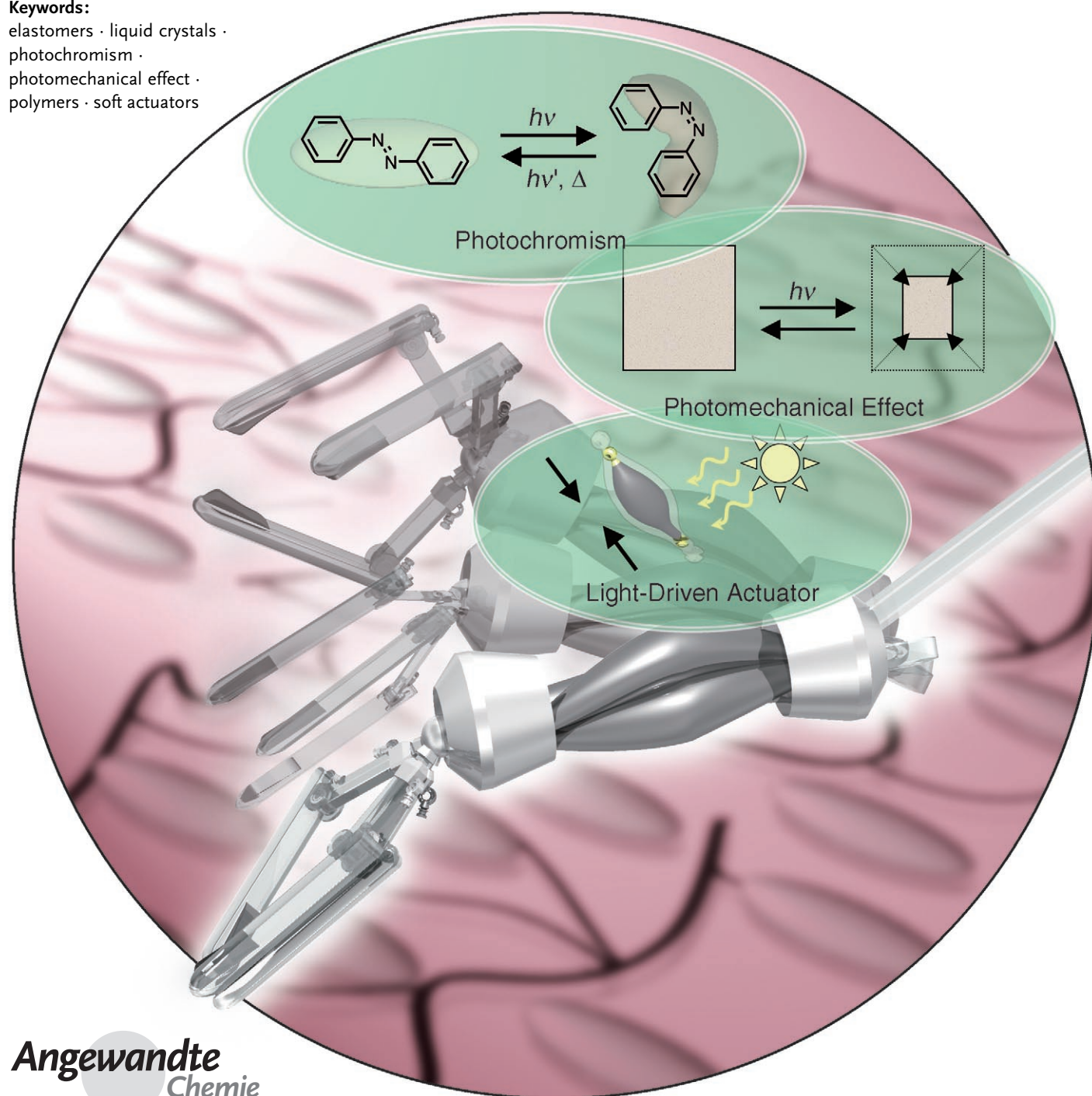


Photomechanics of Liquid-Crystalline Elastomers and Other Polymers**

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Muscle is a transducer that can convert chemical energy into mechanical motion. To construct artificial muscles, it is desirable to use soft materials with high mechanical flexibility and durability rather than hard materials such as metals. For effective muscle-like actuation, materials with stratified structures and high molecular orders are necessary. Liquid-crystalline elastomers (LCEs) are superior soft materials that possess both the order of liquid crystals and the elasticity of elastomers (as they contain polymer networks). With the aid of LCEs, it is possible to convert small amounts of external energy into macroscopic amounts of mechanical energy. In this Review, we focus on light as an energy source and describe the recent progress in the area of soft materials that can convert light energy into mechanical energy directly (photomechanical effect), especially the photomechanical effects of LCEs with a view to applications for light-driven LCE actuators.

1. Introduction

Many studies on actuators for the construction of artificial muscles have been performed recently. An actuator is an energy transducer that can convert input energies of a variety of forms into mechanical quantities such as displacement, strain, velocity, and stress. Many types of materials have already been developed as actuator materials, including inorganic materials such as shape-memory alloys and electrostrictive and piezoelectric materials. However, to realize muscle-like movements in artificial actuators, these should be soft and deform in response to external stimuli such as changes in electric field or temperature.^[1] Polymers are one of the most promising materials for artificial muscles because of their advantageous properties, such as their high processability, softness, easy fabrication characteristics, high corrosion resistance, and low manufacturing costs. Many actuators that respond to various external stimuli have been developed using polymers as base materials: polymer gels,^[2–4] conducting polymers,^[5–7] carbon nanotubes,^[8–11] and dielectric elastomers.^[12] Among these materials, polymer gels have attracted much attention as artificial muscles because polymer gels contain fluid in their three-dimensional network structures, which provides softness as well as high biocompatibility; moreover, large deformations are produced with only a small stress. In particular, electric-field-responsive polymer gels are superior to other materials in view of their high sensitivity to electric fields and the large amount of mechanical energy produced by an electric field. However, polymer gels have some disadvantages: they swell in fluids and require cycles of swelling and shrinking to induce their deformation, which could in general result in slow response times and low fatigue resistance. From this point of view, dry actuators are advantageous. Shape-memory materials consisting of cross-linked polymers function by the combination of cross-linking reactions and polymer crystallization, which fix the shape of the polymers.^[13] Furthermore, a variety of external stimuli that produce effective responses have been examined, for

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example, heat, light, electric field, magnetic field, and concentration of fluids.

Studies on photoinduced deformation (contraction and expansion) of amorphous polymers have been performed intensively since the 1960s.^[14–17] Light as an external stimulus enables the remote control and rapid deformation of materials. Furthermore, no wires or connections are necessary to use light as a stimulus, which enables easy fabrication of the devices and reduces the weight. Light-driven polymer actuators, therefore, are promising in a wide range of micro- and macroscale devices. However, in these amorphous polymer materials, the deformation in response to external stimuli takes place in an isotropic way; there is no preferential direction for the deformation. Also the degree of the deformation is in general small. If the materials possess any anisotropy, their deformation in response to external stimuli could be induced in an anisotropic way with preferential direction of the deformation, which could produce a much larger deformation than that observed in amorphous materials.

Liquid-crystalline elastomers (LCEs) are a new type of material that have properties of both liquid crystals (LCs) and elastomers; the elastomer properties arise from polymer networks. LCEs contain mesogens, which, because of their LC properties, are aligned; this alignment of the mesogens is coupled with polymer network structures and gives rise to the characteristic properties of LCEs. Depending on the mode of alignment of the mesogens, LCEs are classified into nematic LCEs, smectic LCEs, cholesteric LCEs, and so on. If a

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nematic LCE film is heated toward the nematic–isotropic phase-transition temperature, the nematic order decreases, and the mesogens become disordered when the temperature exceeds the phase-transition temperature. With this phase transition, the LCE films in general show contraction along the alignment direction of the mesogens; if the temperature is lowered below the phase-transition temperature, the LCE films revert to their original size (expansion). This anisotropic deformation of the LCE films is sometimes very large, which makes the LCE materials promising as artificial muscles.^[18,19] The incorporation of photochromic moieties into LCEs can induce a reduction in the nematic order (and in extreme cases conversion into the isotropic phase) and causes a contraction of the films upon exposure to UV light as a result of a photochemical reaction of the photochromic moiety.^[20–22] Furthermore, three-dimensional movement (bending) of LCE films was observed by incorporation of photochromic moieties into LCEs.^[23,24] Light-driven actuators based on LCE materials are a topic of recent intensive studies, and a variety of actuation modes have been developed.

In this Review, we describe photomechanical effects observed in many kinds of materials, focusing our attention on light-driven LCE actuators. In Section 2, we summarize the photomechanical effects in monolayers, gels, and polymers. In Section 3, we describe LCEs, their preparation and general properties, and their responses to various external stimuli other than light. In the final section of this Review, we discuss the photoresponsive behavior of LCEs, focusing on recent progress in this field.

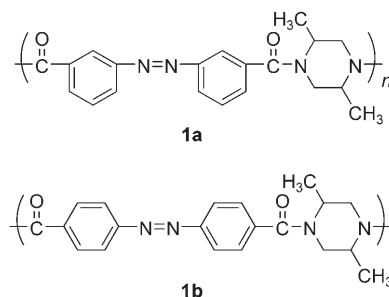
2. Photomechanical Effects in Various Systems

2.1. Monolayers

Azobenzene is a classical photochromic molecule that has been used by many researchers to incorporate photoresponsive properties into materials: its *trans*–*cis* photoisomerization produces a variety of changes in physicochemical properties of the materials, such as molecular length and polarity. The introduction of azobenzene functions to polymers also leads to fascinating photoresponsive systems. Monolayers of the azobenzene polymers are easily prepared at air/water interfaces. In a monolayer, changes in the

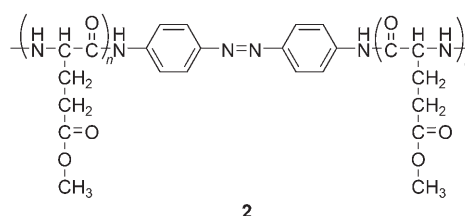
molecular shape and orientation can be directly related to the film properties, such as area and surface pressure. The molecular motion of azobenzene moieties in polymers at a monolayer interface is transferred and amplified to a macroscopic level of the materials.

Photomechanical effects of a monolayer consisting of polyamide with azobenzene moieties in the main chain (**1**)



were first reported by Blair et al.^[25,26] A decrease in stress at the air/water interface was observed upon irradiation of the monolayer with UV light, thus indicating contraction of the monolayer. When the monolayer was in darkness, the stress increased again; this cycle could be repeated many times. For these main-chain type monolayers, the azobenzene moieties are considered to lie flat on the water surface. The photomechanical effects are due to the *trans*–*cis* isomerization of the azobenzene moieties, which occupy a larger area at the interface when they are in the more-linear *trans* form than in the *cis* form.

Higuchi et al. prepared a polypeptide monolayer composed of two α -helical poly(γ -methyl L-glutamate) rods linked by an azobenzene moiety (**2**).^[27] The *trans*–*cis* photoisomerization and the consequent variation in geometry of



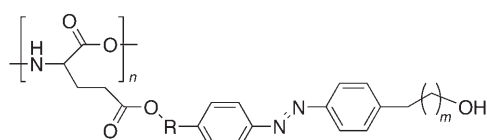
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the azobenzene moiety led to bending of the main chain of the molecule and a decrease in the limiting area per molecule. It was estimated that the bending angle between the two α -helical rods, produced by irradiation with UV light, was about 140° . The photoinduced bent structure of **2** resulted in a decrease of the molecular area of **2** at the air/water interface owing to a decrease in the distance between the ends of the molecule. An important finding was that the photoinduced changes in the area of the monolayer of **2** occurred more slowly than the spectral changes of the azobenzene moieties. The photoinduced changes in the surface area may arise from rearrangement of the bent molecules of **2** induced by photoisomerization of the azobenzene moieties in the main chain. The intermolecular interaction of **2** in the solid condensed monolayer may serve to slow down the rate of their rearrangement.

The photoresponsive behavior of related polypeptides in which the side chains contain azobenzene functions were investigated by Menzel et al.^[28] They prepared poly(L-glutamate)s with azobenzene-containing side chains coupled to the backbone through alkyl spacers (**3**). The monolayers showed



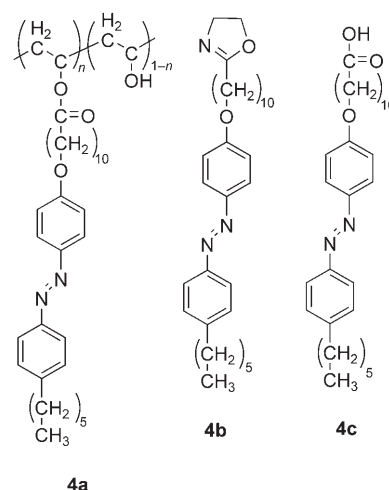
3a: $R = C_6H_{12}$, $m = 2$

3b: $R = C_2H_4$, $m = 6$

3c: $R = C_6H_{12}$, $m = 6$

photoresponsive behavior that was opposite to that of the above-mentioned systems. The monolayers expanded when exposed to UV light and shrank when exposed to visible light. The *trans*–*cis* photoisomerization of the azobenzene moiety upon irradiation with UV light leads to a large increase in the dipole moment of this unit, and this part gains a high affinity for a water surface.^[29]

Seki and co-workers prepared poly(vinyl alcohol)s (**4**) containing azobenzene side chains and observed photoinduced changes in their areas on a water surface.^[29–38] The



monolayers at the air/water interface exhibited a threefold expansion in area upon irradiation with UV light and reversibly shrank by irradiation with visible light (Figure 1).

