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Photochromism and Molecular Mechanical Devices

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It is a dream for chemists to synthesize molecular systems, which can transform changes of molecular shape induced by external stimuli, such as chemicals, photons, and electrons (or holes), to macro-scale motion of the materials and perform mechanical work. To realize this dream we first prepared photoresponsive polyamides having azobenzene chromophores in the main chain. Although the polyamides changed conformation in solution upon photoinduced trans–cis isomerization, we failed to link the conformational change to macro-scale motion of polymer films and gels. During the course of study on photochromism of diarylethene single crystals we found that the surface morphology as well as the bulk shape of the single crystals reversibly changes upon photoisomerization of the component diarylethene molecules in the crystals. The photoinduced shape changes of the molecules in the densely packed crystals give rise to mechanical motion of the crystals and launch a tiny silica-particle. This is the first molecular system, which directly transforms changes of molecular shape to macro-scale motion of the materials and performs mechanical work. This account describes the progress of the research.

1. Introduction

It is of particular interest from both scientific as well as technological points of view to have synthetic molecules make mechanical motion by external stimuli and link the motion to large macro-scale mechanical work of bulk materials. Mechanical work means controlled, large amplitude, or directional motion of the materials, which results in a net task being performed. Most chemical reactions induced by external stimuli, such as chemicals, photons, and electrons (or holes), are accompanied by a change of molecular shape. The shape change results in machine-like motion at the molecular level. In biological systems, the bending motion of myosin upon release of adenosine diphosphate at the molecular level is used to drive muscles and perform large macro-scale mechanical work.[1] On the other hand, there is no man-made molecular machine, which is based on the shape changes of molecules and can perform macro-scale mechanical work in the real world.[2–6] The shape changes of synthetic molecules at the molecular level fail to be linked to the large macro-scale mechanical motion of materials. So far there is no guiding principle which leads to man-made molecular machines.

In this account, our effort to achieve macro-scale mechanical work of molecular materials based on photoinduced molecular shape changes will be described. We first tried to develop photoresponsive polymers having photochromic molecules and induce photomechanical work of polymer films and gels. Although we could connect the shape changes of the photochromic molecules to conformational change of the polymer chains in solution, we failed to link the changes to macro-scale mechanical motion of the solid polymer films or gels. We finally succeeded to transform the shape changes of molecules to the macro-scale mechanical work using photochromic molecular crystals.

2. Photoresponsive Polymers[7]

The first attempt to link photoinduced shape changes of molecules to macro-scale mechanical work of polymer fibers was carried out by Merian[8] in 1966. He assumed that the trans–cis photoisomerization of azobenzene dyes causes shrinkage of the fiber when the dyes are molecularly dispersed in the fiber, because the azobenzene unit is known to change geometrical structure. The length of the dye used changes from 21 to 16.5 Å upon photoisomerization from the trans to the cis form, as shown in Figure 1. Upon photoirradiation the fiber length was found to shrink as much as 0.1%. Although he attributed the fiber shrinkage to the change of the molecular shape, local photo-heating due to non-radiative transition of the photo-excited azobenzene dyes should be taken into account as the main origin of the photoinduced shrinkage, as evidenced later by Matějka et al.[9]

Another approach to use photoisomerization of azobenzene dyes for mechanical work of polymer gels was carried out by Prins et al.[10,11] They reexamined the experiment by Lovrien,[12] who demonstrated that the conformation of poly(methacrylic acid) chains changes upon photoirradiation in the presence of the azobenzene dye chrysophenine G in water, and applied the molecular-scale conformational change to the shape change of the polymer gel. The trans–cis photoisomerization of the azobenzene derivative changes its hydrophobic nature

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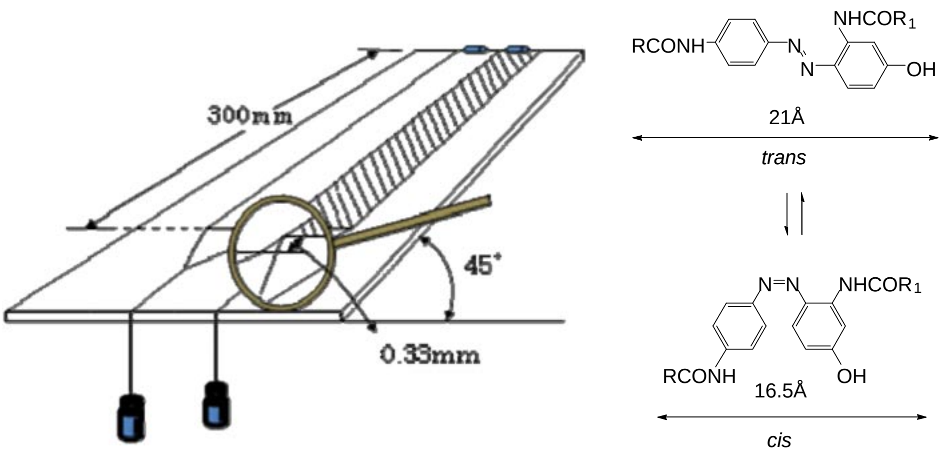


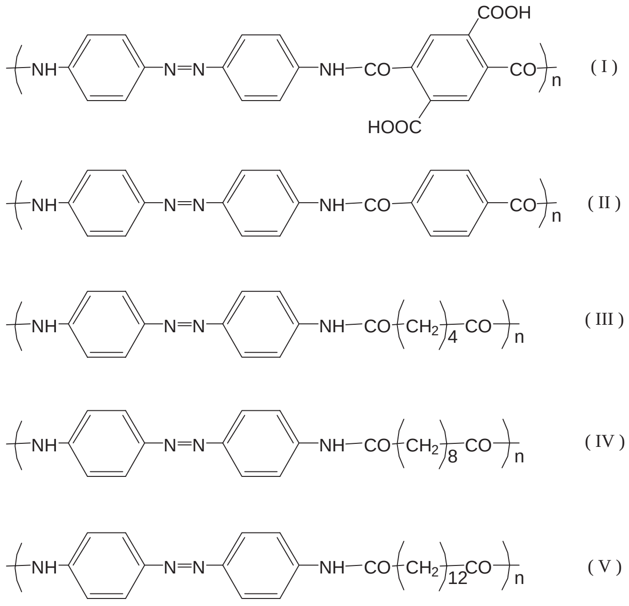
Figure 1. Photoinduced contraction of fabric dyed with trans–cis photoisomerizable dye, shown in the right side.

