Supramolecular halogen bonded liquid crystalline polymers and networks: A study of weak associations on mesophase stability

Wiegel Research: Careening from catastrophe to catastrophe since 2000

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Background

Liquid Crystals

•Materials that exhibit long-range and some short-range directional ordering in a fluid state.

•Composed of mesogens (shaped molecules) and flexible spacers

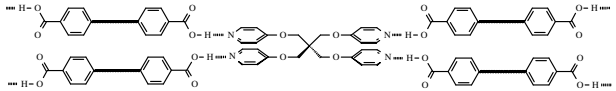
•Different types of mesogens based on molecular shape (calamitic: rod-shaped)

Molecular Self-assembly Through Hydrogen Bonding

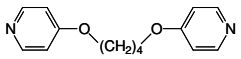
Non-covalent interactions formed between two molecules through a hydrogen-bond resulting in a larger "associated" molecule

Mesogenic Networks

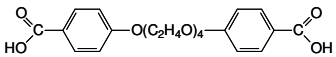
- Combine characteristic of networks and liquid crystals
- Couple physical deformations with liquid crystalline phase behavior
- Thermoreversability through hydrogen bonding would introduce lability and the ability to reorganize to these characteristics



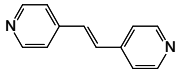
Materials Used



4BPD ((1,4)Diproxidine Butane)

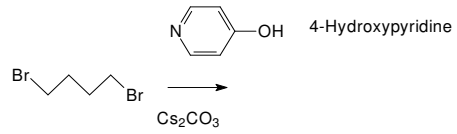


4EOBBA Tetraethyleneglycoxy bis-(4-benzoic acid)

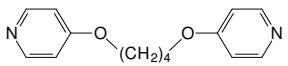


2RP 1,2-Di(4-pyridyl) Ethylene

Synthetic Methodologies



4-Hydroxypyridine



4BPD

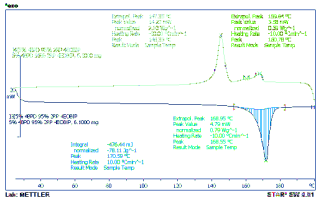
Thermal Analysis

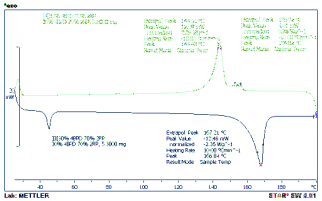
- Complexes synthesized through standard melt-complex methodology
- DSC data determined on a Mettler-Toledo STAR e1 DSC at 10˚C/Min heating rate unless otherwise noted
- Optical micrographs were measured using a Mettler-Toledo FP82 Hotstage Mounted on an Olympus BHT polarizing light microscope at a 10˚C/Min heating rate unless otherwise noted

4EOBBA/4BPD/2RP Networks

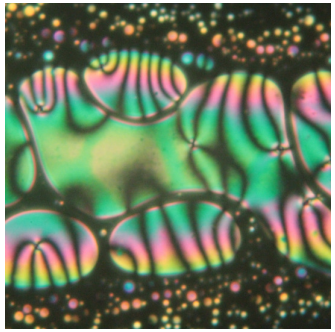
	KI	IN	NS	SK	NK	IK
5%	170.6	168.55	160.8	146.3	X	X
10%	167.2	159	149.3	138.4	X	X
15%	168.5	161.8	153.5	146.4	X	X
20%	168.3	158.4	155.1	143.2	X	X
25%	168.6	161.1	152.6	144.3	X	X
30%	166.8	154.8	X	X	144.8	X
35%	163.1	147.3	X	X	137.6	X
40%	162.3	143.9	X	X	136.6	X
45%	163.5	146.3	X	X	137.9	X
50%	160.5		X	X	X	139.4

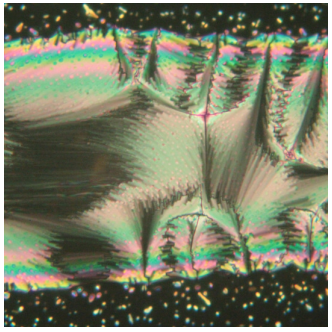
K = Crystal, I = isotropic, N = nematic, S = smectic (often S_A)





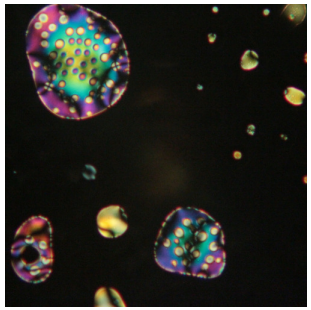
4EOBBA with 5% 4BPD and 95% 2RP

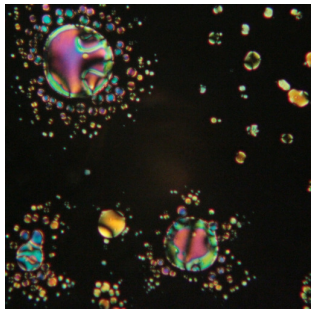




On the left is a nematic phase, and on the right is a smectic phase of a 4EOBBA 5% 4BPD and 95% 2RP complex. Both pictures were taken during the cooling of the complex on the same slide.

Pictures of 15% disruption loading





Nematic phase for 15% disruptor loadings:
Left is warming cycle and right is sample cooling

Results/Observations

General Observations:

- Nematic monotropic phases (cooling)
- Observed in all systems, smectic till 25% (high loadings)
- Almost all samples display a decreasing melting with increasing loading

Specific Observations:

- 4BPD competetor in systems
- Liquid crystal characteristics disappeared 50% loadings
- Smectic phase disappeared at 25%
- Actual disappearance of smectic lie between 25% and 30% of 4BPD disruption (transient phase)

Conclusions

•A series of novel liquid crystalline supramolecular polymers formed through hydrogen bonds have been synthesized.
•Polymers display monotropic nematic characteristics at high concentrations of disrupting hydrogen bond accptors up to 50%
•Decreasing loading concentrations could be a function of decreasing melting temperatures of the non-mesogenic characters
•Increased flexibility allows for the chains to realign and maintain mesogenicity by overcoming localized structural defects and disruptive agents.

Acknowledgements

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