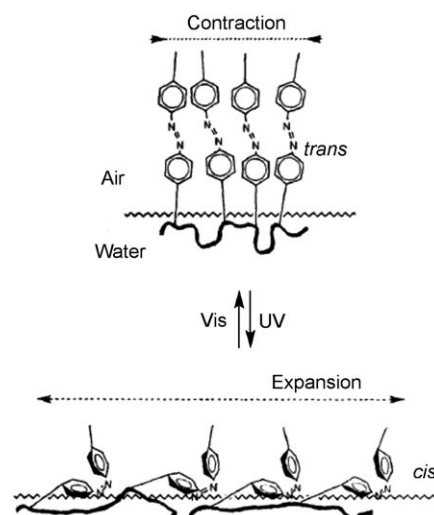
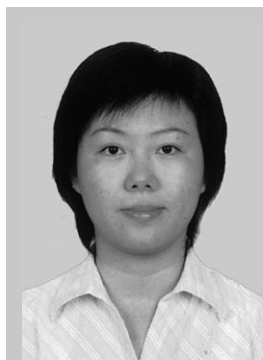


Figure 1. UV- and visible-light-induced deformation of a polymer monolayer containing azobenzene side chains at the air/water interface.

The mechanism of the photoinduced changes in area was interpreted in terms of the change in polarity of the azobenzene moiety: the *trans*–*cis* photoisomerization leads to an increase in dipole moment, thus bringing about a higher affinity of the *cis*-azobenzene for the water surface and the expansion of the monolayers. The *cis*–*trans* back-isomerization by irradiation with visible light leads to the recovery of the monolayers in the initial structure. The XRD data show that the monolayer of the *trans* isomer is thicker than that of the *cis* isomer. The change in thickness by 0.2–0.3 nm as a result of the *trans*–*cis* isomerization in the hydrophobic side chain is observed in situ on the water surface.^[35]

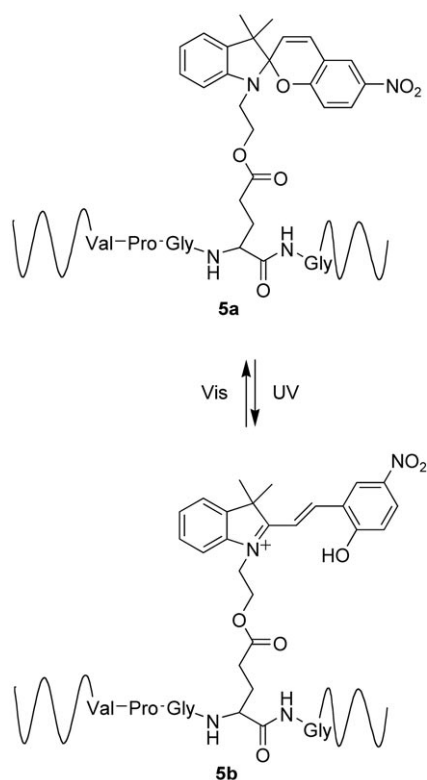
These results indicate that the photoinduced deformations of the azobenzene-containing monolayers strongly depend on the location of the azobenzene moieties in the dark: when the



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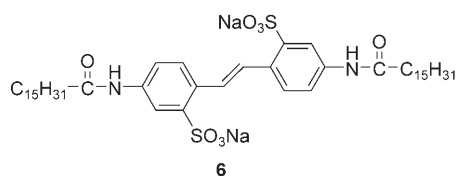
azobenzene moieties are on or in the water subphase, the structural response of the monolayers is determined by the geometrical change of the photochromic units. In contrast, the change in polarity of the azobenzene moieties is more important when they are away from the water subphase in the dark.

In monolayers of polymers with spiropyran chromophores (**5**), the photomechanical effect was unambiguously ascribed to a change in the concentration of the chromophore at the air/water interface.^[39–41] In the dark, the hydrophobic spiropyran species tend to stay away from the water (Scheme 1).^[41]



Scheme 1. Photoisomerization between benzospiropyran and merocyanine derivatives.

In contrast, the photogenerated merocyanine species, which are zwitterionic and highly polar, try to maximize their interaction with the aqueous phase and penetrate the monolayer to the maximum possible extent. Shimomura and co-workers reported a novel design of a stilbene amphiphile (**6**)



in a condensed monolayer and morphological change at the air/water interface.^[42]

As the monolayers are restricted in two dimensions, they offer intriguing systems for understanding macroscopic

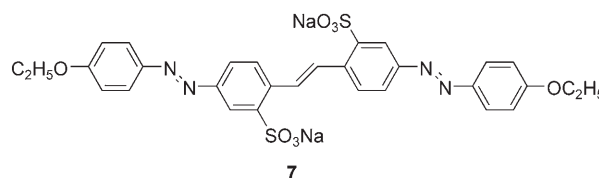
deformations in terms of the processes that take place at the molecular level. Nevertheless, gels and solid films are of greater interest from the viewpoint of applications.

2.2 Gels

A polymer gel consists of a cross-linked network and a liquid filling in the interstitial spaces of the network. Polymer gels can be easily deformed by external stimuli and generate force or perform work in various environments. If such responses can be translated from the microscopic to the macroscopic scale, the conversion of chemical free energy into mechanical work can be realized.^[43] The ability of polymer gels to undergo substantial swelling and shrinkage as a function of their environment is one of the most remarkable properties of these materials.^[43] Volume changes of gels, which can be induced by a change in factors such as temperature, pH, or ionic strength, are quite useful for the applications of the gels as potential actuators, sensors, controllable membranes for separations, and modulators for drug delivery.^[43]

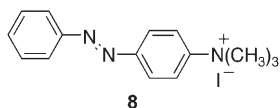
Studies on the stimuli-responsive gels began as early as the 1950s. Kuhn, Katchalsky, and co-workers found that water-swollen gels can reversibly expand and contract by successive addition of alkali and acid. An electrostatic repulsion along the polymer chain is induced by ionization of carboxyl groups of a polyacid and causes an expansion of the originally coiled polymer chain. The stretching and coiling behavior of the charged polymer gel can be translated from the submicroscopic to the macroscopic scale. Therefore, the polymer gels act as a mechanochemical system, which converts chemical energy directly into mechanical energy.^[44–46]

A gel system consisting of a low-molecular-weight chrysophenine dye (**7**) and a water-swollen gel of poly(2-hydrox-



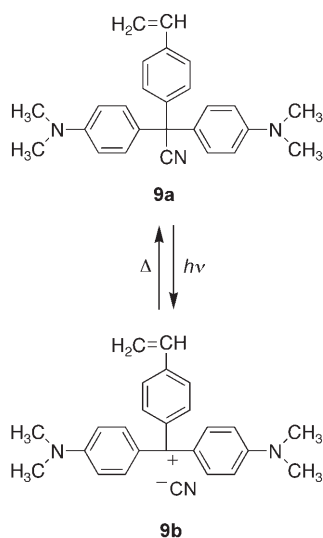
ethyl methacrylate) cross-linked with ethylene glycol dimethylacrylate was prepared by van der Veen and Prins.^[47] The polymer gel was found to contract upon irradiation with UV light, because the *trans*–*cis* isomerization decreases the hydrophobicity of the dye, which leads to liberation of the dyes from the polymer chain into the surrounding solution. The same type of the photoinduced deformations was also observed in cross-linked poly(methacrylic acid) on which chrysophenine was adsorbed.^[48]

In contrast, adsorption of the positively charged dye 4-phenylazophenyl trimethylammonium iodide (**8**) to the cross-linked poly(methacrylic acid) film led to the reverse of the photoresponsive behavior described above.^[49] Swelling occurred upon irradiation with UV light, whereas the sample



relaxed and contracted in the dark. The aqueous polymeric acid gel and the positively charged *trans* isomer take on a more hydrophobic, globular conformation. After irradiation with UV light, the more soluble *cis* isomer is formed. As a result, the polymer relaxes to an extended conformation and the sample swells.

Irie and co-workers demonstrated that triphenylmethane leuco derivatives of polyacrylamide gels (**9**) exhibit a large reversible deformation (Scheme 2).^[50–53] Triphenylmethane leuco derivatives dissociate into ion pairs upon irradiation



Scheme 2. Photochemical reaction of leuco derivative.

with UV light and intensely colored triphenylmethyl cations are produced. Upon irradiation of the triphenylmethane leuco derivatives of polyacrylamide gel with UV light, the weight of the gel increased by as much as 13 times, and the swollen gel contracted in the dark and regained its initial weight.^[51] Furthermore, photoinduced reversible bending under an electric field of rod-shaped polyacrylamide gels with leucocyanide functions was observed.^[52] In the dark, the gel showed no change in shape at an electric field of 10 V cm^{-1} , whereas upon irradiation with UV light the gel bent within 1 minute (Figure 2). The ends of the gel moved

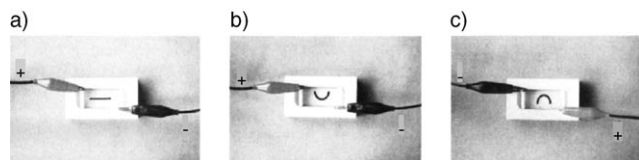


Figure 2. Photoinduced reversible bending of a rod-shaped polyacrylamide gel under an electric field: a) before photoirradiation; b) under irradiation with UV light; c) under irradiation with UV light in the reverse electric field to that in (b).

toward the electrode. When the polarity of the electric field was changed, the gel again became straight and then bent in an opposite direction (Figure 2). The response time of this change in the gel shape was around 2 minutes. The bending of the gel in response to the change in polarity could be repeated many times under UV irradiation. After the light was switched off, the gel slowly returned to its initial (straight) shape in the electric field. This result suggests that photo-dissociation of the leucocyanide moiety in the gel is responsible for the bending motion of the gel.

An *N*-isopropylacrylamide (NIPA) gel undergoes a volume change upon heating.^[54,55] A photoresponsive NIPA gel was first prepared by incorporating a small amount of trisodium salt of copper chlorophylline into the gel. The gel was shown to undergo a phase transition upon exposure to visible light; this transition was due to local heating of the gel by absorption of light by the dye molecule, followed by elimination of heat by a nonradiative process.

2.3. Polymers

Polymers are one of the most superior materials in view of their high processability, ability to form self-standing films with thicknesses from nanometers to centimeters, lightweight, flexibility in molecular design, and precisely controllable synthesis. Many kinds of polymers have been put to practical use in daily life and industry. From this point of view, polymer actuators capable of responding and deforming in response to external stimuli are most desirable for practical applications. Various chemical and physical stimuli have been applied to induce deformation of polymer actuators, for example, temperature changes,^[56] electric fields,^[57,58] and solvent composition.^[59]

The use of structural changes of photoisomerizable chromophores to change the size of polymers was first proposed by Merian.^[60] He observed that a nylon filament fabric dyed with an azobenzene derivative shrank upon photoirradiation. This effect is ascribed to the photochemical structural change of the azobenzene moiety adsorbed on the nylon fibers. However, the observed shrinkage was very small (only about 0.1 %), and, subsequent to this work, much effort was made to find new photomechanical systems with an enhanced efficiency.^[15,61]

Eisenbach investigated the photomechanical effect of poly(ethyl acrylate) networks (**10**) cross-linked with azobenzene moieties and observed that the polymer network contracted upon exposure to UV light (caused by *trans*–*cis* isomerization of the azobenzene cross-links) and expanded upon irradiation with visible light (caused by *cis*–*trans* back-isomerization; Figure 3).^[62] This photomechanical effect is mainly due to the configurational change of the azobenzene cross-links by the *trans*–*cis* isomerization of the azobenzene chromophore. However, the degree of deformation was small (0.2 %).