to hydrophilic and the amphiphilic property change affects the binding of the azobenzene dyes to the polymer chain. The binding force change affects the conformation of the polymer chains as well as the shape of polymer gels. This is the first successful example of photostimulated macro-scale mechanical work.

The attractive reports by Prins et al.[10,11] activated research on the photomechanical effect of polymer films and gels, and various polymers having photochromic chromophores, such as azobenzene or spirobenzopyran derivatives, were prepared.[13–18] Although many polymer films and gels were reported to exhibit macroscopic shape changes upon photoirradiation, there remains the question as to the relative contribution of the local photo-heating and the real photochemical reaction to the observed photoinduced shrinkage. Matějka et al.[9,19] carefully examined the contribution of the local photo-heating effect to the photoinduced shrinkage of a maleic anhydride–styrene copolymer with covalently bound pendant azobenzene groups swollen in diethyl phthalate. They measured the temperature increase of the polymer gel by inserting a thermocouple into the gel along with the photogenerated force. It was found that the force change well correlates with the change in temperature of the gel. The decisive role played in the contraction of the gel is local heating due to light absorption, not ascribed to molecular shape changes of the azobenzene chromophores. The large heat effect observed even in the contraction of the solvent-swollen gel strongly indicates that many works should be carefully reexamined to check and evaluate the real photochemical effect.

Under these circumstances we decided to carry out a fundamental study on the conformational changes of polymer chains in solution upon photoirradiation.[7] If the conformational changes of polymer chains are reversibly induced by photochemical reactions, the changes will probably be linked to macro-scale shape changes of polymer films and gels.

First, we prepared polyamides having azobenzene chromophores in the main chain, as shown in Scheme 1.[20] The most convenient way to know the conformational changes of polymer chains is to measure the viscosity of the polymer solution. The intrinsic viscosity [η] of polyamide **I** in polar *N*,*N*-dimethylacetamide was found to decrease from 1.22 to 0.5 $\mathrm{dL\,g^{-1}}$ upon ultraviolet light (410 nm > λ > 350 nm) irradiation and to return to the initial value in 30 h in the dark at 20 °C. The decrease is ascribed to the geometrical structure change of the azobenzene unit, as shown in Figure 2.



Scheme 1. Photoresponsive polyamides.

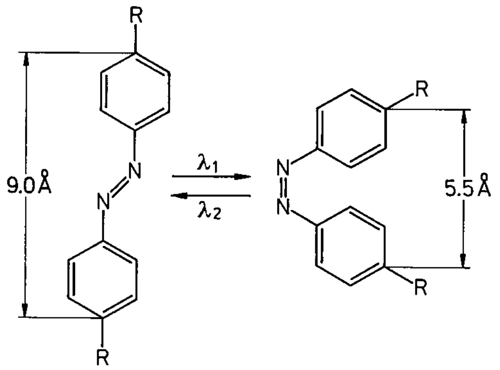


Figure 2. The geometrical structure change of an azobenzene residue along with trans–cis photoisomerization.

The decrease is not due to the intramolecular dipole–dipole

Table 1. Effect of Backbone Structure of the Polymers on the Photodecrease of the Solution Viscosity

Polymer	η_{sp} (UV)/η_{sp}(dark)[a]	$(1 - \varepsilon_c/\varepsilon_t)y$[b]
Polyamide II	0.37	0.47
Polyamide III	0.59	0.79
Polyamide IV	0.80	0.69
Polyamide V	0.96	0.52

a) η_{sp} (UV) and η_{sp} (dark) are specific viscosities under irradiation with ultraviolet light ($410 > \lambda > 350$ nm) and in dark before irradiation in *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M), respectively. Concentration of the polymer was 0.3 g dL^{-1}. b) Relative content of the cis form of the azobenzene residues in the photostationary state under ultraviolet irradiation ($410 > \lambda > 350$ nm). ε_c, ε_t, and y are extinction coefficients of the cis and trans forms at 390 nm and the content of the cis form in the photostationary state.

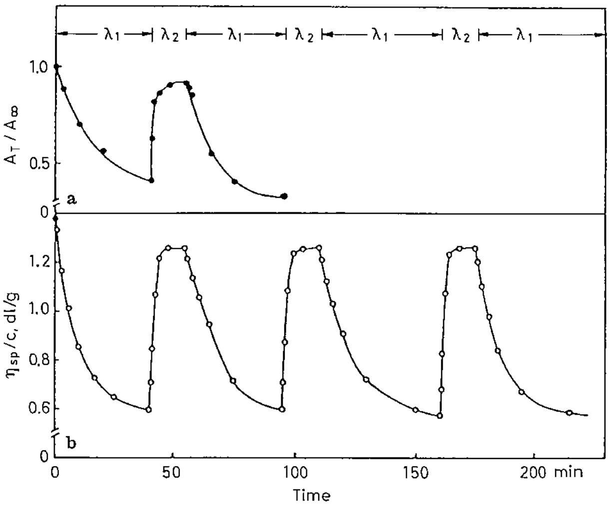


Figure 3. Changes in (●) content of the *trans*-azobenzene residues in polyamide I backbone and (○) viscosity of the polyamide in *N*,*N*-dimethylacetamide on alternate irradiation with ultraviolet ($410 > \lambda > 350$ nm) and visible ($\lambda > 470$ nm) light at 20 °C. Polymer concentration was 0.9 g dL^{-1}.

