Lyotropic chromonic liquid crystalline macromolecules derived from small molecules as functional materials in opto-electronic applications.

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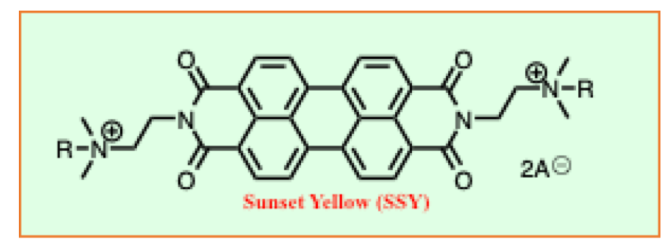
ABSTRACT

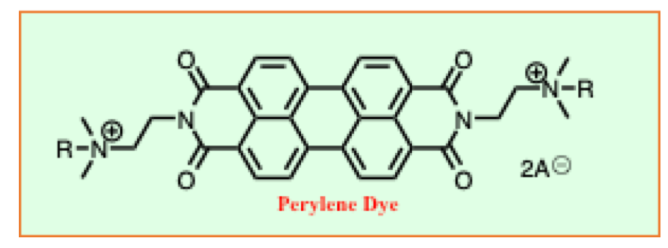
Possessing rigid, plank-shaped aromatic cores and often functionalized at the periphery with ionic groups to aid solubility in aqueous solutions, lyotropic chromonic liquid crystals are a unique subset of liquid crystals. Finding applications in biological fields including drugs to fabrication of devices such as biosensors and use as optical polarizers and compensators, these molecules are promising new breakthroughs in future devices and technologies.

The majority of research has centered on utilizing them as small molecules; but these often presents processing difficulties and a host of other unattractive defects like cracks when they are made into thin films. By transforming these small molecules into large macromolecules, there's a general expectation that some of the current problems can be circumvented.

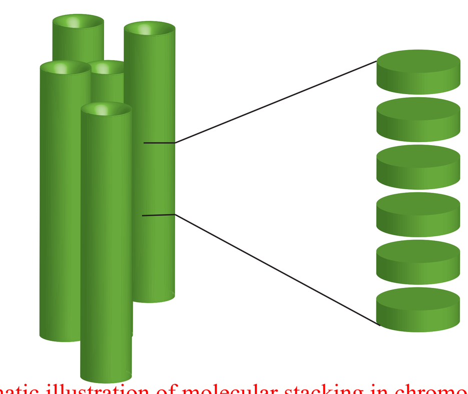
Current experiments show that we can fix the stack lengths of chromonic aromatic cores and thanks to robust ring opening metathesis polymerization friendly monomers designed with the aromatic cores exhibiting chromonic properties, very narrowly dispersed polymers have been realized. With X-ray scattering techniques and a combination of spectroscopy and microscopy techniques, the purity, and structure-property relationship is well characterized.

INTRODUCTION





Examples of common chromonic molecules.



Schematic illustration of molecular stacking in chromonic molecules.

These molecules possesses the following properties:

- Both N and C phases from LCLCs reveal a 0.34nm between aromatic rings
- Aggregation is due to π-π stacking of aromatic cores
- Aggregation is said to be isodesmic

Chromonic polymers can be designed for multiple uses including:

- Photonics
- Sensors
- Nano-templates
- Stimuli responsive materials

Research Motivation, Experimental Design and Results

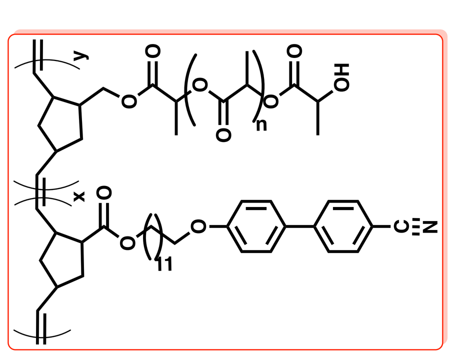
Motivation

Chromonic small molecules suffer from shortcomings such as:

- Poorly formed films due cracks emerging after drying.
- Difficulty retaining chromonic phases as they lack a platform for aligning domains

By controlled order, chromonic polymers provides:

- A handle for fabricating optical materials.
- Ability to dissolve in organic solvents.
- Opens up better methods of fabricating uniform thin films.