Matějka et al. synthesized several types of photochromic polymers based on a copolymer of maleic anhydride and styrene with azobenzene moieties both in the side chains and in the cross-links of the polymer network.^[63–65] The photo-

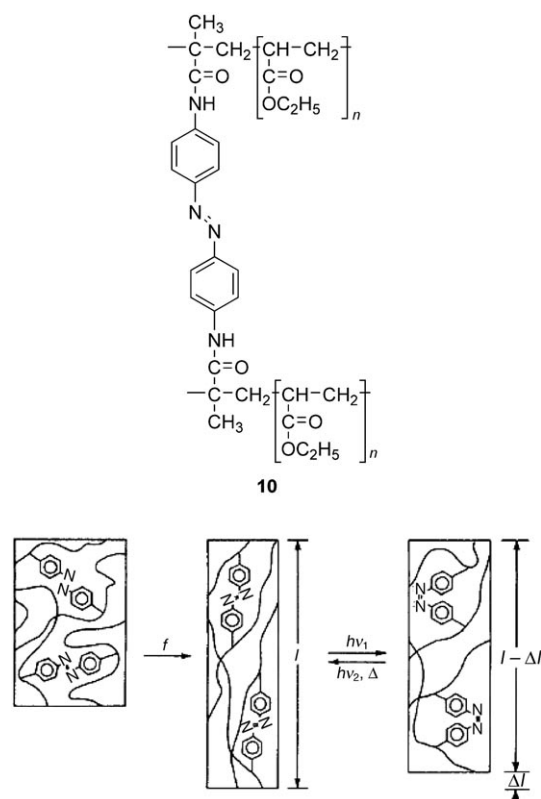
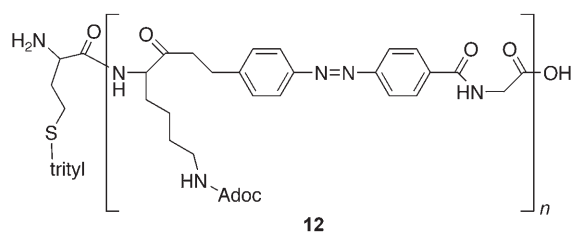


Figure 3. Photomechanical effect in a poly(ethyl acrylate) network with azobenzene cross-links upon irradiation. f = force.

mechanical effect was enhanced by an increase in the number of photochromic groups, and the photoinduced contraction of the sample amounted to 1% for a polymer with 5.4 mol % azobenzene moieties.

The photoinduced expansion of thin films of polymers (**11**) containing azobenzene chromophores was explored in real time by single-wavelength ellipsometry (Figure 4).^[66] The initial expansion of the azobenzene polymer films of thickness ranging from 25 to 140 nm was irreversible and amounted to 1.5–4%. Subsequent, reversible expansion was observed with repeated irradiation cycles; the relative expansion was 0.6–1.6%.

The recent development of single-molecular force spectroscopy by atomic force microscopy (AFM) techniques has enabled measurement of the mechanical force produced at a molecular level. Gaub and co-workers synthesized a polymer with azobenzene moieties in its main chain (**12**; Adoc = 1-adamantyloxycarbonyl).^[67,68] They coupled the ends of the



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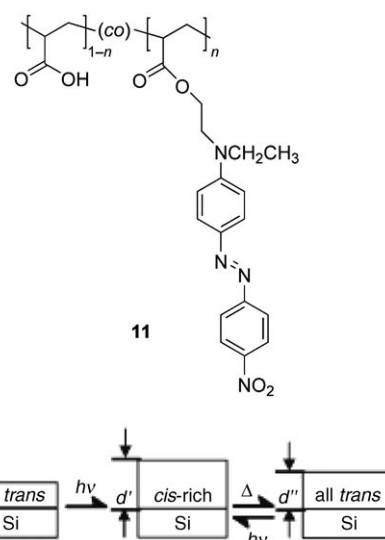


Figure 4. Photoexpansion effect in the thin films.

polymer covalently to the AFM tip and a supporting glass substrate through the formation of Au–S bonds to ensure stable attachment and investigated the force (pN) and extension (nm) of a single polymer in total internal reflection geometry by using the slide glass as a wave guide. This excitation method is very useful for avoiding thermomechanical effects on the cantilever. They were able to lengthen and contract individual polymer chains photochemically by switching the azobenzene moieties between their *trans* and *cis* forms by irradiation with UV ($\lambda = 365$ nm) and visible ($\lambda = 420$ nm) light, respectively. The mechanical work (W) performed by the azobenzene polymer strand by *trans*–*cis* photoisomerization was approximately 4.5×10^{-20} J. This mechanical work at the molecular level results from a macroscopic photoexcitation, and the real quantum efficiency of the photomechanical work for the given cycle in their AFM setup was only on the order of 10^{-18} . However, a maximum efficiency of the photomechanical energy conversion at a molecular level can be estimated as 0.1, if it is assumed that each switching of a single azobenzene unit is initiated by a single photon with an energy of 5.5×10^{-19} J ($\lambda = 365$ nm).^[67,68]

Photoinduced reversible changes in elasticity of semi-interpenetrating network films bearing azobenzene moieties (components **13a,b**) were achieved by irradiation with UV and visible light.^[69] The network films were prepared by cationic copolymerization of azobenzene-containing vinyl ethers in a linear polycarbonate matrix. The network film showed reversible deformation by switching the UV light on and off. The photomechanical effect is attributed to a reversible change between the highly aggregated and disassociated state of the azobenzene groups (Figure 5).^[69–71]

Photomechanical effects have been also explored in detail in other photochromic polymers. Smets et al. studied the mechanical properties of polymer matrices containing spirobenzopyran (**14**) cross-links.^[61] Irradiation with UV light caused isomerization from the spiropyran (closed form) to the merocyanine (open form) and a contraction of more than 2% under isothermal conditions. In the dark, the sample reverted

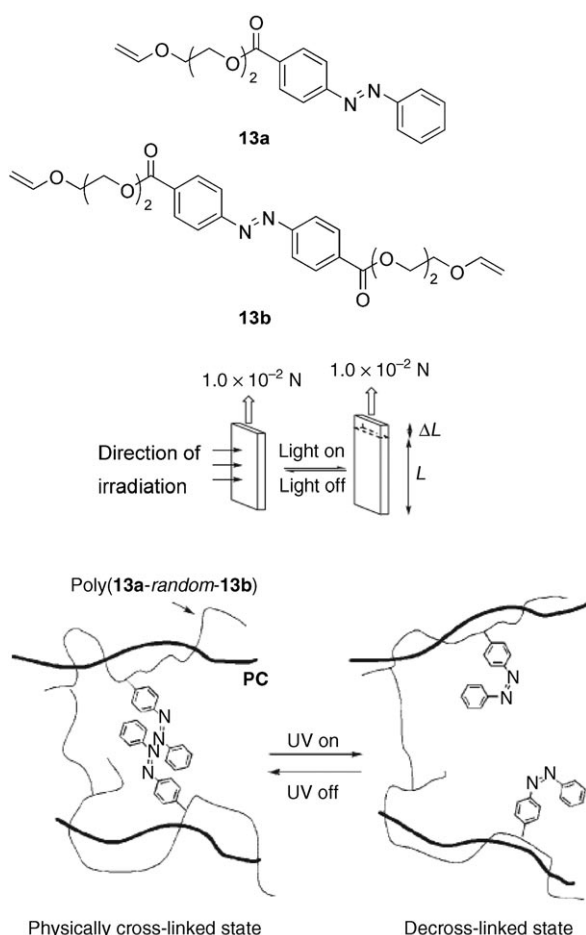
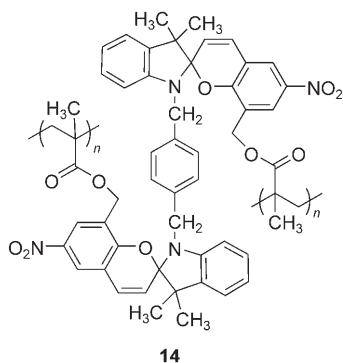
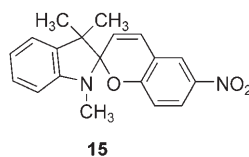


Figure 5. A model for the photoinduced change in the elasticity.



to its initial length.^[61,72,73] The photomechanical response of polystyrene and poly(methyl methacrylate) doped with a spiropyrans derivative (**15**) was investigated by Blair and



Pogue.^[74] They studied the effects of the photoisomerization of the photochromic dopant on the stress of the polymer sample. Upon exposure to UV light to cause the spiropyran–merocyanine isomerization, the initial stress applied to the sample decreased, which indicates expansion of the sample, whereas, in the dark, the length of the sample recovered its initial state by subsequent contraction, which was evidenced by an increase in stress. The spiropyran chromophore exhibited a different effect on the polymer substrates by spiropyran–merocyanine isomerization depending on the site of incorporation: when it is located at the cross-links, it induces contraction of the polymer; when doped into polymer matrices, it causes relaxation of the polymer substrate, which results in a decrease in stress.

In this respect, Athanassiou et al. reported a very interesting result on the effect of photoisomerization of a spiropyran dopant on the photomechanical phenomena of a polymer.^[75] They prepared a polymer film of poly(ethyl methacrylate-*co*-methyl acrylate) doped with 5.0 wt % spiropyran derivative. Figure 6 shows the deformation behavior of

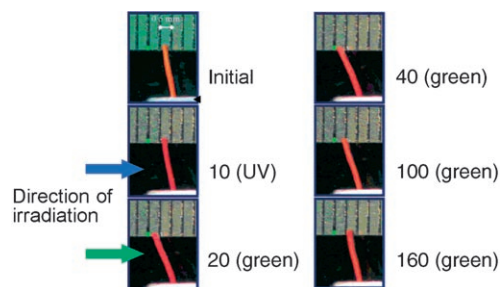
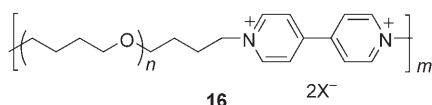


Figure 6. Bending cycle of a spiropyran-doped polymer film. The photographs were taken after irradiation of the film with the number of laser pulses shown.

this film (70 μm thick) upon exposure to laser pulses (UV pulses at $\lambda = 308$ nm with a pulse width of 30 ns and visible (green) pulses at $\lambda = 532$ nm with width of 5 ns) at an intensity of 70 mJ cm^{-2} . Upon exposure to green light, the film bent in the direction of the laser source. The maximum bending was observed after 40 pulses, and continuing green pulses led to the recovery of the film after 160 pulses. However, no deformation was observed when the sample was irradiated with green laser pulses without the preceding UV pulses. The volume remained unaffected by the initial UV pulses, which cause the spiropyran–merocyanine isomerization; only the green pulses caused the contraction and recovery. Thus, they concluded that the formation of the merocyanine does not correspond directly to the bending behavior. By fluorescence spectroscopy, they interpreted the bending behavior of the film in terms of the formation of aggregates of merocyanine isomers. The decrease in the effective partial molar volume of the merocyanine molecules owing to formation of aggregates results in an increase in the effective free volume of the polymer, which leads to a decrease in the effective glass-transition temperature (T_g) and allows a greater motion of the

polymer chains, thus causing macroscopic contraction. Continuous irradiation with pulses of green light causes merocyanine–spiropyran back-isomerization, which destroys the aggregation, and the film recovers its initial volume. The photomechanical effects occurring in polymers doped with spiropyrans seem to be more complicated than those observed in the azobenzene-containing systems.

Viologen is an organic chromophore that is susceptible to oxidation–reduction reactions. Under suitable conditions, irradiation with light leads to reduction of the colorless dication to a green or violet radical cation. The photomechanical effect on the relaxation behavior of the stress of the viologen polymer (**16**) in a dry solid state was inves-



tigated.^[76,77] This phenomenon was considered to be induced by a decrease in the total number of ionic charges of the polymer by photoreduction of the viologen groups, followed by a change in the state of ionic clustering in the polymer matrix.

Ahir and Terentjev reported a unique phenomenon of the photoinduced mechanical actuation in polymer composites consisting of poly(dimethylsiloxane) and multiwalled carbon nanotubes under infrared irradiation.^[78] At small strains, the sample expanded upon irradiation to a size that is orders of magnitude larger than the initial polymer; at larger strains, the sample contracted. This behavior is dependent on the orientation of nanotubes within a homogenous polymer matrix and is modeled as a function of orientational ordering of nanotubes induced by the uniaxial extension.

Lendlein et al. prepared polymers containing cinnamic acid groups (**17**).^[79] Similar to thermally induced shape-memory polymers, the photoresponsive polymer film was first stretched by an external force. Then exposure to UV light with $\lambda > 260$ nm led to fixation of the elongated shape by a photoinduced [2+2] cycloaddition reaction. After the external stress was released, the film stayed in the elongated form for a long period of time. Irradiation of the elongated sample with UV light with $\lambda < 260$ nm at ambient temperature brought about the cleavage of the cross-links and the recovery of the original shape of the film (Figure 7). When only the top of a polymer film in a stretched state was irradiated with UV light of $\lambda > 260$ nm, a spiral shape was obtained. Two layers are formed: the elongation is fixed well for the top layer and the bottom layer retains its elasticity (Figure 7).