interactions, because the polarity of the solvent used is high enough and the photo-effect was not observed for polymers with flexible methylene chains, as shown in Table 1. Although the specific viscosity of stiff polyamide II decreased as much as 63% upon ultraviolet irradiation, the photo-effect decreased with increasing number of methylene units in the main chain. The photodecrease of the specific viscosity was scarcely observed for polyamide V having 12 methylene units. When alternatively irradiated with ultraviolet (410 nm $> \lambda >$ 350 nm) and visible ($\lambda > 470$ nm) light, the viscosity of *N*,*N*-dimethylacetamide solution of polyamide I reversibly changed as much as 60%, as shown in Figure 3.

It is of particular interest to know how fast long polymer chains change their conformation in response to a light pulse. The photoisomerization of azobenzene chromophores can be induced in less than 10^{-8} s with a short laser pulse. The conformational change subsequent to the photoisomerization can be followed with a time-resolved light-scattering system combined with the laser pulse source.[21] The Debye eq 1 relates light-scattering intensity R_θ to the mean square radius of gyration $\langle s^2 \rangle$.

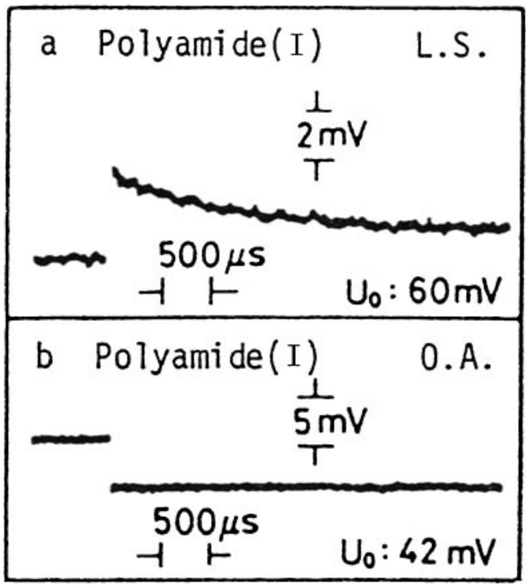


Figure 4. Chain unfolding and cis to trans photoisomerization of polyamide I in *N*,*N*-dimethylacetamide solution (0.31 g dL^{-1}). The oscillograms illustrate changes of light-scattering intensity at 514 nm (a) and optical absorption at 514 nm (b) during and after 20 ns flash of 530 nm light.

$$\frac{K_c}{R_\theta} = \frac{1}{\overline{M}_w} + \frac{16\pi^2 \langle s^2 \rangle}{3\lambda_0^2 \overline{M}_w} \sin^2(\theta/2) + 2A_2 \tag{1}$$

Polyamide I was irradiated with a 20-ns laser pulse (530 nm) in *N*,*N*-dimethylacetamide. The cis to trans photoisomerization of the backbone azobenzene units was followed by time-resolved optical absorption and subsequent conformational change of the polymer chain by time-resolved light scattering. Before each laser experiment the polymer was pre-irradiated with ultraviolet light and brought to a compact conformation, and then the unfolding process was traced by laser photolysis. The optical absorption change indicated that the cis to trans isomerization is completed in 100 ns. Figure 4a shows a typical oscilloscope trace illustrating the change in light-scattering intensity during and after the laser pulse. The change of the light-scattering intensity R_θ reflects the conformational change involving the change in $\langle s^2 \rangle$, as shown in eq 1. The initial rapid increase is due to a concurrent decrease in the optical absorption, as depicted in Figure 4b. The slow decrease of the scattering intensity indicates that the conformational change from the compact to the extended conformations takes place in about 1 ms.

The large difference in the response times for the optical absorption and the light scattering suggests a two-step mechanism for the photostimulated unfolding process. During the isomerization of the backbone azobenzene residues, the total chain conformation remains in the initial compact conformation. After the isomerization is completed, the conformation relaxes to a more stable extended conformation in 1 ms

Compact Conformation
10^{-7} s ↓ cis to trans photoisomerization
Compact Conformation
10^{-3} s ↓ unfolding
Extended Conformation

Chart 1.

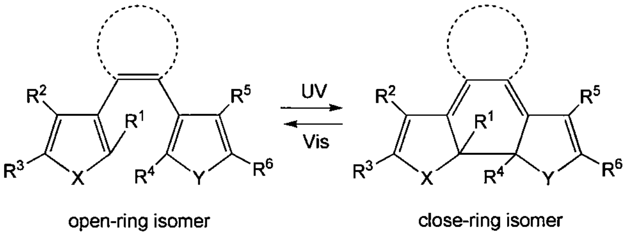
(Chart 1).

The above scheme implies that the trans–cis photoisomerization applies stress to the polymer chain and the compact conformation having *trans*-azobenzene residues stores a certain amount of strain energy. The strain energy causes the expansion, and it is released during the unfolding process in about 1 ms.[22]

The photoinduced conformational change of polyamide chains encouraged us to examine the possibility to link the change to macro-scale mechanical motion of polymer films. We prepared films of the polyamides and investigated the shape change upon photoirradiation. Although a self-standing thin film was successfully prepared with a solvent cast method on a glass plate, we failed to observe a photoinduced shape change even for a solvent-swollen film. Any appreciable change of the shape was not observed. The reason is as follows. As described above, the strain energy of the polymer chain generated by the geometrical structure change of the azobenzene units is easily released when the azobenzene units are connected by flexible methylene chains. In the flexible polymer systems, the total conformation is not affected by the isomerization. When a polymer film has large free volume, the strain energy generated by the photoisomerization is also released by the free volume and the bulk shape of the polymer film does not change. The molecular shape change is not effective to induce macro-scale shape change of polymers. To link the molecular shape change to macro-scale motion of materials, we need densely packed and well-organized molecular systems, such as crystals.

