’ (26). Furthermore, the macromolecules must also be strongly associated, that is, by covalent or non-covalent (H-bonds) cross-linking in order to eliminate the possibility that individual molecules change their shapes and reorient individually by sliding.

Several methods have been used to prepare light-responsive monodomain LC elastomers: two step cross-linking of LC polysiloxanes under mechanical stress (19); simultaneous photopolymerisation/ photocross-linking (21, 22) or thermal radical polymerisation (23, 25) of an LC monomers mixture aligned by surface effects in an LC cell.

On the other hand, Naciri *et al.* (27) have reported recently the fabrication of thermo-responsive LC fibres made of a nematic side-on LC elastomer.

Combining these different approaches, we have prepared light-responsive wires from a side-on LC azo copolymer (Scheme 1).

The LC azo copolymer is a random copolymer of an LC azo monomer (MAazo444, 90 mol%) and hydroxyethyl methacrylate (HEMA, 10 mol%), which was obtained by atom transfer radical polymerisation (ATRP) following Deng *et al.* (28). The polymer PMAazo444<sub>48</sub>-r-PHEMA<sub>10</sub> has a molecular weight of 30700 and a polydispersity  $M_w/M_n = 1.14$ . From the first heating and cooling cycles (temperature variation rate: 10°C/minute) of the differential scanning calorimetry (DSC) curves, the phase transition temperatures of PMAazo444-r-PHEMA were determined as Cr 70 N 88 I 84 N 50 G (°C).



Scheme 1. Chemical structure of the compounds used in this study.

Two kinds of wires have been prepared, uncross-linked and cross-linked with hexamethylene diisocyanate (HDI) (Scheme 1).

The uncross-linked wires were made only of the LC azo copolymer. After heating the polymer to its isotropic phase for 1 minute to equilibrate the system, the viscous liquid was cooled down to the nematic phase (80°C). The wires were drawn from the nematic melt with tweezers. By varying the drawing speed, wires with diameters from 0.2 to 2 mm were obtained. Figure 6 shows micrographs of the wires observed by polarised optical microscopy. The uniform alignment of the wires is probed by the bright (top) and dark (bottom) images obtained for different orientations of the polarisers.

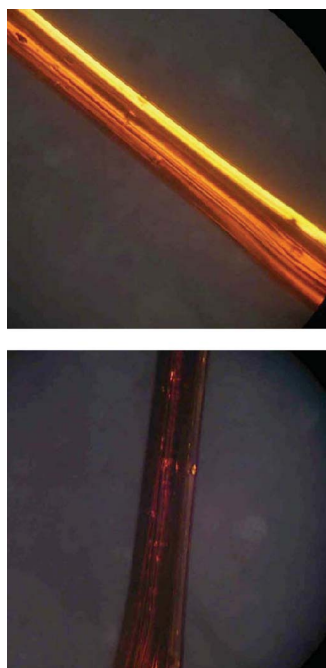


Figure 6. Typical POM pictures of the uncross-linked liquid crystalline polymer wires. The angle between the fibre long axis and one of the polariser is 45° in the top image. This angle is 0° or 90° in the bottom image.

When irradiated sideways at room temperature with UV light (55 mW cm<sup>-2</sup> at 365 nm from a high pressure mercury lamp), the initially straight wires (Figure 7 center) bent towards the direction of the incident UV light (Figure 7, top). In order to rule out

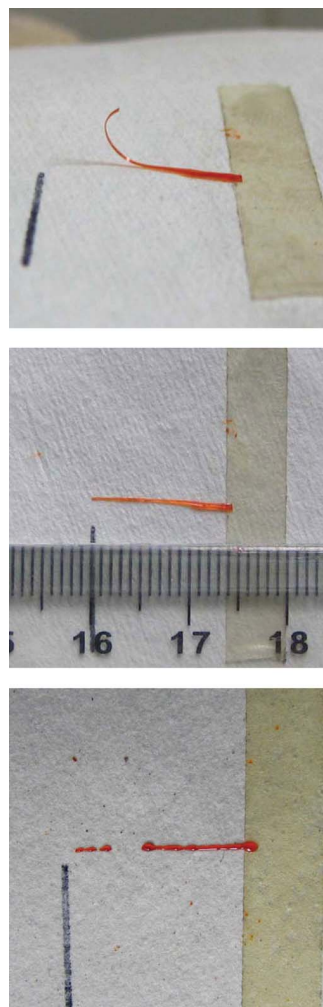


Figure 7. Uncross-linked liquid crystalline polymer wires before light irradiation (center), after irradiation with UV light for 10 minutes (top), and after heating with hot air (bottom).

bending caused by a thermal effect, the wires were heated sideways with hot air from a heating gun. No bending was observed before the wires started to melt (Figure 7, bottom). These results indicate that the bending of the wires was caused by the photo-effect of the UV light.