An interesting mode of deformation of polymer colloidal particles by light was reported by Wang and co-workers.^[80] They observed that the spherical polymer particles containing azobenzene moieties changed from a sphere into an ellipsoid upon exposure to interfering linearly polarized laser beams. The elongation of the particles was induced along the polarization direction of the laser beam.

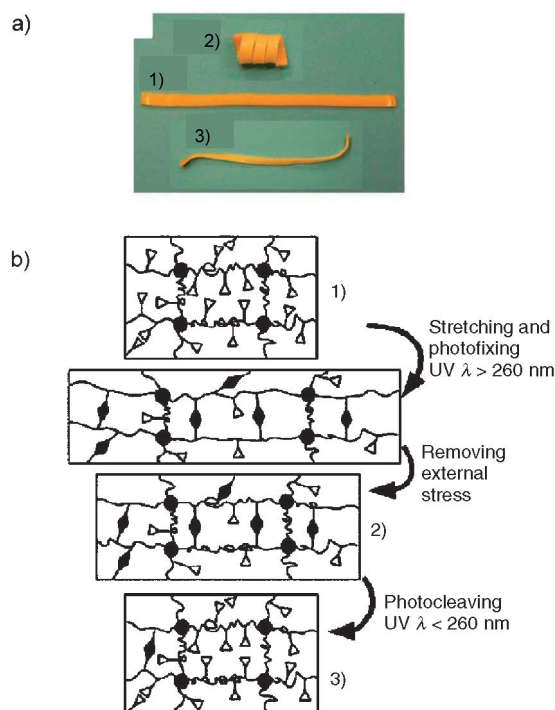
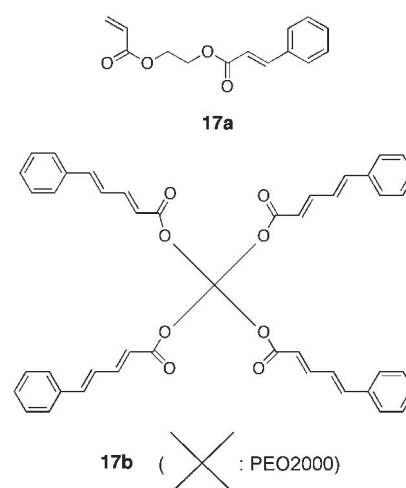


Figure 7. Shape-memory effect of photoresponsive polymers: a) A polymer film doped with **17b**: 1) original shape; 2) a corkscrew shape obtained; 3) the original shape recovered by photoirradiation at $\lambda < 260$ nm. b) Mechanism of the shape-memory effect of the grafted polymer network.

As mentioned above, azobenzene-containing gels and polymer films are especially interesting for applications. However, previous studies have shown that in general the response of the gels is slow and the degree of deformation of the polymer films is too small to be practically utilized. Therefore, it is of great importance to develop novel photomechanical systems that can undergo fast and large deformations. The gels and polymer films used in the studies described above were amorphous, without microscopic or macroscopic order, and thus their deformations are isotropic. If materials with anisotropic physical properties are used, the mechanical power produced could increase significantly.

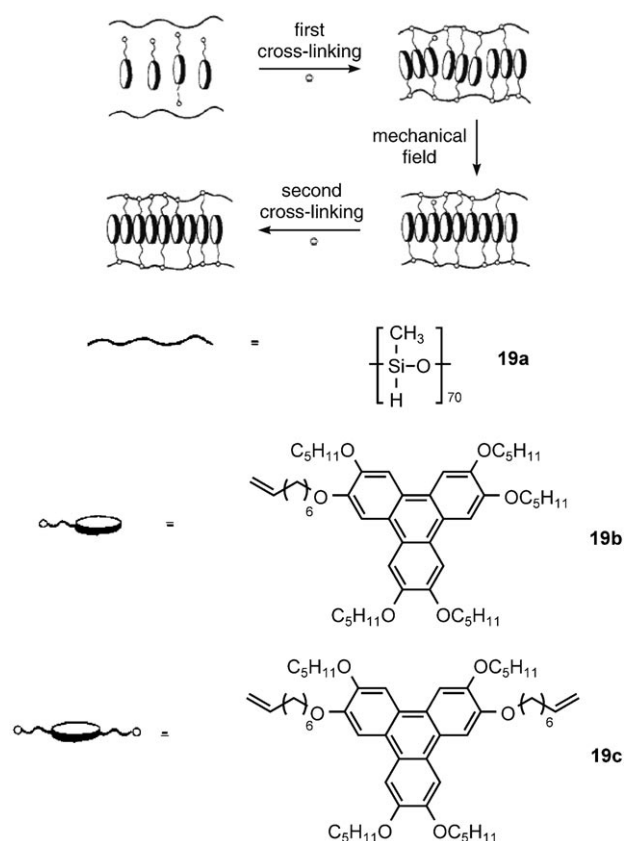


Figure 9. Synthesis of discotic LCEs.

mesogens when the alignment of mesogens before polymerization was low.

Serrano and co-workers studied the photopolymerization of mixtures of mono- and difunctional LC monomers to yield polymer materials with differing degrees of cross-linking.^[113] Oriented films can be prepared by controlling the alignment of the monomers. The birefringence of photopolymerizable samples and polymer films, as well as its temperature dependence, was evaluated. The birefringence of the films increased as the content of the monofunctional LC monomer increased.

Furthermore, LCEs have been prepared by block copolymerization and hydrogen bonds.^[114,115] Li et al. proposed a muscle-like material with a lamellar structure based on a nematic triblock copolymer (components **20a–c**, Figure 10). The material consists of a repeated series of nematic (N) polymer blocks and conventional rubber (R) blocks.^[114] The synthesis of block copolymers with well-defined structures and narrow molecular-weight distributions is a crucial step in the production of artificial muscles based on triblock elastomers. Talroze and co-workers studied the structure and the alignment behavior of LC networks stabilized by hydrogen bonds under mechanical stress.^[116] They synthesized poly[4-(6-acryloyloxyhexyloxy)benzoic acid] (**21**), which exhibits a smectic LC phase over a broad temperature range. Addition of up to 10 mol % of any low-molecular-weight benzoic acids and, as a result, the formation of mixed dimers does not influence the smectic C_A structure (Figure 11). The amor-

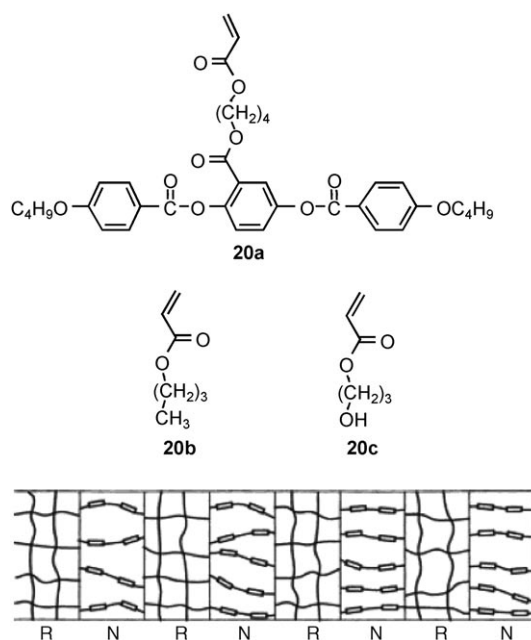


Figure 10. Chemical structures of a side-on nematic monomer (**20a**) and a striated artificial muscle with a lamellar structure based on a nematic triblock copolymer, RNR.

phous azopyridine polymer can easily be converted to LC polymers through hydrogen bonding with a series of commercially available aliphatic and aromatic carboxylic acids.^[117] The pure acids have only a crystal phase that melts at high temperatures; after mixing them with the azopyridine polymer, the complex formed showed a new LC phase. This observation is strong evidence for the formation of hydrogen-bonded complexes, because neither the pure acids nor the azopyridine polymer show any LC phase.

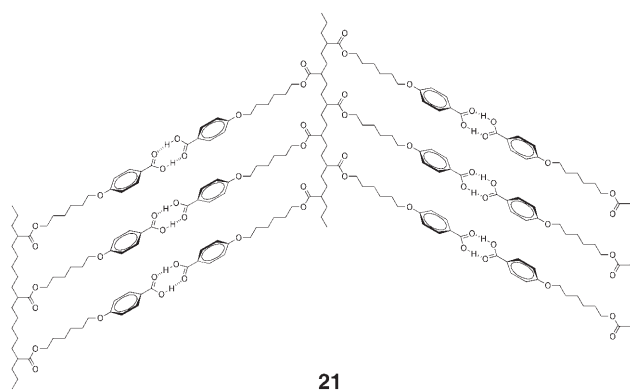


Figure 11. Plausible structure of polymer network based on H-bonded rodlike dimers formed by carboxyl monomer units incorporated in the polymer side chains.

3.2. Deformation of Liquid-Crystalline Elastomers by External Stimuli

Anisotropic deformation of monodomain LCEs by a thermal phase transition from an LC into an isotropic state

was first reported by K pfer and Finkelmann.^[18] A nematic LCE prepared by the two-step process contracted by about 26% owing to the change in order parameter as a result of the change in molecular alignment of mesogens.^[18] This anisotropic deformation behavior of LCEs has been a subject of extensive experimental and theoretical studies.^[118–120] The possibility of using LCEs as artificial muscles, by taking advantage of their substantial uniaxial contraction in the direction of the director axis, was proposed by de Gennes.^[91] The origin of the contraction is a subtle decrease in microscopic order upon nematic–isotropic phase transition; however, this deformation is closely related to coupling between the LC order of mesogens and the elastic properties of the polymer network. Warner and Terentjev established a relation between the nematic order parameter S and the effective backbone anisotropy of polymer chains forming the rubbery network. The relation is expressed by a dimensionless ratio of the principal step lengths parallel and perpendicular to the nematic director ($R_{\parallel}/R_{\perp}$).^[83,88] In the nematic phase, this ratio is larger than unity ($R_{\parallel}/R_{\perp} \approx 1.3$),^[83] but, after a nematic–isotropic phase transition, this ratio approaches unity as a result of the formation of a random coil of polymer chains, which makes the polymer material contract along the director axis of LCEs. In the smectic A phase, the ratio $R_{\parallel}/R_{\perp}$ is in general smaller than unity because the polymer chains are likely to exist between the smectic layers.^[84]

There have been a number of efforts to develop artificial muscle-like materials.^[19,114,121–126] LCE films with a splayed or twisted molecular alignment display a well-controlled deformation as a function of temperature (Figure 12).^[124] The twisted films show a complex macroscopic deformation owing to the formation of saddle-like geometries, whereas the deformation of the

splayed structured is smooth and well controlled.^[124] Wermter and Finkelmann reported a new type of LC coelastomers composed of LC side chains and LC main-chain polymers (components **23a–c**) as network strands.^[19] Thanks to the direct coupling of the LC main-chain segments to the network anisotropy, the thermoelastic response was increased remarkably with an increase of the concentration of these segments. An elongation in the direction of the director by up to a factor of 4 relative to the length of the networks in an isotropic state

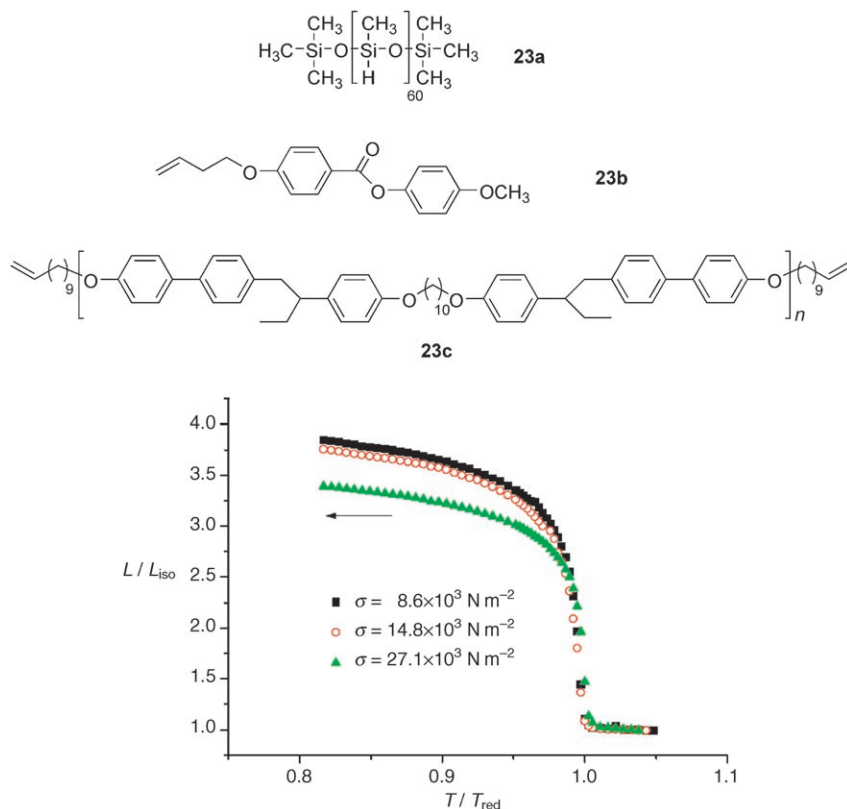


Figure 13. Thermoelastic response of an LCE prepared from **23**. σ : mechanical field; L : length of the network in the nematic state; L_{iso} : length of the network in the isotropic state; T_{red} : reduced temperature.