We inferred from the study on the conformation changes in solution that the electrostatic repulsion between photogenerated charges is more effective than the trans to cis isomerization for the design of photo-deformable polymers.[23–25] On due consideration, we took advantage of photogenerated long-range electrostatic repulsive forces for the shape change and succeeded to prepare gels exhibiting large macro-scale mechanical motion upon photoirradiation,[26–28] but in this account we will not discuss these topics, because the mechanical motion does not directly correlate with the change of molecular shape.

Recently, another approach to induce the photomechanical effect of polymers was reported by Finkelmann et al.[29] They applied the photoinduced order–disorder phase transition of nematic elastomers crosslinked with azobenzene units to the photomechanical effect. This effect again does not directly correlate with the change of molecular shape of azobenzene units, because phase transition or photo-shrinkage can also be induced just by heating the elastomer. The contraction of the polymer film is not due to the change of the molecular shape but the geometrical shape change is only the trigger to induce the phase transition. The photoinduced shape change is relatively slow and observed only near the phase-transition temperature.



Scheme 2. Photocyclization and photocycloreversion of diarylethene derivatives.

3. Photoresponsive Crystals

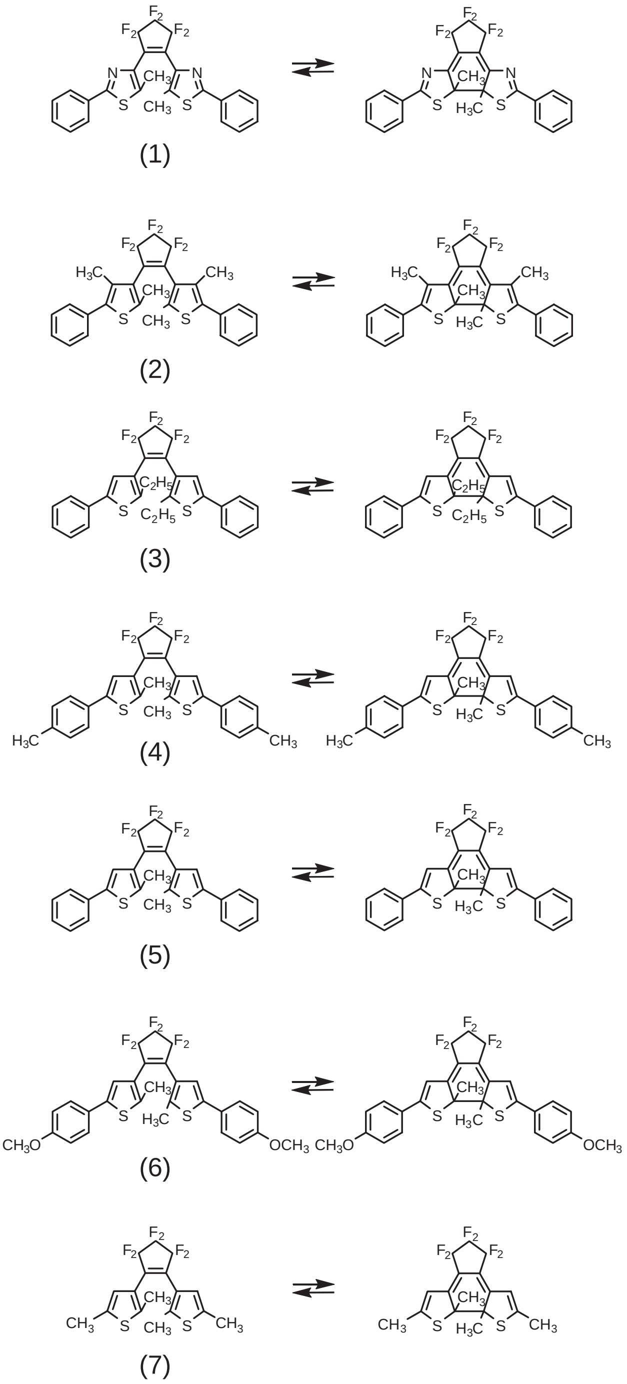
In general, photochromic reactions rarely occur in crystals.[30,31] Photoisomerizations of ordinary photochromic compounds, such as azobenzene and spirobenzopyran derivatives, require relatively large geometrical structure changes and such structure changes are prohibited in densely packed crystal lattices. Therefore, photochromic reactions accompanying large structure changes can not take place in crystals. Although molecular crystals which exhibit photochromism are very rare, there exist some compounds which show photochromism even in crystals. If photochromic reactions take place in crystals, the crystals exhibit efficient and fatigue-resistant color changes and provide characteristic optical-properties. It is strongly desired to develop molecular crystals which undergo photochromism. During the course of study of diarylethene photochromism, we accidentally found that some diarylethene derivatives undergo photochromism even in the single crystalline phase.[32] The crystals undergo thermally irreversible and fatigue-resistant photochromic reactions with a very high cyclization quantum yield. The photochromic reaction of diarylethene derivatives is expressed as shown in Scheme 2.[33]

The colorless open-ring isomer converts to the colored closed-ring isomer upon irradiation with ultraviolet light and the colored isomer returns to the initial colorless isomer upon irradiation with visible light. The colored isomer is stable in the dark. The characteristic properties of the diarylethene derivatives and their crystals are summarized as follows.

