Photoinduced Deformation of Crosslinked Liquid Crystal Polymers: from Ultraviolet to Near-infrared Light

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Crosslinked Liquid Crystal Polymers (CLCPs)

**Polymer networks**
- Heat resisting, Solvent resistant, Elasticity, et al.

**Liquid crystals**
- Self organization, External responsive, Anisotropic, et al.

**Thermal-induced Contraction of CLCP**
- Polymer backbone
- Mesogens
- Isotropic Phase

UV/Vis photoisomerization of trans-cis isomerization.

Photoinduced Contraction of CLCP Films

- Photoisomerization
- Photoinduced Contraction
- Photochemical Phase Transition

Nematic Phase (Order) → Isotropic Phase (Disorder) upon UV irradiation.

UV


Photoinduced Contraction of CLCP Films

UV Light Induced Bending of CLCP Films

Visible Light Induced Bending and Unbending

Long Conjugated Mesogens

- azobenzene
- tolane

Red Shift

Wavelength (nm)

Absorbance

436 nm → 436 nm → 577 nm

Sunlight Induced Reversible Bending

Solar Energy

Mechanical Work

\[ \lambda = 450-550 \text{ nm} \]
\[ \lambda > 570 \text{ nm} \]

Visible-Light-Driven Microrobot

CLCP films weight: 1 mg
Object weight: >10 mg

Plastic Light-Driven Microrobots

This work presents unique significant advances in both materials design, using visible light activation instead of UV, and device design with unique bimorph structures," comments Patrick Mather, an expert in functional polymeric materials at the Syracuse Biomaterials Institute. 'Indeed, the field of smart polymers is transforming from studies of composition variation to more device-based research and this will certainly lead to such applications as the robotic platform envisioned by Yu,' he adds.

Yu's microrobot can lift objects weighing ten times the combined mass of the active nano, wrist and elbow polymer parts and the force-per-unit-area generated (300kPa) compares to that produced by muscles in the human body (320kPa). As light energy is safe, abundant, renewable, and clean, Yu sees it as an ideal potential substitute for electrical power. "Our research focuses on how to convert the light energy directly into 'real' mechanical work," she says.

Yu, believes that this type of robot could be used in mass manufacturing. Robots that pick and place microelectronic components are currently widely used in assembly lines and Yu envisions a future for light driven robots in similar roles. "Maybe one day when the sun is rising up, light-driven microrobots will work regularly doing picking and placing jobs in industry or in our daily life," she says.
Fast liquid-crystal elastomer swims into the dark

Dye-doped LCE sample floating on the water surface moves away from the area of sustained illumination with an argon-ion laser.

Irregular rectangular LCE sample floating on ethylene glycol first folds then swims away when illuminated.

*Miguel Camacho-Lopez, Heino Finkelmann, Peter Palffy-Muhoray* and Michael Shelley

Full-Light-Driven Soft Actuators

Motor

Creeper


Light-Driven Cantilever Oscillator

(1) Light source: 1.42 W/cm² Ar⁺ laser beam
(2) Amplitude of the oscillation: >170 °
(3) Frequency: 270 Hz
(4) Energy conversion efficiency: ~ 0.1%
(5) Film size: 2.7 mm × 0.8 mm × 50 μm

Printed artificial cilia from liquid-crystal network actuators modularly driven by light

Casper L. van Oosten\textsuperscript{1*}, Cees W. M. Bastiaansen\textsuperscript{1,2} and Dirk J. Broer\textsuperscript{1,3}
## This Work

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Near-Infrared Light Induced Bending

Upconversion nanophosphors (UCNPs)

The principle of upconversion fluorescence is emitting higher-energy photons after absorbing lower-energy photons.
Upconversion Luminescence (UCL) of UCNPs

NaYF$_4$: Yb (30 mol%), Tm (0.5 mol%)

CW excitation at 980 nm (power density = 15 W/cm$^2$)

Emission Spectra of UCNPs + Azo Monomers

UCNPs : Monomer mixture (wt : wt )

- 1 : 0
- 1 : 0.5
- 1 : 1
- 1 : 1.5
- 1 : 2

Absorption Spectra of UCNPs + Azo Monomers

CW excitation at 980 nm

300 400 500 600 700 800
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Absorbance
Wavelength (nm)

[WU min]

30 min

0 min

[Azo monomer] = 0.8 × 10^{-5} \text{ mol/L}
[UCNPs] = 0.02 \text{ mg/mL}

UCL of UCNPs induces the trans-cis photoisomerization of the azotolane moieties.