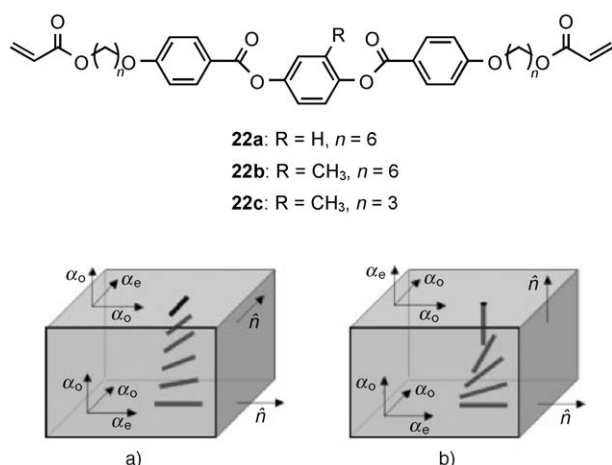


Figure 12. LCE films with a splayed or twisted molecular alignment. a) Twisted; b) splayed. $\hat{n}$: director; α_o , α_e : perpendicular and parallel coefficients of thermal expansion.

was observed in the nematic state (Figure 13).^[19] Ratna and co-workers prepared LCEs with laterally attached side-chain mesogens (**24**) and studied their thermoelastic properties across a nematic–isotropic phase transition.^[122] The LCEs showed a large contraction (strain change) of 35–40% through the phase transition, and the maximum retractive force generated was 270 kPa, which is comparable to that of a skeletal muscle (Figure 14). This increase in the stress during the isostrain measurements is related to the entropy change of the polymer chains and was interpreted as a result of the initial work of the wormlike (prolate) to coil transition in the polymer backbones with laterally coupled mesogenic side chains.

Skeletal muscles are anisotropic, that is, they exhibit contraction and elongation along the fiber axis. Naciri et al. described a method of preparing LC fibers from a side-chain LC terpolymer containing two side-chain mesogens and a nonmesogenic group that acts as a reactive site for cross-linking (Figures 14 and 15).^[123] Fibers were drawn from a melt

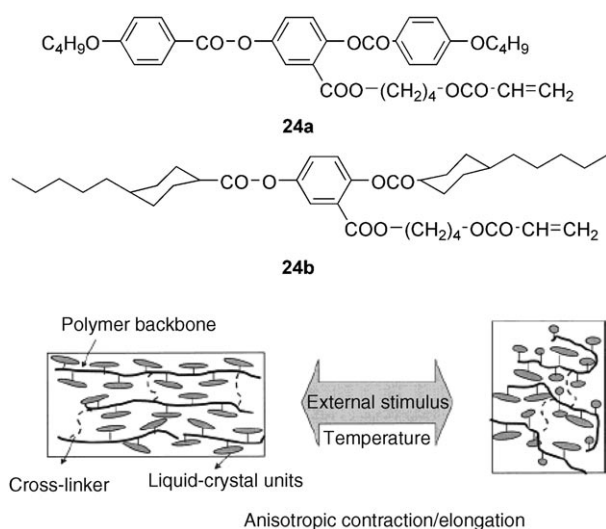


Figure 14. LCEs with laterally attached side-chain mesogens and their deformation behavior.

of the polymer and a cross-linker. The fibers formed showed high LC alignment when observed by polarizing optical microscopy. The thermoelastic response exhibited strain changes through the nematic–isotropic phase transition of about 35 %. A retractive force of nearly 300 kPa was also observed in the isotropic phase.

Many kinds of external stimuli have been applied to induce deformation of LCEs, such as electric field and humidity.^[107,127] Kremer and co-workers developed a new material that showed high and fast strains of 4 % by electrostriction under a much lower applied electric field (by 2 orders of magnitude) than those reported previously. It consists of ultrathin ferroelectric LCE films, which exhibited 4 % strain at only 1.5 MV m^{-1} (Figure 16).^[107] The thinning of the film by 4 % in the ferroelectric LCE corresponds to an electrically induced tilt angle of $\theta = 16^\circ$ in the sample cosine model. If the molecular tilt is regarded as the cause of the spontaneous polarization in the ferroelectric smectic C^* phase, an externally induced electric polarization may in turn be used to induce a tilt θ of the mesogenic side chains in the paraelectric smectic A^* phase. This electrically induced tilt (electroclinic effect) of the mesogens is proportional to the externally applied electric field.

Broer and co-workers proposed pH- or water-con-

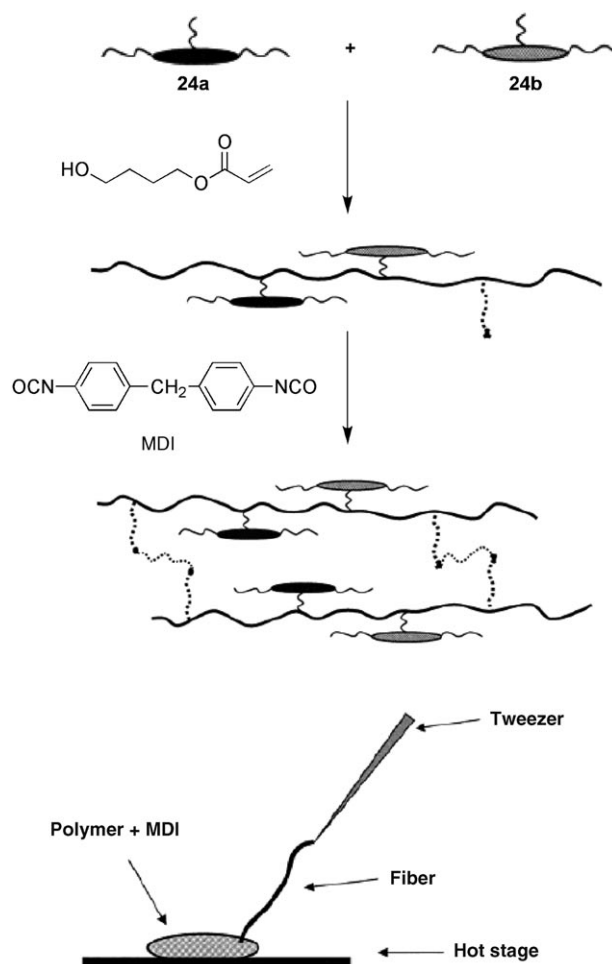


Figure 15. Preparation of the LCE fiber. MDI: 4,4'-methylenebis(phenyl isocyanate).

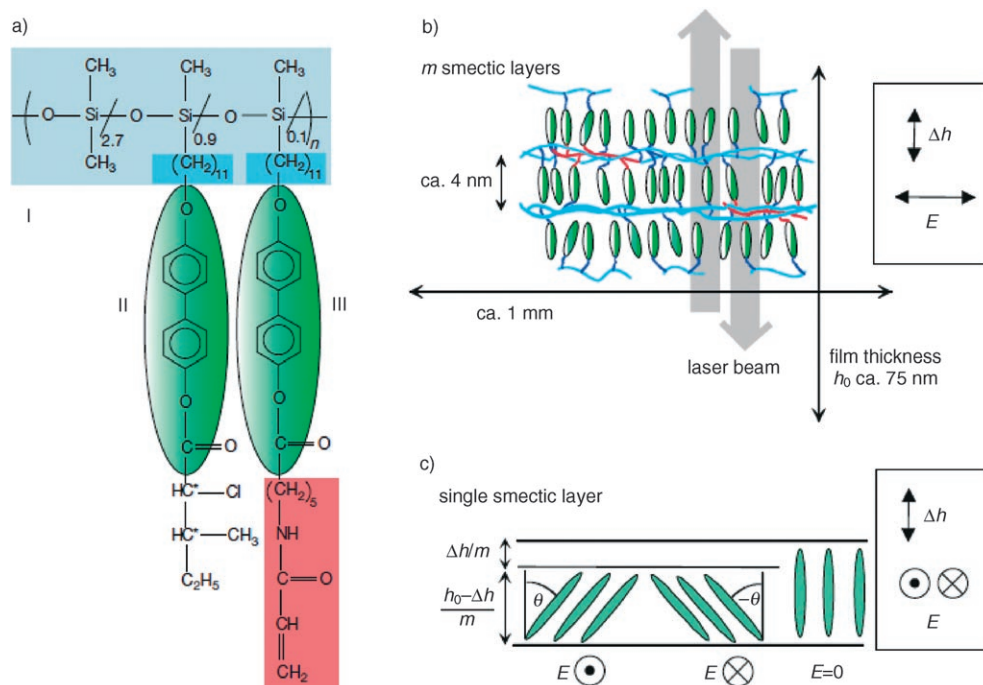


Figure 16. Electroclinic effect in ferroelectric LCEs: a) Chemical structure of sample. b) Measurement geometry: The beam in the interferometer passes twice through the film to measure the electrically induced thickness modulation. c) The viewing angle is turned by 90° around the layer normal relative to that in (b).

trolled actuators based on two simple concepts: an aligned LC network consisting of both covalent and secondary bonds, and stimulus-controlled molecular switching between acidic and neutral states (Figure 17).^[127] The uniaxially aligned film responded equally to water or pH changes in all regions of the

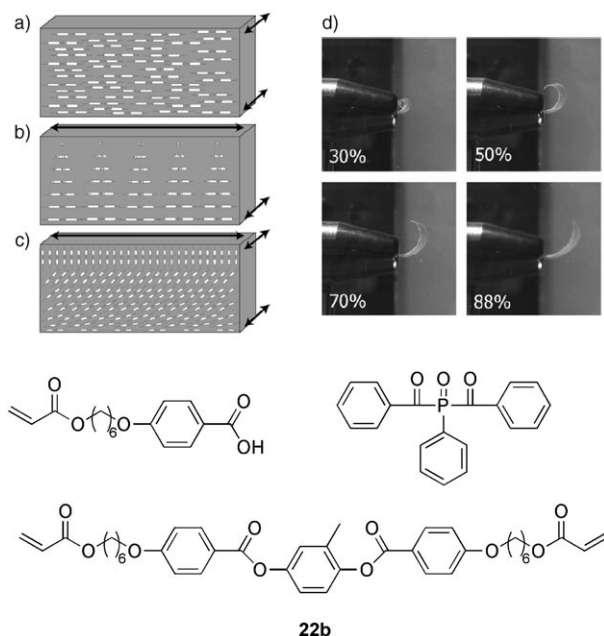


Figure 17. Director-orientation configurations for bending motion: a) uniaxially, b) twisted, and c) splayed aligned network film. The arrows indicate the preferred expansion directions. d) Photographs of the twisted film under the relative humidity conditions shown.

film and only elongated by a small amount when exposed to a uniform stimulus. Differences in the pH value or humidity of the upper and lower surfaces induced a large degree of bending of the film. The twisted and splayed configurations do not require environmental gradients to produce macroscopic motion. In both cases, the preferred expansion directions on the opposite sides of the film were offset by 90°, and a uniform stimulus resulted in expansion gradients over the thickness of the film and bending behavior similar to the thermal deformation in a metallic bilayer.

Yusuf et al. investigated the swelling behavior of the LCE films in low-molecular-weight LCs.^[128–130] Figure 18 shows the shape changes of dry LCEs during heating and cooling of planar and homeotropic samples. The planar sample contracted parallel to the director and expanded perpendicular to the director upon heating. The homeotropic sample expanded on heating. All samples reverted to their initial shapes upon cooling. Furthermore, the swelling behavior of both polydomain and monodomain LCE films was studied. Polydomain LCEs swell equally in all three dimensions, whereas monodomain LCEs swell isotropically in only two dimensions, but not in three dimensions.

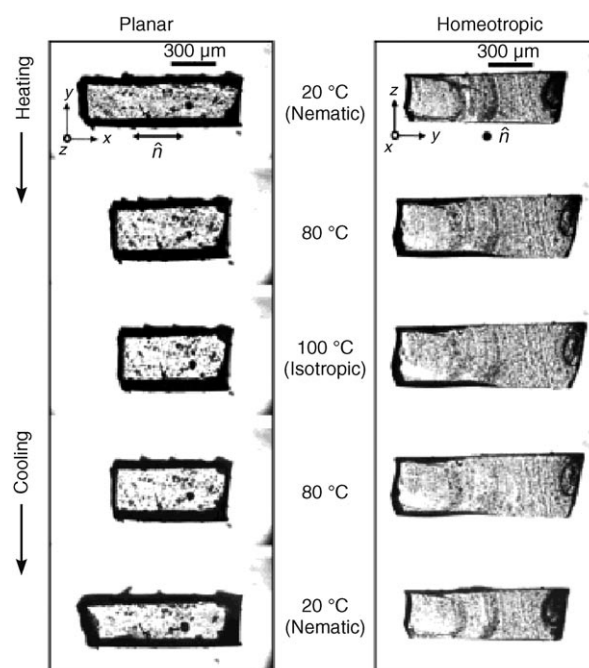


Figure 18. Shape change of an LCE (planar and homeotropic samples) as a function of temperature.