1. Both isomers are thermally stable. For example, the half-life time of the colored isomer of 1,2-bis(2-phenyl-5-methyl-4-thiazolyl)perfluorocyclopentene (**1**) is estimated to be as long as 4.7×10^5 years.[34]

2. Coloration/decoloration cycles of diarylethene derivatives, such as 1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene, can be repeated more than 10^4 times.[35] In crystals, the cycles can be repeated more than 10^5 times.

3. The photocyclization quantum yields of the derivatives are relatively high. Especially, 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2**), 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3**), 1,2-bis(2-methyl-5-tolyl-3-thienyl)perfluorocyclopentene (**4**), 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**5**), and 1,2-bis[2-methyl-5-(4-methoxyphenyl)-3-thienyl]perfluorocyclopentene (**6**) show the quantum yields close to 1.0 in the crystalline



Scheme 3. Photochromic diarylethene derivatives.

phase.[36]

4. The reaction rates of both photocyclization and photocycloreversion are very fast. The photocyclization of derivatives such as 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**7**), completes in less than 10 ps in solution as well as in the crystalline phase.[37]

5. In crystals the diarylethene molecules are regularly packed. Therefore, the crystals exhibit dichroism.[38,39]

6. When three different kinds of diarylethene derivatives with different colors are packed in a single crystal, the crystal exhibits multi-colors, such as yellow, red, and blue, upon irradiation with appropriate wavelengths of light.[40–42]

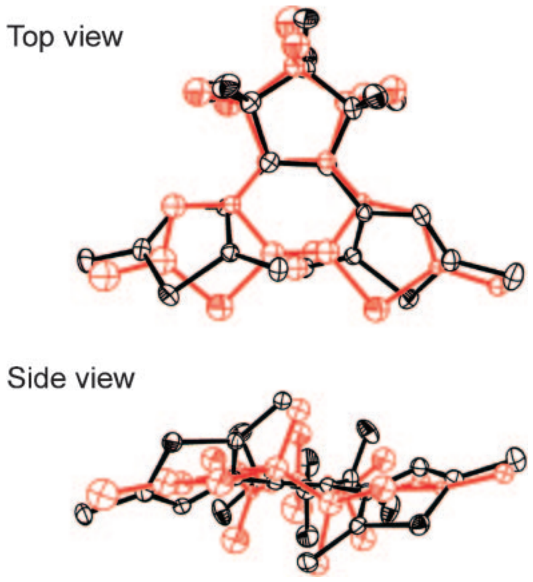


Figure 5. The molecular structure change of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**7**) in the crystal upon irradiation with 360 nm light for 24 h. The occupancy of the closed-ring isomer was 8%.

7. Some achiral diarylethene derivatives form chiral crystals. In these chiral crystals, enantioselective photocyclization reactions take place.[43–45] Scheme 3 shows the structures of diarylethene derivatives.

The definitive evidence for single crystalline photochromism is obtained by X-ray crystallographic analysis of the photoirradiated crystal.[46,47] Figure 5 shows the ORTEP drawings of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**7**) irradiated with ultraviolet light. The black drawing shows the structure of the open-ring isomer, while the red one shows the structure of the photogenerated closed-ring isomer. Although sulfur atoms and reactive carbons change their positions, other atoms remain almost the same. The favorable reactivity of the diarylethene derivative in the single crystalline phase is attributed to the small structure change during the photoisomerization.[48,49]

The interesting result revealed by the X-ray crystallographic analysis is that the molecule shrinks upon photocyclization, though the change is very small. The distance between the tail-end methyl groups shortens and the molecular thickness becomes thinner, as shown in Figure 5. The component molecules, which construct the crystal, shrink in size upon photocyclization. This means that the crystal bulk shape should follow the molecular size change to avoid breaking of the crystal. The most convenient way to know the crystal shape change is to measure the surface morphology by using an atomic force microscope (AFM).[50]

Figure 6 shows the morphology changes of the (100) and (010) surfaces of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2**) upon irradiation with ultraviolet (366 nm) and visible ($\lambda > 500$ nm) light measured with AFM. Upon irradiation with 366-nm light, new steps appeared on the (100) single crystalline surface that disappeared upon irradiation with visible ($\lambda > 500$ nm) light. The step height, about 1 nm, corresponds to one molecular layer. When the

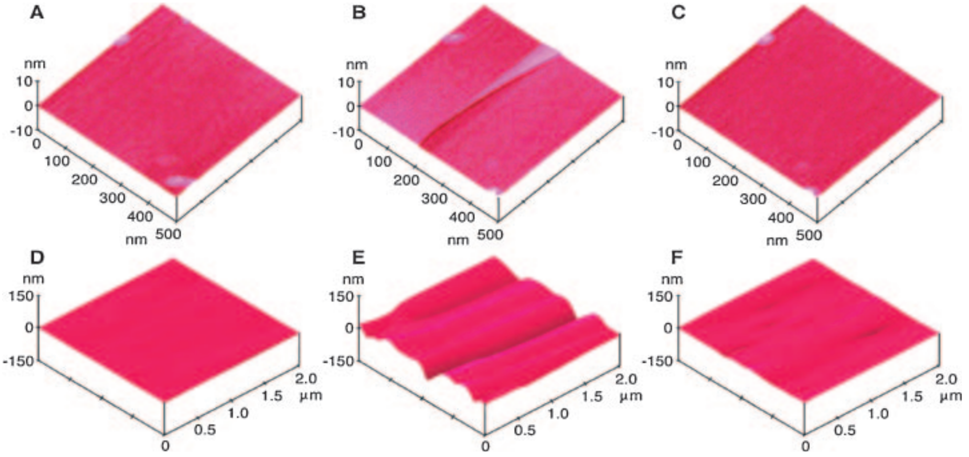


Figure 6. AFM images of the (100) crystal surface (A–C) and the (010) crystal surface (D–F) of 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**2**): before photoirradiation (A and D), after irradiation with 366-nm light for 10 s (B) and 15 s (E), and after irradiation with visible light ($\lambda > 500$ nm) (C and F).