- Cyanobiphenyl possesses magnetic anisotropy
- Optical, thermal and electrical properties
- Macroscopically aligned LCs obtained.
- BCPs offer access to mesoscopic length scales

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Experimental strategy

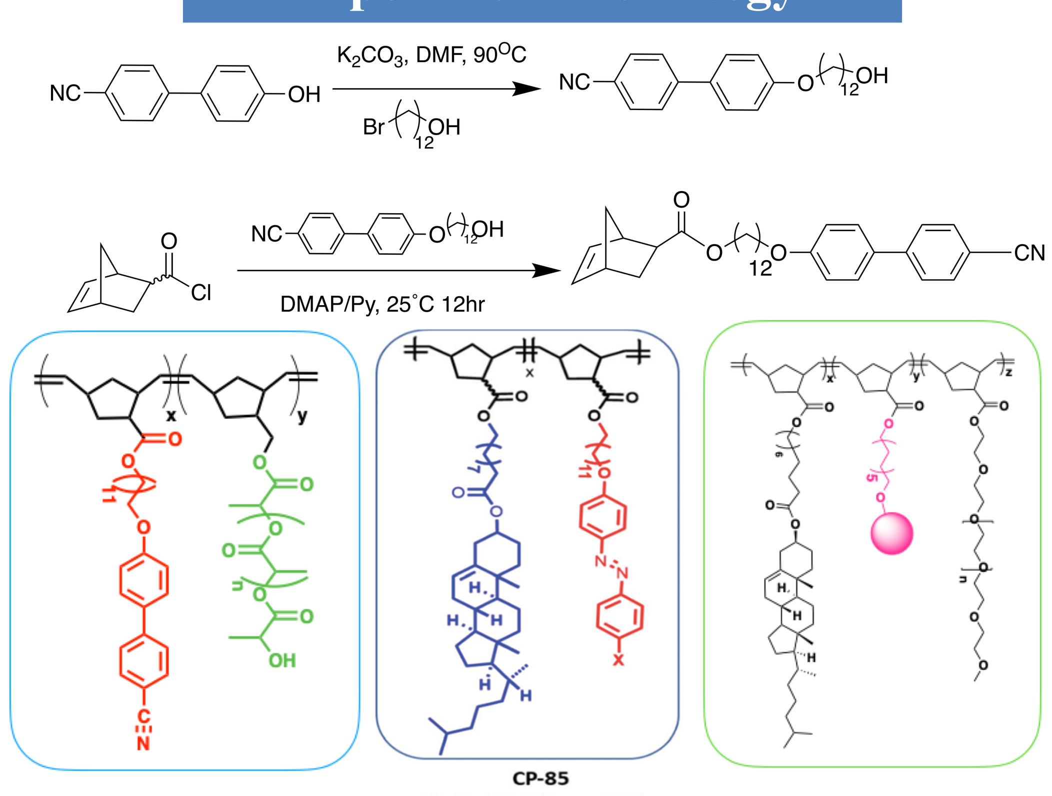
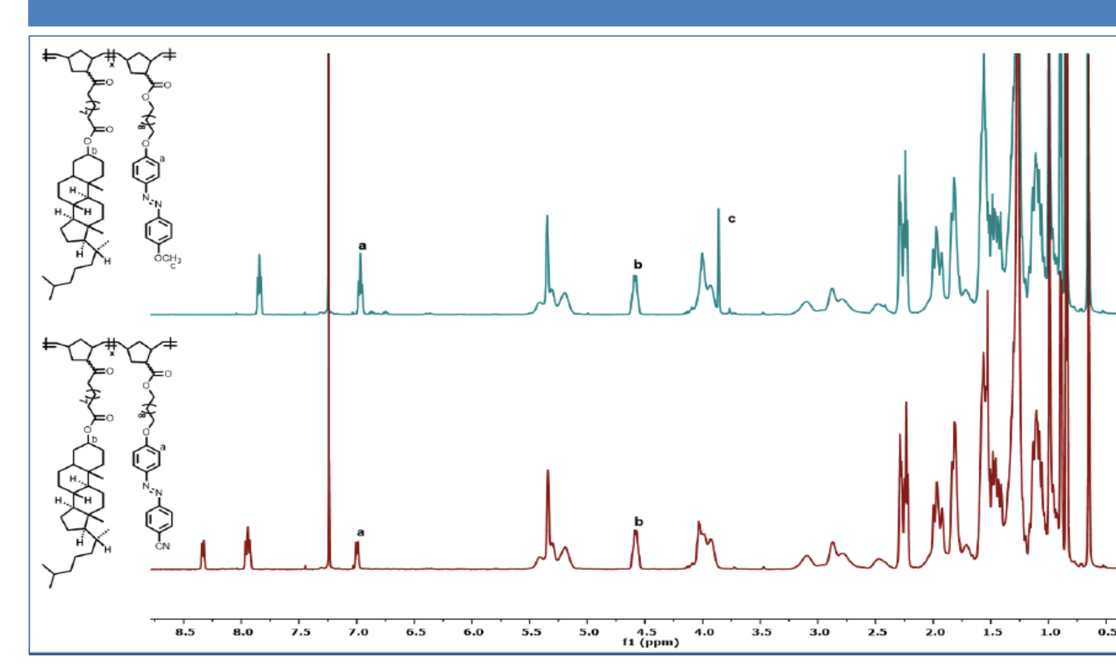