3.3. Photoresponsive Behavior of Liquid Crystals Containing Photochromic Molecules

Cooperative motion of molecules in LC phases may be most advantageous in changing the molecular alignment by external stimuli. If a small portion of LC molecules change their alignment in response to an external stimulus, the other LC molecules also change their alignment. This phenomenon means that only a small amount of energy is needed to change the alignment of all LC molecules: the energy required to induce an alignment change of only 1 mol% of the LC molecules is enough to bring about the alignment change of the whole system. In other words, a huge amplification is possible in LC systems. When a small amount of a photochromic molecule such as an azobenzene, stilbene, spiro-pyran, or fulgide derivative is added to LCs and the resulting guest/host mixture is irradiated to cause photochemical reactions of the photochromic guest molecules, an LC–isotropic phase transition of the mixtures can be induced isothermally. The *trans* form of the azobenzenes, for example, has a rodlike shape, which stabilizes the phase structure of the LC phase, whereas its *cis* isomer is bent and tends to destabilize the phase structure of the mixture. As a result, the LC–isotropic phase transition temperature (T_c) of the mixture with the *cis* form (T_{cc}) is much lower than that with the *trans* form (T_{ct}) (Figure 19). If the temperature of the sample (T) is set at a temperature between T_{ct} and T_{cc} and the sample is irradiated to cause *trans*–*cis* photoisomerization of the azobenzene guest molecules, T_c decreases with an accumulation of the *cis* form. When T_c becomes lower than the irradiation temperature T , an LC–isotropic phase transition of the sample is induced. Photochromic reactions are usually reversible, so the sample reverts to the initial LC

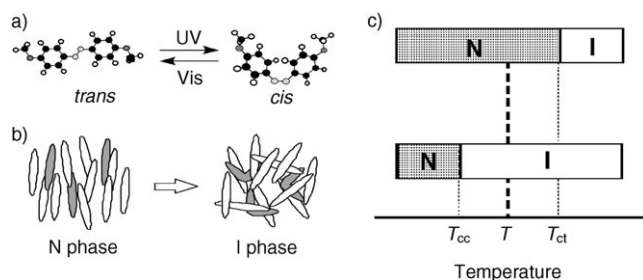


Figure 19. Photoisomerization of a 4,4'-disubstituted azobenzene derivative (a) and phase diagram of the photochemical phase transition of azobenzene/LC systems (b, c). N, nematic; I, isotropic.

phase through *cis*–*trans* back-isomerization. Thus, phase transitions of LC systems can be induced isothermally and reversibly by photochemical reactions of photoresponsive guest molecules (Figure 19). Tazuke et al. reported the first explicit example of a nematic–isotropic phase transition induced by *trans*–*cis* photoisomerization of an azobenzene guest molecule dispersed in a nematic LC.^[131]

Advantages of using photochromic molecules as a trigger include:

- 1) Such molecules change their molecular shapes upon photoirradiation, which usually leads to changes in other properties such as polarity.
- 2) Photochromic reactions are reversible; thus, two isomers can be interchanged effectively by light with different wavelengths.
- 3) Photochromic reactions are very fast in most cases and occur on a timescale of picoseconds (ps).

The photochemically induced phase transitions (“photochemical phase transitions”) are interpreted in terms of a change in the phase-transition temperature of LC systems upon accumulation of one isomer of the photochromic guest molecule.^[132, 133]

Various photochromic molecules have been examined for their ability to induce phase transitions upon photoirradiation. Kurihara et al. investigated the photochemical phase transition behavior of mixtures of spiropyran and nematic LCs and found that the merocyanine (open form), owing to its linear molecular shape, stabilizes the LC phase, whereas the spiropyran (closed form) destabilizes the LC phase.^[134] Photoirradiation with visible light of a mixture of merocyanine and a nematic LC to cause merocyanine–spiropyran isomerization induces a nematic–isotropic phase transition; irradiation with UV light caused the mixture to revert to its initial nematic phase.^[134]

Fulgides are extensively studied photochromic molecules. Allison and Glesson investigated the effect of photoisomerization on the T_c of a mixture of furylfulgide dispersed in a cyanobiphenyl nematic LC (E7) at a concentration of less than 2 wt %. The effect of photoirradiation on T_c was very small.^[135] They also studied the effect of photoisomerization on the physical properties of the nematic LC (dielectric constants^[136] and elasticity^[137]) and ascribed the observed change in these properties to the change in T_c upon photoisomerization.

Photochromic reactions can also strongly influence the phase structures of various LCs. Ferroelectric LCs exhibit spontaneous polarization (P_s) and show microsecond responses to changes in applied electric fields in a surface-stabilized state (flip of polarization).^[138] A mixture of an azobenzene (**25b**; 3 mol %) and a ferroelectric LC (**25a**; Figure 20) was prepared in a very thin LC cell in a surface-

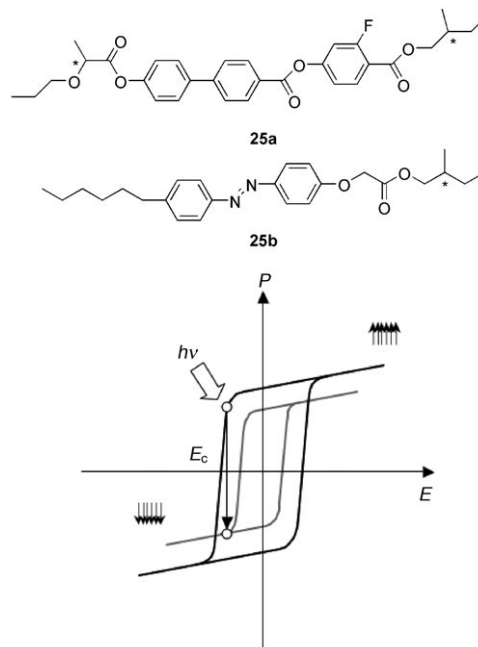


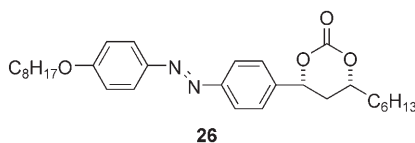
Figure 20. Photochemical flip of polarization in ferroelectric LCs.

stabilized state. The mixture was then irradiated with UV light ($\lambda = 366$ nm) to cause *trans*–*cis* photoisomerization of the azobenzene molecule. The threshold electric field for the flip of polarization (coercive force, E_c) of the ferroelectric LCs was changed upon photoirradiation.^[139] Ferroelectric LCs in the surface-stabilized state show a hysteresis between the applied electric field and polarization.^[138] The hysteresis of the *trans*-azobenzene/ferroelectric LC mixture was different from that of the *cis*-azobenzene/ferroelectric LC. This effect of molecular shape on the coercive force is very similar to that observed for the different T_c values of the azobenzene/nematic LC mixtures described above. In the azobenzene/ferroelectric LC mixture with the azobenzene in the *trans* form, the phase structure of the chiral smectic C phase of the ferroelectric LCs is not disorganized significantly. However, when the azobenzene is in the *cis* form, the phase structure of the smectic C* phase is seriously affected and the threshold value for the flip of polarization is reduced significantly as a result of the decrease in order. In view of these properties, a new mode of optical switching of ferroelectric LCs (photochemical flip of polarization of ferroelectric LCs) has been proposed (Figure 20).^[139, 140] A flip of polarization is induced at the irradiated sites, which leads to a change in alignment of the ferroelectric LCs. These changes in polarization and alignment of ferroelectric LCs produce an optical contrast

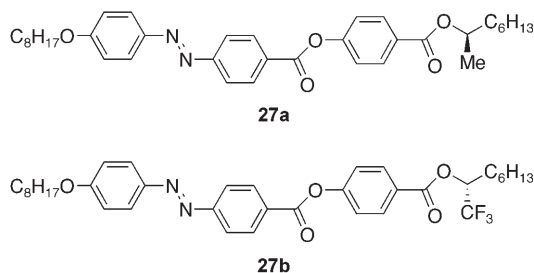
between the irradiated and nonirradiated sites, which remain unchanged (memory effect).

The flip of polarization in the photochromic guest/ferroelectric LC host systems has been investigated in detail. Studies include the effects of the structure of ferroelectric LC hosts,^[141a,b] the structure of photochromic guests,^[141c] temperature,^[141d] bias voltage,^[140] and the change in spontaneous polarization.^[141d] The photochemical flip of polarization was also examined in antiferroelectric LCs. It was found that the flip of polarization can be induced similarly in the azobenzene/antiferroelectric LC mixtures upon irradiation to cause *trans*–*cis* photoisomerization of the guest molecule.^[142]

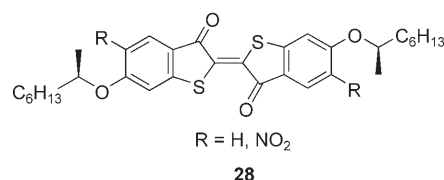
An azobenzene derivative was designed with a chiral cyclic carbonate group (**26**) to induce a large value of



polarization and examined as a chiral dopant to induce a smectic C* phase.^[143] In this system, the chiral dopant also acts as a photoresponsive molecule; therefore, it is expected that a change in molecular shape of the dopant would affect significantly the phase structure of the smectic C* phase because the molecular shape of the dopant is crucial for the induction of the smectic C* phase. The azobenzene with a cyclic carbonate is quite effective at inducing the photochemical flip of polarization of the ferroelectric LC mixture.^[143] Furthermore, azobenzene derivatives that exhibit antiferroelectric properties were developed and their photoresponsive behavior was examined (**27a,b**).^[144] The photochemical flip of polarization in these antiferroelectric LCs is induced very effectively,^[144] and a device fabricated with these antiferroelectric LCs was explored.^[145]



Another interesting approach to affect the properties of ferroelectric LCs is the use of a photochromic dopant that shows a large change in the dipole moment upon photoirradiation but a small change in its molecular shape.^[146,147] Thioindigo is a good candidate: it has two isomers with parallel (*cis* form) and antiparallel (*trans* form) arrangements of carbonyl moieties attached to α -carbon atoms of the double bond (**28**). The *cis* form possesses a large dipole moment owing to the parallel arrangement of the carbonyl moieties, whereas the antiparallel arrangement of the two



carbonyl moieties in the *trans* form produces a very small overall dipole moment. Furthermore, thioindigo shows a small change in its molecular shape upon isomerization. For these reasons, thioindigo derivatives are superior to other compounds as photoresponsive dopants in guest/ferroelectric LC systems. Photoirradiation of a mixture of thioindigo/ferroelectric LC at $\lambda > 550$ nm caused isomerization of the guest molecule and resulted in optical modulation of the spontaneous polarization of the ferroelectric LC mixture, which was enhanced 1.5-fold owing to an increase in dipole moment of the guest thioindigo molecule.^[146,147]

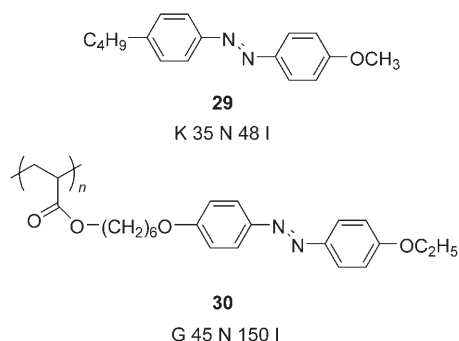
LC polymers possess properties of both polymers and LCs and currently are regarded as promising photonic materials because of their advantageous properties mentioned above. Heat-mode processes were exclusively employed in early studies of the photoresponsive behavior of LC polymers for optical image storage: exposure of LC polymer films to laser light increases the temperature at the irradiated sites and causes an LC–isotropic phase transition. Rapid cooling of the irradiated films below the T_g value of the polymer quenches the isotropic phase at the irradiated sites, thus producing a contrast between the irradiated and nonirradiated sites.^[148,149]

Wendorff and co-workers reported the first example of a photon-mode photoresponse in LC polymers, namely, holographic recording in LC polymer films containing azobenzene moieties and mesogenic groups.^[150,151] Ikeda et al. reported the first example of the photochemical phase transition in LC polymers; they demonstrated that irradiation of LC polymers doped with low-molecular-weight azobenzene derivatives with UV light to cause *trans*–*cis* isomerization led to a nematic–isotropic phase transition; upon *cis*–*trans* back-isomerization, the LC polymers reverted to the initial nematic phase.^[152–154] However, it soon became apparent that LC copolymers are superior to doped systems because phase separation was observed in the doped systems when the concentration of the photochromic molecules was high. A variety of LC copolymers were prepared, and their photochemical phase transition behavior was examined.^[154–157] One of the important factors of the photoresponsive LCs is their response to optical stimuli. In this respect, the response time of the photochemical phase transition has been explored by time-resolved measurements.^[156,158]

Photochromic reactions are in general very fast, occurring on a timescale of picoseconds. If an ultrafast laser with a pulse width on the picosecond scale is used as an excitation light source to induce phase transitions of LC systems containing photochromic molecules, photochemical reactions of the photochromic molecules can be completed within picoseconds, and the T_c of the system can be decreased below the irradiation temperature on this timescale. This means that immediately after pulse irradiation, a nonequilibrium state is

produced, which is thermodynamically an isotropic phase in its equilibrium state but shows an anisotropy because orientational relaxation of mesogens is not completed. The response of the whole LC system depends strongly on this orientational relaxation of the mesogens, which in fact is the rate-determining step, especially in highly viscous LC polymers that require a relatively long time.^[159]

A new system has been developed in which every mesogen in the LC or LC polymer is photosensitive.^[160–163] In azobenzene derivatives that form LC phases, the azobenzene moiety could play roles as both a mesogen and a photosensitive moiety (Scheme 3). These azobenzene LCs show a stable LC phase only when the azobenzene moiety is in the *trans* form, but show no LC phase when all the azobenzene moieties are in the *cis* form. Examination of these azobenzene LCs revealed that a nematic-isotropic phase transition is induced in the azobenzene LC polymers within 200 ns over a wide temperature range under optimized conditions.^[162]



Scheme 3. Azobenzene LCs.