(010) surface was irradiated with 366-nm light, valleys were formed, and they disappeared by bleaching upon irradiation with visible light. The surface morphology changes can be explained by the molecular structure changes of diarylethenes regularly packed in the single crystal. The shape changes of the component molecules induced the surface morphology changes of the bulk crystal. This result indicates that the small shape changes of molecules are directly linked to the shape changes of the bulk crystal.

So far, molecules in crystals are considered to be stationary and they never move in the crystals. However, recently some crystals have been reported to readily change shape under stress.[51] Molecules in crystals have potential for movement when external or inner stress is applied. The photoinduced shape changes of the molecules can apply the inner stress. As discussed in the previous section, in polymer films and gels the strain energy generated by the molecular shape change is released by the free volume. On the other hand, in densely packed molecular crystals, the strain energy is considered to directly influence the shape of the bulk crystal.

In order to modulate the shape of bulk crystals upon photoirradiation without breaking, the following conditions are required.

1. The whole crystal undergoes a homogeneous photoreaction. In other words, the whole crystal is homogeneously illuminated.
2. Phase separation does not take place between the photoreacted isomers and unreacted isomers.
3. The photoreactions randomly take place. In other words, local or co-operative reactions are avoided.
4. The conversion efficiency is high.

The most convenient way to fulfill the above conditions is to use small size crystals. When the crystal size is 10–100 micrometers and the thickness is less than 1 micrometer, UV irradiation can induce homogeneous reaction. We prepared such small size crystals by sublimation.

Figure 7 shows 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3**) and 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**1**) used in this study and illustrates their structural transformations and single crystal deformations

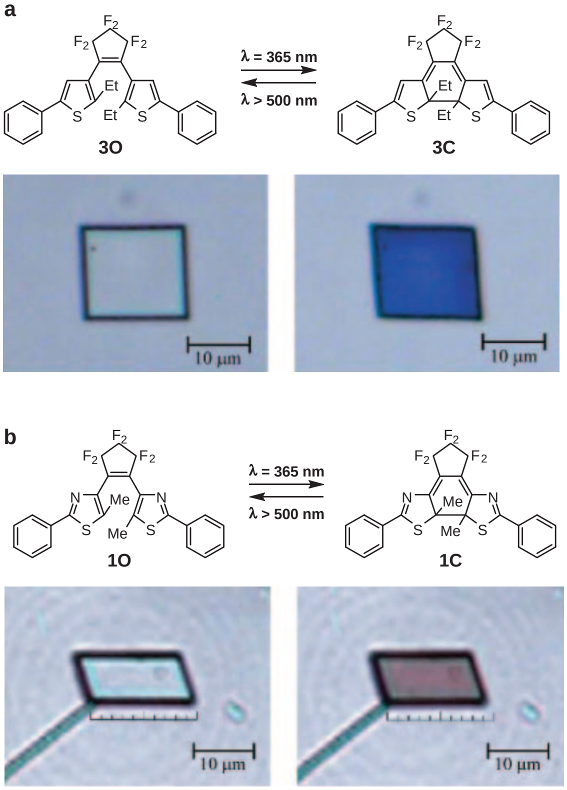


Figure 7. Chemical structures and deformation of the two diarylethene compounds. Molecular structures of the open- and closed-ring isomers of the two compounds along with images illustrating the deformation of their single crystals on irradiation with ultraviolet (365 nm) and visible (>500 nm) light. (a) A square single crystal of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3O**) with corner angles of 88 and 92° reversibly changed to a lozenge shape with corner angles of 82 and 98°. The thickness of the crystal was 570 nm. (b) A rectangular single crystal of 1,2-bis(5-methyl-2-phenyl-4-thiazolyl)perfluorocyclopentene (**1O**) reversibly contracted and expanded by as much as 7%. The thickness of crystal was 330 nm.

upon alternate irradiation with UV (365 nm) and visible ($\lambda > 500$ nm) light.[52] Upon irradiation with UV light, the molecules in the crystals undergo a cyclization reaction that transforms open-ring isomers into closed-ring isomers and change the colors to blue (compound **3**) and violet (compound **1**). The colors were stable in the dark, but disappeared upon irradiation with visible light. UV irradiation of the single crystal **3** changed its corner angles from 88 and 92 to 82 and 98°, respectively, and hence its shape from a square to a lozenge. Figure 8 shows the time dependence of the color and shape changes on alternate irradiation with UV and visible light by showing the relation between the absorption intensity of the crystal at 600 nm and its corner angle. The data shown in Figure 8 show the angle initially remains unchanged and then decreases by as much as 5 to 6°. We found no evidence of hysteresis between the forward and reverse processes.

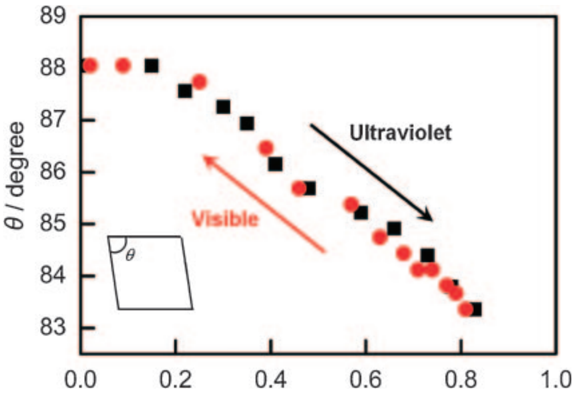


Figure 8. Time dependence of the photoresponse of the single crystal of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3**). Relationship between the corner angle of the single crystal and the absorption intensity measured at 600 nm on alternate irradiation with ultraviolet (365 nm, filled black squares) and visible (>500 nm, filled red circles) light.