Since the azobenzene groups have a large extinction coefficient at 372 nm ( $\lambda_{\text{max}}$ ), and the wires have a relatively large diameter ( $>0.2$  mm), only the azobenzene groups located near the surface facing the UV light can undergo an efficient trans-cis isomerisation (self-screening effect) (29). The photochemically induced nematic to isotropic transition occurring in this thin layer results in a contraction of the surface layer. This unsymmetrical contraction could explain the bending of the wires towards the incident direction of the UV light.

In a first attempt, cross-linked wires were prepared by reacting the hydroxyl-functionalised LC polymer with the diisocyanate cross-linker HDI. Figure 8 shows the FTIR spectra of the LC polymer and cross-linker mixture. The peak at  $2275\text{ cm}^{-1}$ , which corresponds to the stretching vibration peak of the isocyanate group, decreases quickly after heating at  $90^\circ\text{C}$  for 20 seconds. It indicates that the cross-linking reaction occurs rapidly in the sample. After thermal equilibrium at  $90^\circ\text{C}$  for 20 seconds, no wires could be drawn from the rubber-like material.

However, the relatively high  $T_g$  of the LC polymer requires heating the mixture to a high temperature (around  $80^\circ\text{C}$ ) for the processing. To lower this processing temperature, 5CB (Scheme 1) was added as a plasticiser. Thus, in the presence of 5CB, the processing temperature could be lowered to  $65^\circ\text{C}$ , limiting the cross-linking reaction during the drawing of the fibres.

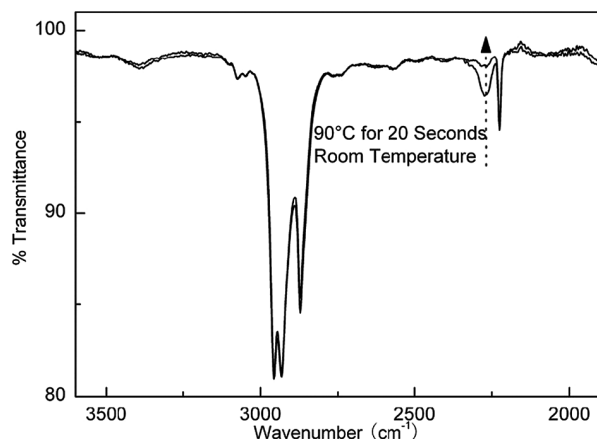


Figure 8. FTIR spectra of the liquid crystalline copolymer and cross-linker mixture. The characteristic absorption peak ( $2275\text{ cm}^{-1}$ ) of the isocyanate group decreased quickly after heating the mixture at  $90^\circ\text{C}$  for 20 seconds.

The components were dissolved in anhydrous dichloromethane (molar ratio of AZO:OH:NCO:5CB = 48:10:3:5) and the solvent removed under vacuum. The mixture was melted at  $90^\circ\text{C}$  and the temperature was quickly lowered to  $65^\circ\text{C}$ . The wires were drawn from the melt at this temperature. To get full cross-linking, the wires were kept in the dark at room temperature for a week. Figure 9 (top and middle) presents typical images of the cross-linked LC wires, obtained from polarised optical microscopy. The images indicate that the cross-linked wires have anisotropic alignment, but the degree of orientation is not as high as for the uncross-linked wires. After being irradiated at room temperature with UV light for 10 minutes, the cross-linked fibres bent towards the incident light (Figure 9, bottom).