3.4. Photomechanical Effect in Liquid-Crystalline Elastomers

Light is a clean energy source that can be controlled rapidly, precisely, and remotely. Therefore, photodeformable LCEs have attracted increasing attention. As described in Section 3.2, LCEs show thermoelastic properties: upon transformation from the nematic into the isotropic phase, they contract along the alignment direction of mesogens and upon cooling below the phase-transition temperature they expand. If this property of LCEs is combined with the photochemical phase transition (or photochemically induced decrease of nematic order), it is expected that deformation of LCEs can be induced by light.^[20–22] In fact, Finkelmann et al. succeeded in inducing a contraction by 20% of an azobenzene-containing LCE (components **31a–f**) upon exposure to UV light to cause the *trans*–*cis* isomerization of the azobenzene moiety (Figure 21).^[20] They synthesized monodomains of nematic LCEs with polysiloxane main chains and azobenzene chromophores at the cross-links. From the viewpoint of photomechanical effects, the subtle variation in nematic order upon *trans*–*cis* isomerization causes a significant uniaxial deformation of the LCs along the director axis when the LC molecules are strongly associated by covalent cross-linking to form a three-dimensional polymer network. Terentjev and co-work-

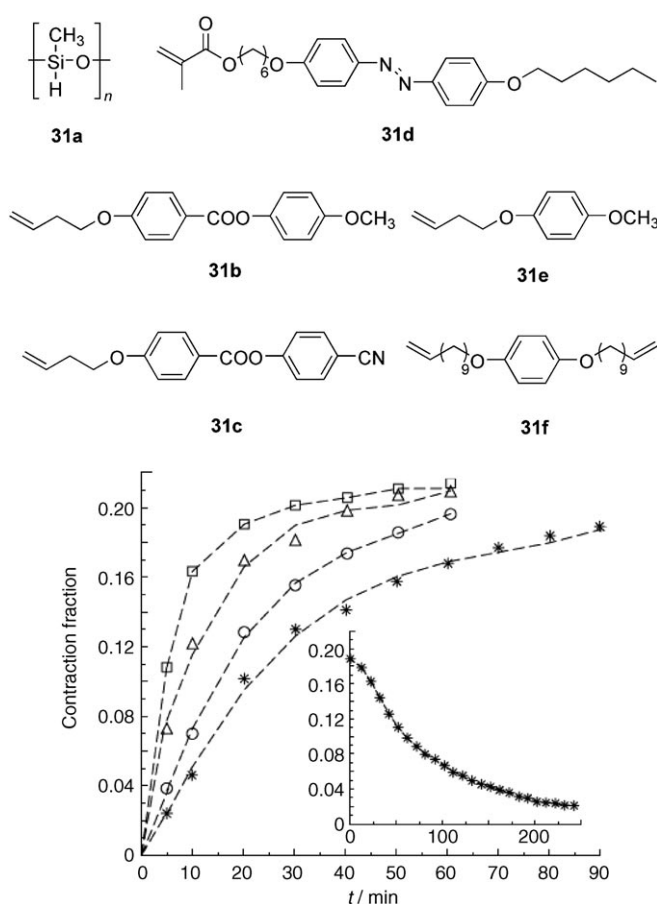
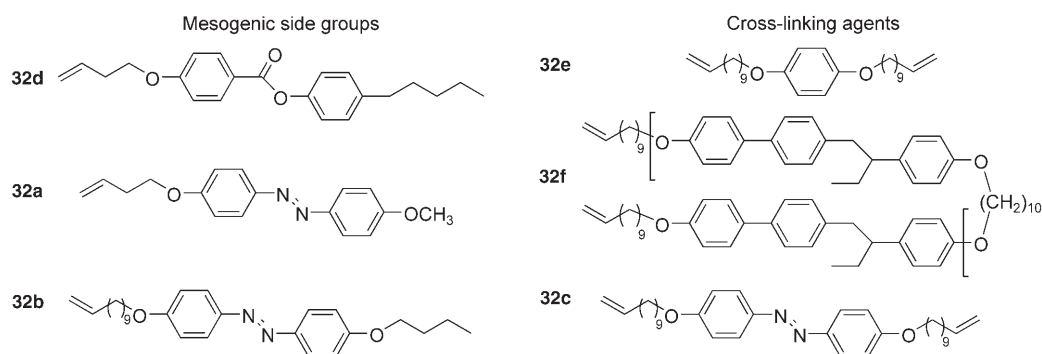


Figure 21. Photoinduced contraction of the LCE prepared from **31a–f**. □ = 313 K, △ = 308 K, ○ = 303 K, * = 298 K. Inset: recovery of the contracted LCE at 298 K after irradiation was switched off.

ers incorporated a wide range of azobenzene derivatives (**32a–c**) into LCEs as photoresponsive moieties and examined their deformation behavior upon exposure to UV light (Scheme 4).^[21,22]

Keller and co-workers synthesized monodomains of nematic azobenzene side-on elastomers (components **33a,b**) by photopolymerization with a near-infrared photoinitiator.^[164] The photopolymerization was performed on aligned nematic azobenzene monomers in conventional LC cells. Thin films of these LCEs showed fast (<1 minute) photochemical contraction of up to 18% upon irradiation with UV light and a slow thermal back reaction in the dark (Figure 22).

Three-dimensional movements of LCE films have been demonstrated. Ikeda and co-workers observed photoinduced bending behavior of LC gels^[23] and LCEs^[23,24,165,166] containing azobenzenes. The bending mode, which is a three-dimensional movement, could be advantageous in the construction of artificial hands and microrobots that are capable of particular manipulations. Figure 23 shows the bending and unbending processes induced by irradiation with UV and visible light, respectively. The monodomain LCE film bent along the rubbing direction toward the irradiation source, and the bent film reverted to the initial flat state upon exposure to visible light. This bending and unbending behavior was



Scheme 4. Azobenzene derivatives (**32a–c**) examined for their ability to induce deformation upon exposure to UV light, along with mesogenic group **32d** and cross-linking agents **32e,f**.

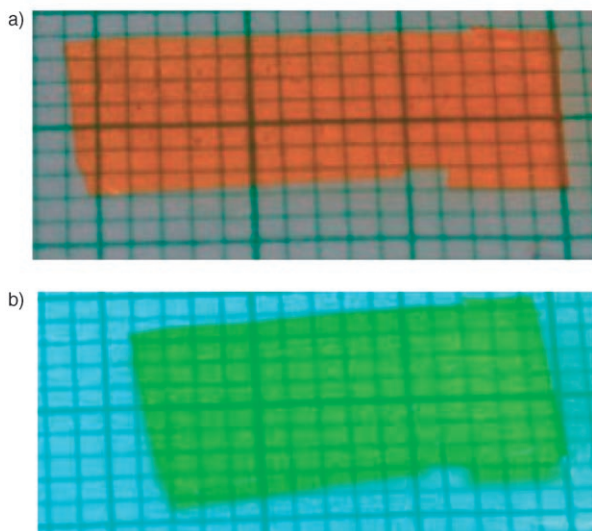
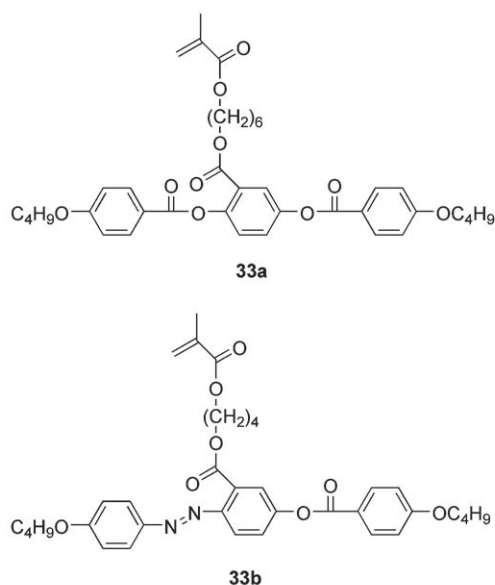


Figure 22. Photographs of photodeformation of azobenzene LCE before (a) irradiation and under (b) irradiation with UV light.

reversible and could be controlled by simply changing the wavelength of the incident light. Furthermore, when the film

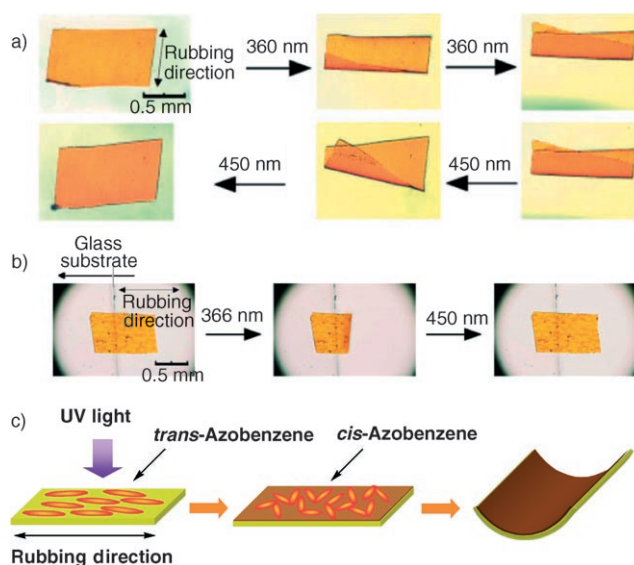


Figure 23. Bending and unbending behavior of an LC gel in toluene (a) and an LCE film in air (b). c) Plausible mechanism of the photo-induced bending of LCE films.

was rotated by 90°, the bending was again observed along the rubbing direction. These results demonstrate that the bending is anisotropically induced and occurs only along the rubbing direction of the alignment layers.

Irradiation with UV light gives rise to the *trans*–*cis* isomerization of azobenzene moieties and thus destabilization of the nematic phase (decrease in nematic order) even as far as to produce a nematic–isotropic phase transition of the LC systems, as mentioned in Section 3.3. However, the extinction coefficient of the azobenzene moieties at around 360 nm is large and thus more than 99% of the incident photons are absorbed by a surface with a thickness less than 1 μm. As the thickness of the films used was 20 μm, the decrease in nematic order occurs only in the surface region facing the incident light, but in the bulk of the film the *trans*–azobenzene moieties remain unchanged. As a result, the volume contraction is generated only in the surface layer, thus causing the film to bend toward the irradiation source (Figure 23). Furthermore, the azobenzene moieties are preferentially aligned along the rubbing direction of the align-

ment layers, and the decrease in the alignment order of the azobenzene moieties is thus produced only along this direction, which contributes to the anisotropic bending behavior.