The appearance of the induction period is explained as follows. In the initial stage of photoirradiation photogenerated closed-ring isomers are isolated. As long as the reacted molecules are isolated, the crystal keeps the initial shape. When the conversion exceeds around 10%, the photogenerated isomers become laid side-by-side and the neighboring closed-ring isomers are closely packed. The contraction induces the shape change.

Figure 9 shows the molecular packing of the crystal **3** before UV irradiation, as seen when viewed from the (100) and (010) faces. The change from a square to a lozenge shape indicates that the crystal contracts along the *c* axis and expands along the *b* axis. The molecular structures of the open- and closed-ring isomers within the crystal indicates that the twisted thiophene rings become coplanar and that the thickness of each molecule is reduced as the molecule converts from the open- to the closed-ring isomer. The cofacial packing of the thin layers of the planar closed-ring isomers along the *c* axis allows the molecules to be stacked one-by-one, resulting in contraction along the *c* axis.

As shown in Figure 7b, irradiation of the rectangular single crystal **1** with UV and visible light induced contraction and expansion by as much as 7%. We also prepared a rod-like crystal of compound **1**. X-ray crystallographic analysis revealed that the thin plate-like crystal shown in Figure 7b and the rod-like crystal have the same crystal structure. The rod-like crystal bends upon irradiation with UV light, with the bending moving toward the direction of the incident light, as shown in Figure 10. We ascribed this effect to a gradient in the extent of photoisomerization caused by the high absorbance of the crystal, so that the shrinkage of the irradiated part of the crystal causes bending, just like a bimetal. The bent rod-like crystal became straight again on irradiation with visible light. The re-

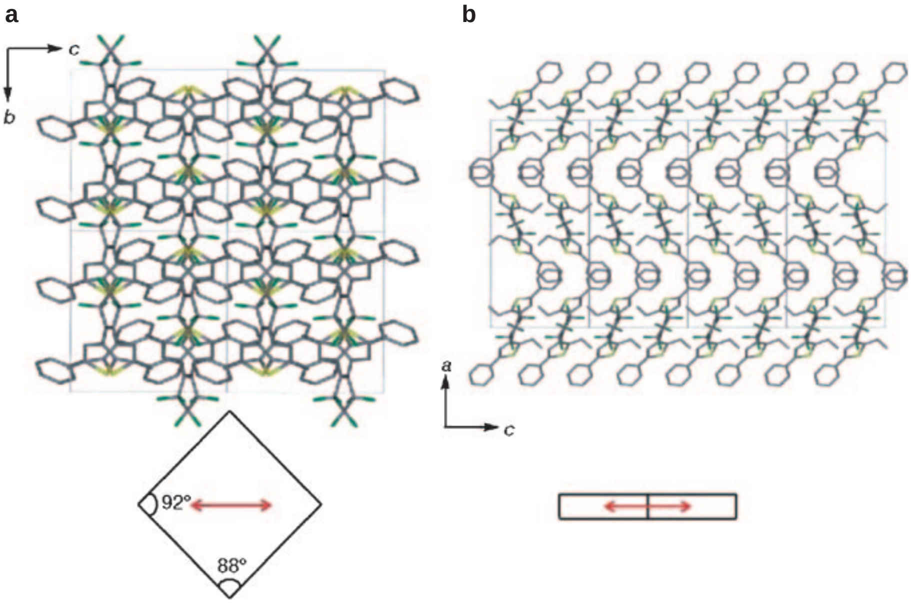


Figure 9. Molecular packing of the single crystal of 1,2-bis(2-ethyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3**). Crystalline packing of the molecules in the crystal before ultraviolet irradiation and outlines of the crystal morphology as viewed from the (100) face (a) and the (010) face (b).

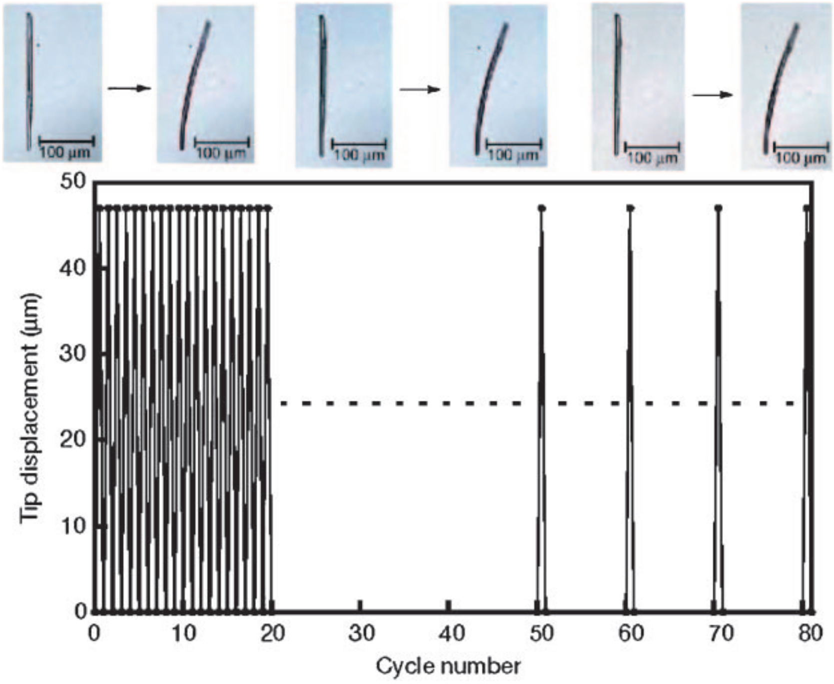


Figure 10. Reversible bending of crystal rod **1** on alternate irradiation with ultraviolet (365 nm) light and visible (>500 nm) light. On irradiation with ultraviolet light, the crystal rod ($225 \times 7.5 \times 5\,\mu m^3$) bent and the head moved as far as 47 µm. The bent crystal rod straightened again on irradiation with visible light. Top panel, pairs of images showing the first, fiftieth, and eightieth cycles (left to right).