Table 1: Thermal properties of newly synthesized polymers

Entry	Tm(°C)	Tg(°C)	T_{lc1},°C (ΔH)	T_{lc2}, °C (ΔH)	T_{c1}, °C (ΔH)	T_{c2}, °C (ΔH)
TTPX85R	51.97 (3.209)	37.16	62.96 (0.4624)	87.72 (1.143)	-23.57 (1.668)	-41.64 (0.6256)
TPX85B	48.50 (6.980)	30.28	80.96 (1.246)	100.65 (0.6736)	-	-
TPX75R	52.19 (4.950)	28.64	83.54 (0.9741)	-	-21.77 (2.479)	-37.88 (2.798)
TPX75B	44.80 (9.533)	31.35	80.65 (1.186)	100.93 (0.8059)	-34.48 (3.737)	-
CPXPEG85B	-	26.61	80.03 (1.319)	99.71 (0.6963)	-	-

- ❖ Magnetically responsive polymers shows interesting LC transitions with different colors as shown by color plates.
- ❖ BCP architecture is amenable to microphase segregation
- ❖ Varying χ parameter and volume fraction (*f*) for different morphologies
- ❖ ROMP chosen for its versatility (Low Đ values)

[1]H NMR and UV-Vis Characterization



Representative [1]H NMR spectrum of copolymer (CP-85, X=CN or OCH3) in CDCl3 at rom temperature
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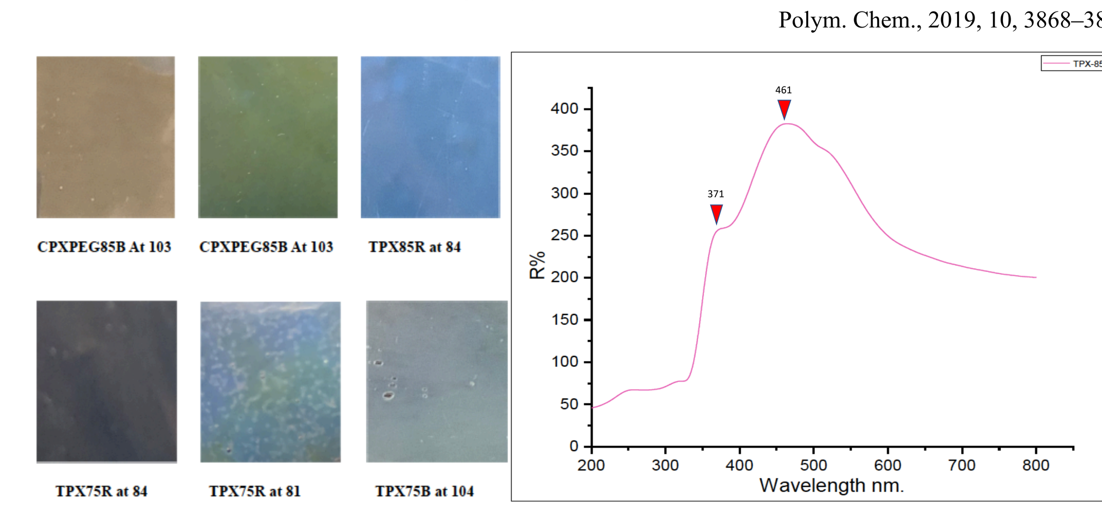
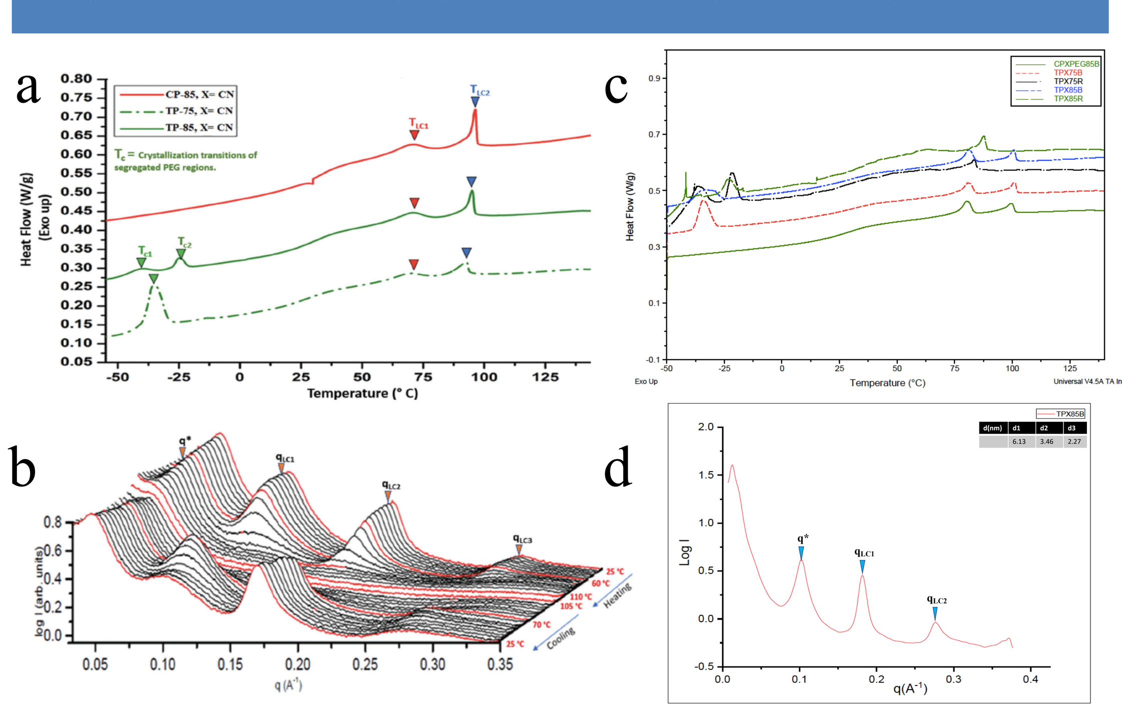
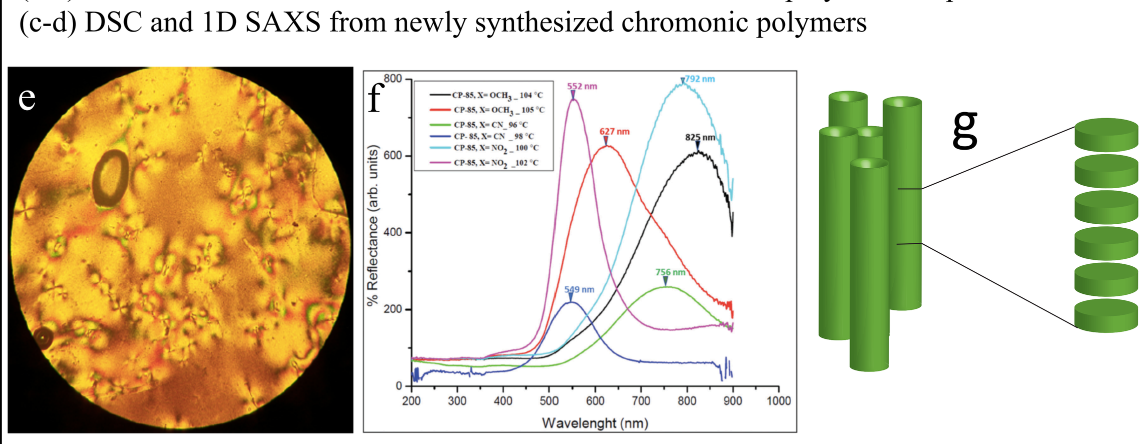