Monodomain LCE films with different cross-linking densities were prepared by copolymerization of **34a** and **34b**.^[165] The films showed the same bending behavior, but the maximum extents of bending were different among the films with different cross-linking densities (Figure 24). Because

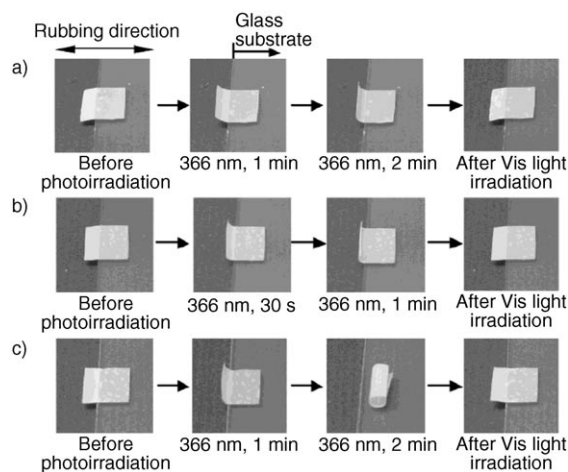


Figure 24. Photographs of monodomain LCE films with different cross-linking densities exhibiting photoinduced bending and unbending behavior. Cross-linker concentration: a) 5 mol%; b) 10 mol%; c) 50 mol%.

films with higher cross-linking densities show higher order parameters, the decrease in alignment order of the azobenzene moieties gives rise to a larger volume contraction along the rubbing direction, thus contributing to a larger extent of bending of the film along this direction. By means of the selective absorption of linearly polarized light in polydomain LCE films, Ikeda and co-workers were able to control the direction of photoinduced bending so that a single polydomain LCE film could be bent repeatedly and precisely along any chosen direction (Figure 25).^[24] The film bent toward the irradiation source in a direction parallel to the polarization of the light.

Palfy-Muhoray and co-workers demonstrated that the mechanical deformation of an LCE sample in which azobenzene dyes are dissolved (components **35a–d**) in response to nonuniform illumination by visible light becomes very large (the sample bends by more than 60°).^[167] When laser light is shone from above onto a dye-doped LCE sample floating on water, the LCE swims away from the laser beam—the action resembles that of flatfish (Figure 26).

An azobenzene LCE film with an extraordinarily strong and fast mechanical response to laser light was developed.^[168] The direction of the photoinduced bending or twisting of LCE can be reversed by changing the polarization of the laser beam. The phenomenon is a result of photoinduced reorientation of azobenzene moieties in the LCE (Figure 27).

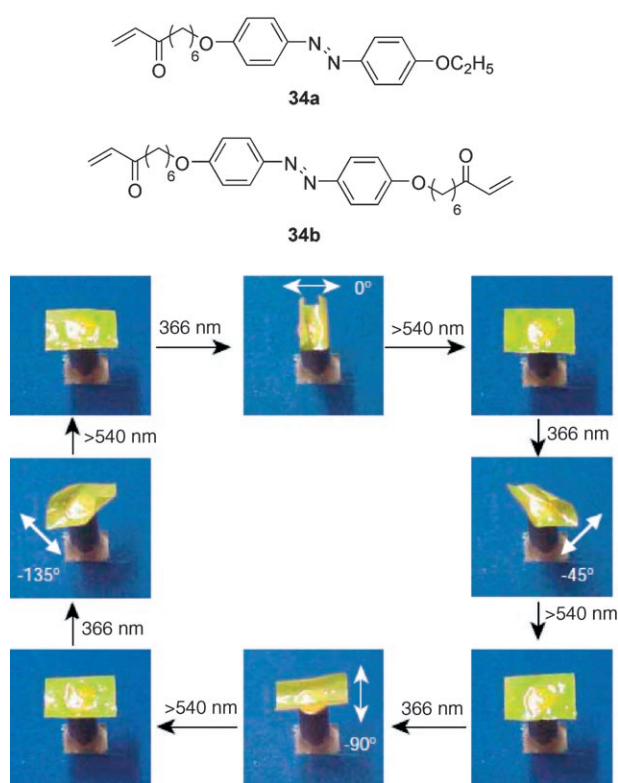


Figure 25. Precise control of the bending direction of a film by linearly polarized light. Top: Structures of the LC monomer (**34a**) and cross-linker (**34b**) used for preparation of the film. Bottom: Photographs of the film in different directions in response to irradiation by linearly polarized light at different angles of polarization (white arrows) at $\lambda = 366$ nm; the bent films are flattened by irradiation with visible light at $\lambda > 540$ nm.

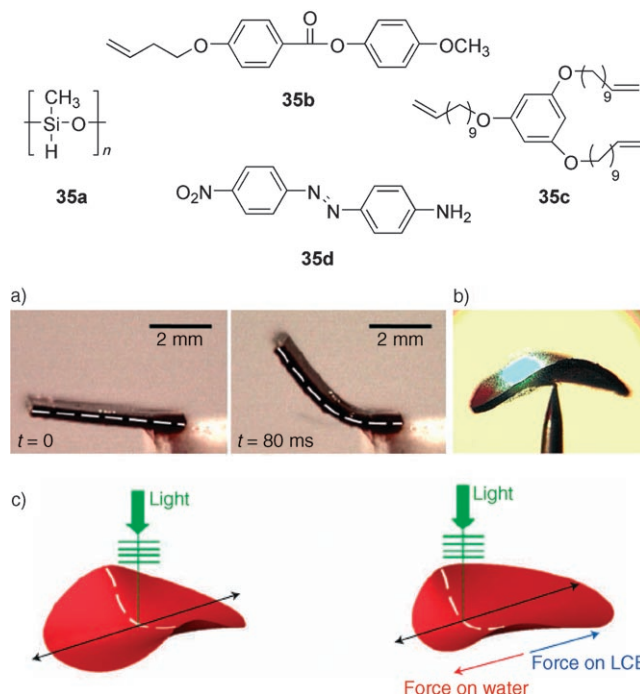


Figure 26. a) Photomechanical response of an LCE sample. b) The shape deformation of an LCE sample upon exposure to light at $\lambda = 514$ nm. c) Mechanism of the locomotion of the dye-doped LCE sample.

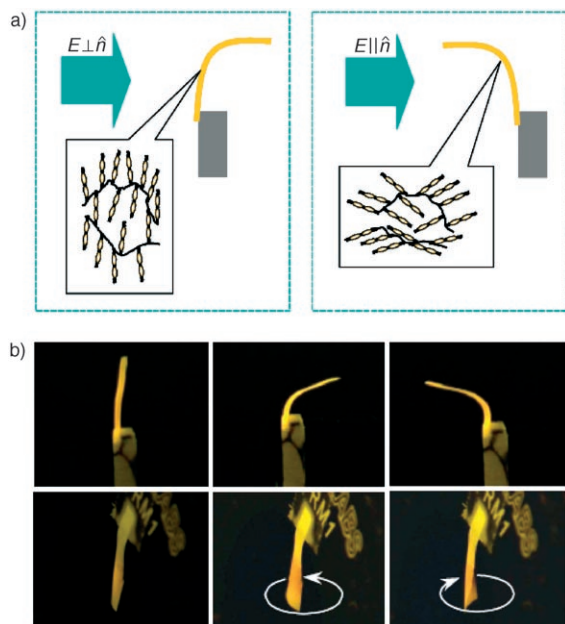


Figure 27. a) The effect of the photoinduced change in LC alignment. E : Polarization direction of laser beam. b) Photoinduced deformation of the polymer film.

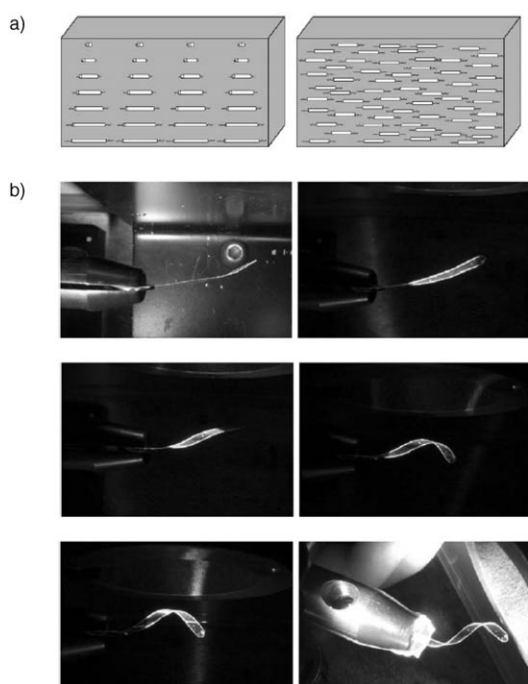
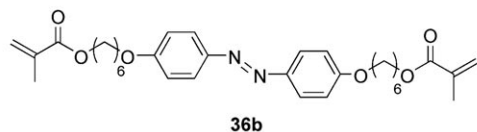
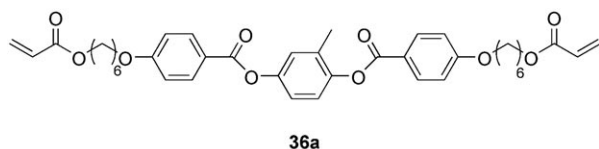


Figure 28. a) Twisted and uniaxial arrangements. b) UV-induced coiling of a film in the twisted configuration.

Broer and co-workers prepared LCE films with a densely cross-linked, twisted configuration of azobenzene moieties.^[169] The films showed a large amplitude bending and coiling motion upon exposure to UV light which results from the 90° twisted configuration of the LC alignment (Figure 28).

The effect of the alignment of the azobenzene mesogens on the photoinduced bending behavior of LCE films was examined. Homeotropically aligned films were prepared and exposed to UV light. The homeotropic LCE films showed a completely different bending; upon exposure to UV light they bent away from the actinic light source (Figure 29).^[170]

Ferroelectric LCE films with a high LC order and a low T_g value were prepared.^[171] Irradiation with UV light caused the films to bend at room temperature toward the actinic light source along the direction with a tilt to the rubbing direction of the alignment layer. The bending process was completed within 500 ms of irradiation from a laser beam. Moreover, the

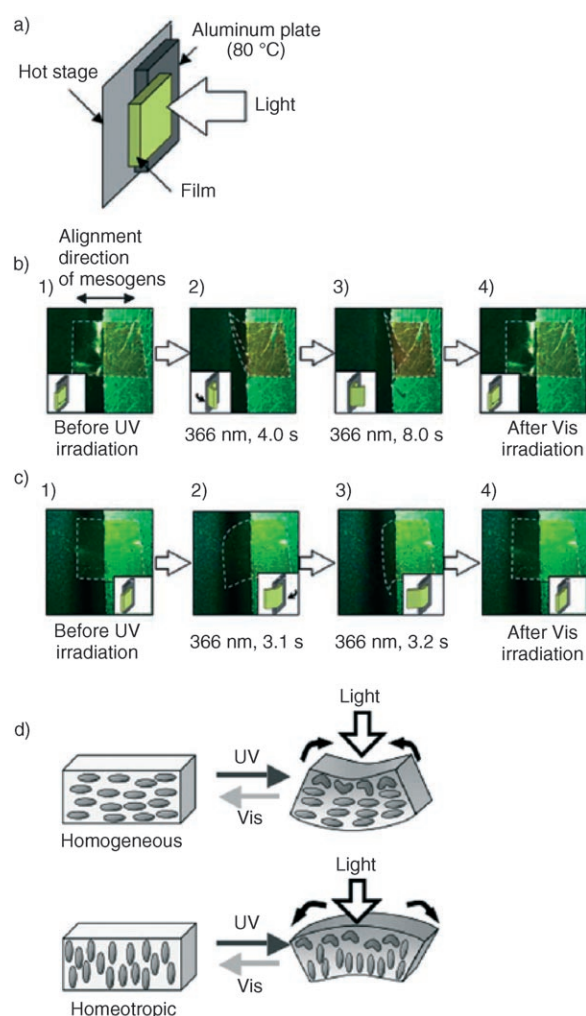


Figure 29. a) Experimental setup and photographs of films with b) parallel (homogeneous) and c) perpendicular (homeotropic) alignment of the mesogens that exhibit photoinduced bending and unbending behavior. The white dashed lines show the edges of the films and the inset of each photograph is a schematic illustration of the film state. d) Bending mechanism in the homogeneous and the homeotropic films.

mechanical force generated by photoirradiation reached about 220 kPa, which is similar to the contraction force of human muscles (ca. 300 kPa).

4. Summary and Outlook

Muscles are responsible for all the movements in our daily lives. The mechanism by which muscles produce mechanical forces has been explored in detail. This force arises from a transformation of chemical into mechanical energy triggered by the brain and precisely controlled at a molecular level. Well-defined, precisely stratified structures are essential for this minute action. The construction of artificial muscles requires: 1) effective elements that exert two- and three-dimensional actions at nano- and microlevels, and 2) well-designed stratified structures of these elements to put their forces together toward macroscopic movements.

This Review describes the photomechanical effects observed in monolayers, gels, polymers, and LCEs. Light-driven actuation has been achieved in many systems; however, the mechanical forces produced and the efficiency of the energy conversion are far from satisfactory. Among the materials investigated, LCEs are promising materials for the construction of artificial muscles driven by light; however, their photomechanical characteristics must be improved, especially the alignment of mesogens, the coupling of LC order with polymer networks, and the change in order by light. Not only two-dimensional but also three-dimensional motions have been achieved which are useful for applications as soft actuators. However, many problems remain unsolved, such as fatigue resistance and the biocompatibility of these materials, and need further intensive investigation.

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