DSC experiments on cross-linked wires demonstrated that the nematic phase was considerably destabilised after UV irradiation. After 15 minutes of irradiation, the TNI transition peak was not visible (Figure 10, curves A and B). However, after annealing,

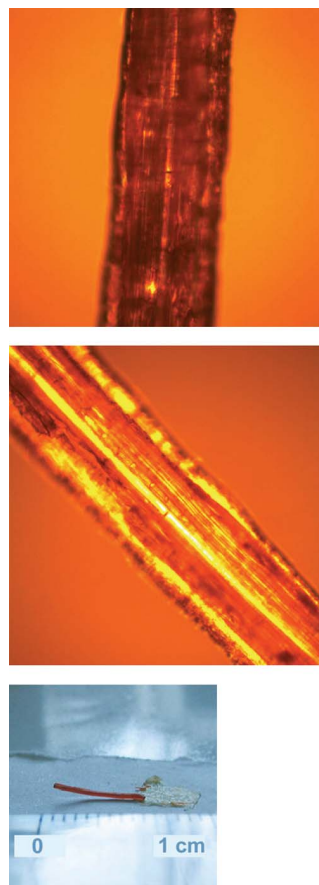


Figure 9. Typical POM pictures of the cross-linked wires different orientations with respect to the polariser (top and centre), and the cross-linked fibre after irradiation with UV light for 10 minutes (bottom).



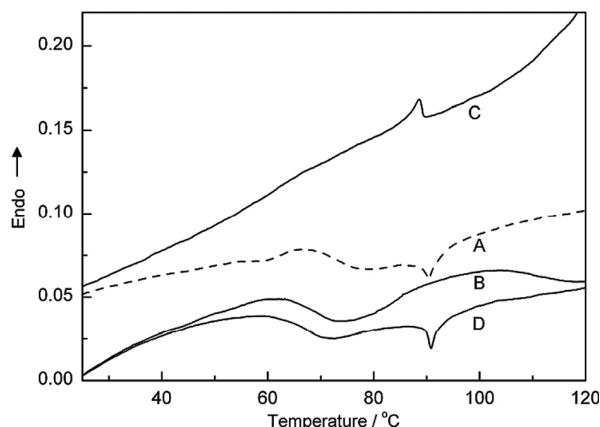


Figure 10. Differential scanning calorimetry curves of cross-linked wires. Curve A: 'native' cross-linked liquid crystalline polymer wires; curve B: cross-linked liquid crystalline polymer wire after UV irradiation (first heating); curve C: same wire as B (first cooling); curve D: same wire as B and C (second heating).

the TNI transition peak was restored for the previously UV irradiated fibre (Figure 10, curve D).

In comparison with the polymer wires without cross-linking (Figure 7, top), the degree of bending is smaller. It could be attributed to the fact that the cross-linked wires are more rigid than the uncross-linked ones and the mechanical resistance to overcome would be larger.

As for all the light-responsive LC elastomers described in the literature, thermal back reaction was observed for the cross-linked fibres, leading back to straight fibres. However, as observed previously for our azo side-on LC elastomer films (21), no back reaction was observed by irradiating the bent wires with visible light.

#### 4. Conclusions

In summary, uncross-linked and cross-linked light-responsive LC wires were prepared from an azobenzene-containing nematic side-on LC polymer. Incorporation of 5CB as a plasticiser, which can decrease the processing temperature, was necessary for drawing fibres from the mixture containing the cross-linker. Under UV light irradiation and at room temperature, the LC polymer wires bent towards the direction of the incident light.

The work presented here as well as all the papers describing artificial muscles made of LC elastomers are the direct applications, sometimes even without knowing it, of the pioneering contributions of Professor P.-G. de Gennes in this field. His enthusiasm for the subject and deep knowledge of chemistry, transmitted through enlightening discussions,

convinced us to start and pursue our research work in LC elastomer actuators.

#### Acknowledgements

Part of this manuscript was prepared during a visit of P. Keller to Professor Wang's laboratory at Tsinghua University. This visit was financially supported by the Department of Chemical Engineering, Tsinghua University, through the Tsinghua-Shell Chair on Chemical Engineering.