Color plates of newly synthesized polymers annealed at different temperatures. b). UV-Vis spectrum from one of the terpolymers is shown.

Thermal and microstructural characterization



(a-b) DSC and 1D T-SAXS from Cholesteric-azobenzene LC copolymers for photonics
(c-d) DSC and 1D SAXS from newly synthesized chromonic polymers



e). POM textures indicating co-exististence of cholesteric and smectic phase in azo copolymers
f). UV-Vis from cholesteric-azo polymers
g). Schematic illustration of new molecular packing in lyotropic chromonic molecules.

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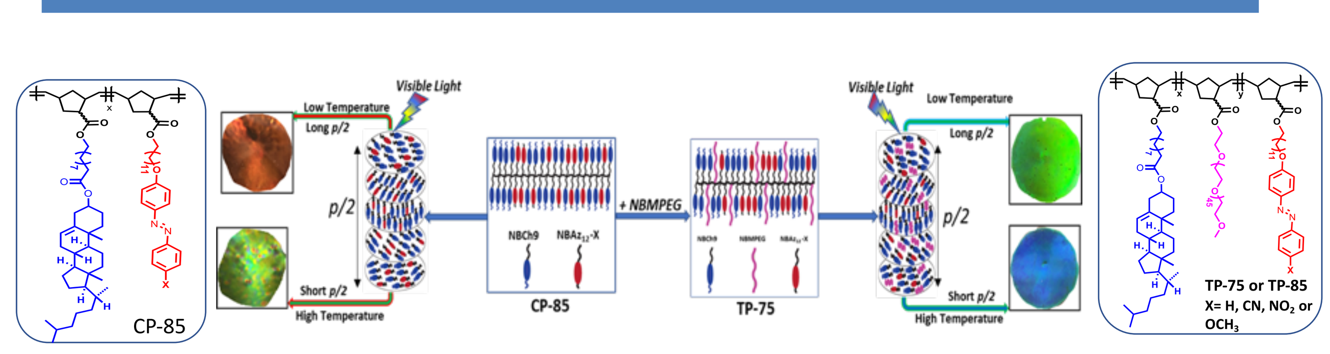
Discussion.



Like thermo-responsive cholesteric-azobenzene liquid crystalline polymers, initial results from chromonic polymers show comparable optical properties.

Both diblock and triblock copolymers exhibit unique optical properties.

- Lyotropic chromonic monomers replace azobenzene and cholesterol to synthesize Lyotropic chromonic polymers.
- Azobenzene and cholesterol monomers are employed in studying polymers for photonic applications.
- Robust polymers are developed by crosslinking olefinic groups in norbornene backbone.
- Spectroscopic, thermal analysis are used to analyze structural and thermal properties.

Summary

- Synthesis of both thermotropic and lyotropic LC polymers is presented
- Monomer selection is based on possession of magnetic anisotropy, refractive index and birefringence
- Applications in photonics, sensors and nanopatterning are envisioned.
- Control of polymer morphology, careful choice of monomers and good chemical and mechanical robustness is employed.
- Microstructural analysis using WAXS, SAXS, TSAXS: long/short range order, domain spacing and morphology.
- Microscopy techniques such as SEM, TEM and are used to support light scattering techniques

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