CLCP Nanocomposite Film

NaYF₄: Yb (30 mol%), Tm (0.5 mol%)

UCNPs solution → coated → Azotolane CLCP film → CLCP nanocomposite film

POM observation

θ = 0°
θ = 45°
Near-Infrared Light Induced Bending

Up-conversion Luminescence
980 nm

Photoisomerization

Phase Transition

Photoinduced Bending

UCNPs

Blue Light

cis-azotolane

trans-azotolane

CW excitation at 980 nm (power density = 15 W/cm²)

This Work

1. Photoinduced Deformation via Upconversion Luminescence
2. No-Loss Transfer of Microdroplet on Micro/Nano Structured Interfaces
3. Photodeformation of an Uncrosslinked Liquid Crystal Polymer
No-Loss Transfer of Microdroplet

Photodeformable CLCPs

Micro/Nano Structured Interfaces

No-loss microdroplet transfer

Superhydrophobic Surfaces

Controllable Adhesion
Superhydrophobic Surfaces

Rose Surface (High Adhesion)

Contact angle (CA) > 150°
Sliding angle (SA) ≥ 90°

Lotus Leaf (Low Adhesion)

CA > 150°
SA < 5°

Micro-Arrayed Azobenzene CLCP Film

Photoresponsive Wettability

*Trans-azo*

- Low adhesion
- 365 nm
- High adhesion
- 530 nm

*Trans-azo*

CA: (trans) $150.9 \pm 1.5^\circ$/ (cis) $150.8 \pm 0.8^\circ$
SA: (trans) $\geq 90^\circ$/ (cis) $\geq 90^\circ$

*Trans-azo*

CA: (trans) $74.3 \pm 0.2^\circ$/ (cis) $70.6 \pm 0.6^\circ$
SA: (trans) $\geq 90^\circ$/ (cis) $\geq 90^\circ$

*Trans-azo*

CA > 150°
Superhydrophobic Surface

*Trans-azo*

d5

*Trans-azo*

CA: (trans) $152.8 \pm 0.7^\circ$/ (cis) $151.4 \pm 1.2^\circ$
SA: (trans) $37.7 \pm 0.6^\circ$/ (cis) $49.3 \pm 1.2^\circ$

*Trans-azo*

d15

Smooth surface

Light Driven Microdroplet Transfer

Pinned ($\geq 90^\circ$)  
Rolling ($67.7 \pm 1.2^\circ$)

Micro-nanopost-arrayed Silicon Wafer with Azo-polymer Coating

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Crosslinked Liquid Crystal Polymers (CLCPs)

- Elasticity
- External responsive
- Anisotropic
- Poor Processability
Preparation of Linear LCP (LLCP) with ROMP

Why choose Ring-Opening Metathesis Polymerization (ROMP)?

- Living polymerization (Linear control of molecular weight)
- High polymerization yield (Approximate to 100%)
- High activity Grubbs catalyst (Tolerant towards functional groups)

Unpublished data

Unpublished data

M_n = 9.3 \times 10^4
M_w = 1.6 \times 10^5
M_w/M_n = 1.69
Molecular Design Strategy for the LLCP

- Processability and Stability of LC Phase
- Rubber Elasticity
- Photoresponsiveness + LC Phase
DSC and POM of the LLCP

Temperature (°C)

Heat Flow (W/g)

Cooling

Heating

Unpublished data
Small Angle x-Ray Scattering Pattern of the LLCP

SAXS

Intensity

$q_1 = 1.38$

$q_2 = 2.76$

$q_1 : q_2 = 1:2$

(60-94 °C)

Long-range ordered lamellar structure (smectic C phase)

Unpublished data
Preparation of the LLCP Film

PC11AB6

= Glass Sheet

Hot-pressing

Melting (110 ºC)

Smectic C (annealing at 70 ºC)

= Glass Sheet

Free-standing (Room temp.)

Unpublished data
Photoinduced Reversible Bending of the LLCP Film

Film size: 2 mm × 8 mm × 10 μm

Unpublished data

- λ = 365 nm
- λ = 540 nm

Keep in the dark

Response time (s)

UV Intensity (mW/cm²)
Preparation and POM of the UCLCP Fiber

θ = 0°

θ = 45°

Toothpick

PC11AB6 fiber

Heating

PC11AB6

20 μm

Unpublished data
Bending of LLCP Fiber toward Different Directions

Unpublished data
Conclusion

Photoresponsive Azo-Containing CLCP Systems

- Photoinduced bending and unbending behavior of CLCP films
- Without the Aid of Batteries, Motors and Gears

New Micro Opto Mechanical Systems (MOMS)

Photoswitching of No-loss Microdroplet Transfer

Future applications?
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