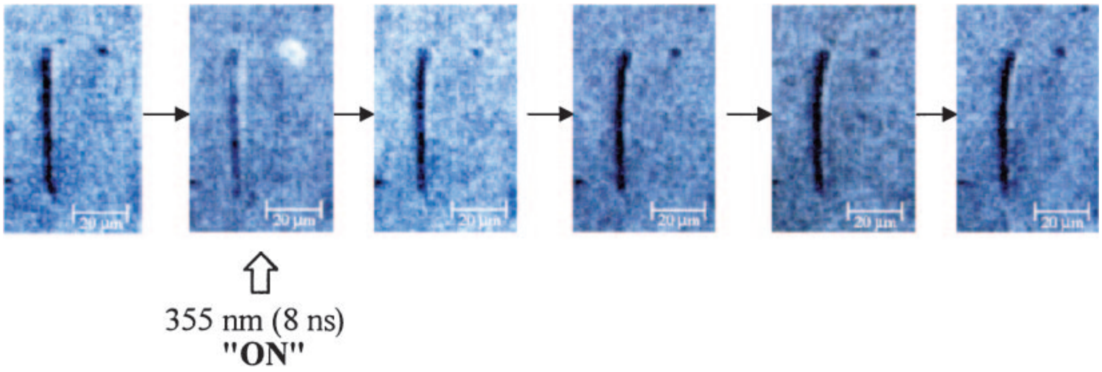


Figure 11. Images of bending behavior of crystal rod **1** ($53 \times 3 \times 3\,\mu m^3$) measured with a high-speed camera. The exposure time of each frame was 25 microseconds. The crystal was irradiated with a single pulsed laser (355 nm, pulse width = 8 ns, power = 60 mJ pulse^{-1}) at the second frame. The bright spot was an anthracene crystal, which gave fluorescence upon the pulsed laser irradiation. Before the pulse irradiation the crystal rod was straight, while it bent after the irradiation and the bending was almost completed in one frame (in the third frame).

versible bending upon alternate irradiation with UV and visible light could be repeated more than 80 cycles without breaking of the crystal rod.

The crystal rod was used for response time measurement, because even low power single pulse laser can induce bending of the crystal rod. The bending behavior induced by the single pulsed laser was measured using a high-speed camera. Figure 11 shows the images of the bending behavior of the crystal. The exposure time of each frame was 25 microseconds. Upon irradiation with a short pulse (355 nm, 8 ns) the component diarylethene molecules convert to the closed-ring isomers during the pulse. The straight crystal rod bent subsequent to the pulse and the bending was almost completed in the first frame. This indicates that the bending rate or the response time of the bending shape change is around 25 microseconds (Chart 2).

The change of the molecular shape along with the photocyclization reaction applies inner stress to the crystal and the crystal stores a certain amount of strain energy. The strain energy causes the bending of the crystal rod. The changes of molecular shape at the molecular level induce the mechanical motion of the crystal rod.

A rod-type crystal (about 200 micrometers long and 5 micrometers diameter) was grown by sublimation on a glass plate so as to attach at one end to the glass plate. When illuminated from the side by an UV pulse light, the crystal rod bent and

Straight crystal rod

10^{-8} s ↓ photoisomerization from
the open- to the closed-ring isomers

Straight crystal rod

10^{-5} s ↓ bending

Bended crystal rod

Chart 2.

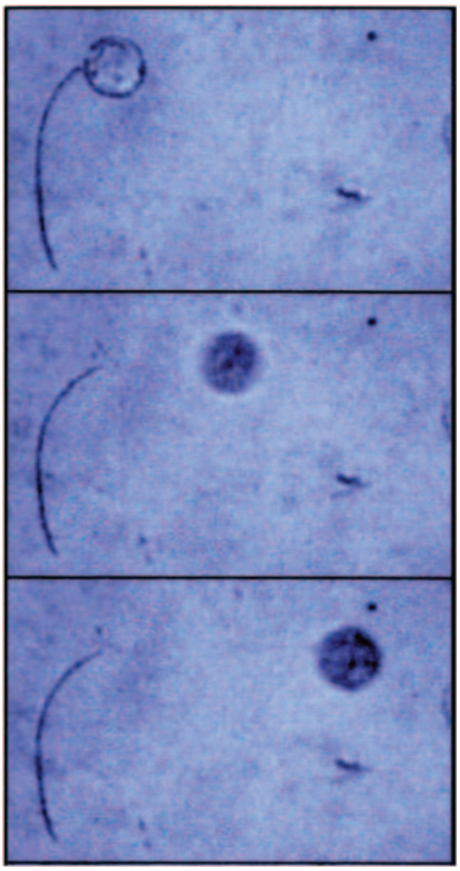


Figure 12. A shot of a silica micro-particle by crystal rod **1** upon irradiation with 365 nm light pulse.

displaced the free end by 50 micrometers. The crystal rod can launch a tiny silica-particle (diameter: 80 micrometers) as if it were a tennis ball, as shown in Figure 12.

4. Conclusion

Photoresponsive polymers having azobenzene chromophores in the main chain changed conformation upon trans–cis photoisomerization of the chromophores in solution. However, the photostimulated conformational changes could not induce macro-scale mechanical motion of solid polymer films or gels. On the other hand, photoisomerization of diarylethene derivatives in densely packed single crystals induced surface morphology as well as shape changes of the single crystals. The changes of molecular shape at the molecular level were successfully linked to the macro-scale mechanical motion of the solid crystal and resulted in a net task to launch a tiny silica-particle. The photoinduced shape change of crystals was also observed for crystals of anthracene carboxylates.[53,54]

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