#### References

- (1) Madden, J.D.W.; Vandesteeg, N.A.; Anquetil, P.A.; Madden, P.G.A.; Takshi, A.; Pytel, R.Z.; Lafontaine, S.R.; Wieringa, P.A.; Hunter, I.W. *IEEE J. Ocean Eng.* **2004**, *29*, 706–728.
- (2) Bar-Cohen, Y. *Electroactive Polymer Actuators as Artificial Muscles: Reality, Potential and Challenges*; SPIE Press: Bellingham, WA, 2004; 2nd Ed.
- (3) Liu, Z.S.; Calvert, P. *Adv. Mater.* **2000**, *12*, 288–291.
- (4) Pelrine, R.; Kornblum, R.; Pei, Q.; Joseph, J. *Science* **2000**, *287*, 836–839.
- (5) Xie, P.; Zhang, R. *J. Mater. Chem.* **2005**, *15*, 2529–2550.
- (6) Li, M.-H.; Keller, P. *Philos. Trans. R. Soc. Lond. A* **2006**, *364*, 2763–2777.
- (7) Yu, Y.; Ikeda, T. *Angew. Chem. Int. Ed. Engl.* **2006**, *45*, 5416–5418.
- (8) de Gennes, P.G. *Phys. Lett. A* **1969**, *28A*, 725–726.
- (9) de Gennes, P.G. *C. R. Acad. Sci. B* **1975**, *281*, 101–103.
- (10) de Gennes, P.G. In *Polymer Liquid Crystals*, Cifferi, A., Krigbaum, W.R., Meyer, R.B., Eds.; Chapter 5: Mechanical properties of nematic polymers. Academic Press: New York, 1982; 115–131.
- (11) d'Allest, J.-F.; Maissa, P.; Ten Bosch, A.; Sixou, P.; Blumstein, R.B.; Teixeira, J.; Noirez, L. *Phys. Rev. Lett.* **1988**, *61*, 2562–2565.
- (12) Li, M.-H.; Brület, A.; Davidson, P.; Keller, P.; Cotton, J.-P. *Phys. Rev. Lett.* **1993**, *70*, 2297–2300. Li, M.-H.; Brület, A.; Cotton, J.-P.; Davidson, P.; Strazielle, C.; Keller, P. *J. Phys. II France* **1994**, *4*, 1843–1863.
- (13) Wermter, H.; Finkelmann, H. *e-Polymers* **2001**, *13*, 1–13.
- (14) Thomsen, III, D.L.; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B.R. *Macromolecules* **2001**, *34*, 5868–5875.
- (15) de Gennes, P.G. *C. R. Acad. Sci. Iib* **1997**, *324*, 343–348.
- (16) Li, M.-L.; Keller, P.; Yang, J.-Y.; Albouy, P.-A. *Adv. Mater.* **2004**, *16*, 1922–1925.
- (17) Leier, C.; Pelzl, G. *J. Prakt. Chem.* **1979**, *321*, 197–204.
- (18) Tsutsumi, O.; Shiono, T.; Ikeda, T.; Galli, G. *J. Phys. Chem.* **1997**, *101*, 1332–1337.
- (19) Finkelmann, H.; Nishikawa, E.; Pereira, G.G.; Warner, M. *Phys. Rev. Lett.* **2001**, *87*, 015501/1–015501/4.
- (20) Hogan, P.M.; Tajbakhsh, A.R.; Terentjev, E.M. *Phys. Rev. E* **2002**, *64*, 061702/1–061702/8.
- (21) Li, M.-H.; Keller, P.; Li, B.; Wang, X.; Brunet, M. *Adv. Mater.* **2003**, *15*, 569–572.

- (22) Yamada, M.; Kondo, M.; Mamiya, J.-I.; Yu, Y.; Kinoshita, M.; Barrett, C.J.; Ikeda, T. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 4986–4988.
- (23) Yu, Y.; Nakoto, M.; Ikeda, T. *Nature* **2003**, *425*, 145.
- (24) Yu, Y.; Nakoyo, M.; Ikeda, T. *Pure Appl. Chem.* **2004**, *76*, 1467–1477.
- (25) Tabiryán, N.; Serak, S.; Dai, X.-M.; Bunning, T. *Opt. Express* **2005**, *13*, 7442–7448.
- (26) Küpfer, J.; Finkelmann, H. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 717–726.
- (27) Naciri, J.; Srinivasan, A.; Joen H.; Nikolov, N.; Keller, P.; Ratna, B.R. *Macromolecules* **2003**, *36*, 8499–8505.
- (28) Deng, W.; Albouy, P.-A.; Lacaze, E.; Keller, P.; Wang, X.; Li, M.-H. *Macromolecules* **2008**, *41*, 2459–2466.
- (29) Ikeda, T.; Mamiya, J.-I.; Yu, Y. *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 506–528.