Hydrogen-bonded liquid crystals: Distonic mesogenic acceptors with increasing flexibility

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Wiegel Research: Careening from catastrophe to catastrophe

Background

Liquid Crystals

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

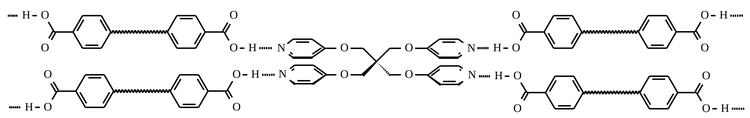
•Composed of mesogens (shaped molecules) and flexible spacers

Molecular Self-assembly Through Hydrogen Bonding

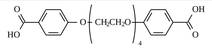
Non-covalent interactions formed between two molecules through a hydrogen-bond resulting in a larger "associated" molecule

Mesogenic Networks

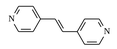
- Combine characteristic of networks and liquid crystals
- Couple physical deformations with liquid crystalline phase behavior
- Thermoreversability through hydrogen bonding would introduce lability and the ability to reorganize to these characteristics



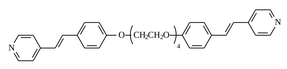
Materials Used



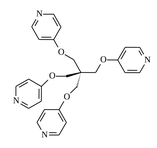
Tetraethyleneglycoxy bis-(4-benzoic acid)
4 EO BBA



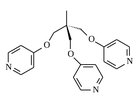
1,2-Di(4-pyridyl)ethylene
2 RP



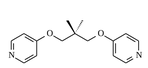
Tetraethyleneglycoxy bis-4-(4-oxystyryl)pyridine)
4EO BSB



Tetrakis(4-pyridyoxymethane)
4PD

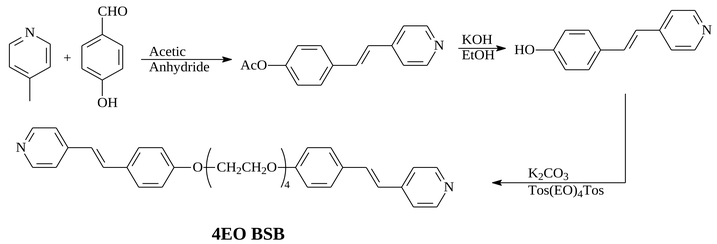


1,1,1-Tris(4-pyridloxymethylene)ethane
(3 PD)



2,2-Dimethyl-1,3-di-(4-pyridyloxy)propane
(2 PD)

Synthetic methodologies



4EO BSB

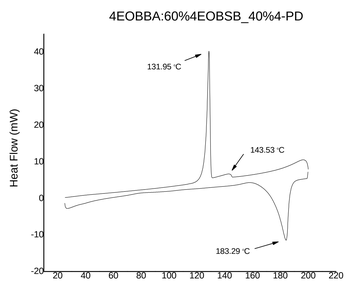
Thermal Analysis

- 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/$EOBSB/4PD Networks

4EOBBA:4EOBSB/4-PD

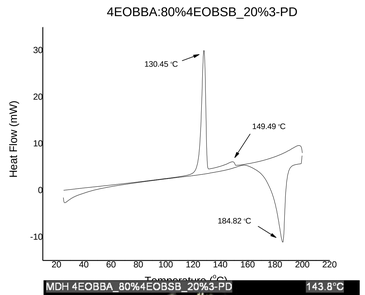
	KI	IN	NK	IK
0%	183.8	158.7	125.4	
5%	185.0	156.3	129.0	
10%	185.3	156.6	129.1	
15%	186.0	153.7	130.1	
20%	184.1	152.1	129.1	
25%	184.8	149.9	130.3	
30%	182.8	144.8	129.6	
35%	182.8	144.4	130.1	
40%	183.3	143.5	132.0	
45%	181.4	137.1	129.5	
50%	181.3	138.1	131.3	
55%	180.6	134.8	129.5	
60%	178.9	131.5	128.3	
61.5%	177.2			128.2
62.5%	178.5			127.6
65.0%	177.3			129.0

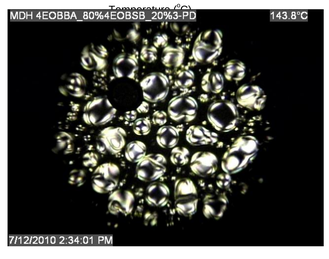


4EOBBA/$EOBSB/3PD Networks

4EOBBA:4EOBSB/3-PD

	KI	IN	NK	IK
0%	183.8	158.7	125.4	
5%	187.0	157.7	128.8	
10%	184.2	154.1	128.0	
15%	183.2	150.6	129.2	
20%	184.8	149.5	130.5	
25%	183.8	144.6	130.3	
30%	183.2	145.2	128.9	
35%	183.9	141.0	130.9	
40%	182.4	136.8	129.6	
45%	180.2	132.3	129.2	
50%	178.3	131.0	128.4	
52.5%	179.5			128.34
55%	178.7			129.2

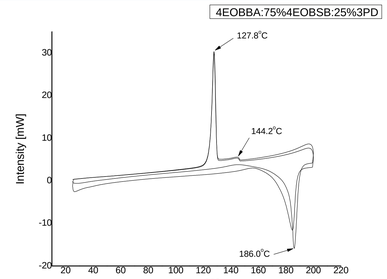


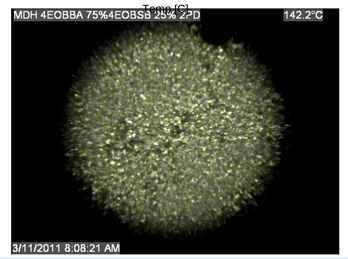


4EOBBA/4EOBSB/2PD Networks

4EOBBA:4EOBSB/2-PD

	KI	IN	NK	IK
0%	183.7	158.6	125.4	
5%	184.3	155.5	128.0	
10%	184.5	152.8	126.7	
15%	184.1	152.1	124.8	
20%	181.4	148.2	123.4	
25%	181.0	136.2	126.5	
30%	180.2	136.9	124.6	
35%	179.8	131.5	125.0	
40%	178.4	128.4	123.9	
42.5%	177.9	128.1	124.5	
45%	176.9			125.0
50%	176.8			124.0





Results/Observations

•4PD-Containing Systems:
-LC character destroyed at 60% loading
-Much higher than previously observed 4PD system with 4PD
•3PD-Containing Systems:
-LC character destroyed at 50% (vs 33%)
•2PD-Containing Systems:
-LC Character destroyed at 42.5% (vs 22.5%)

General Observations:
Nematic monotropic phases (cooling) observed in all systems
All systems displayed clearing concentrations markedly higher than those observed in 2RP containing systems
Increased flexibility of 4EO BSB system attributed to his increase

Conclusions

•A series of novel liquid crystalline supramolecular networks formed through hydrogen bonds have been synthesized.
•Networks display monotropic nematic character at high concentrations of disrupting netpoints
60% for tetrapyridyls (4PD)
50% for tripyridyls (3PD)
42.5% for bipyridyls (2PD)
•Decreasing loading concentrations could be a function of decreasing melting temperatures of the crosslinking agent.
•Loadings in systems are markedly higher than those seen utilizing a smaller, more rigid bis- pyridyl.
•Increased tolerance for disruptive agents can be attributed to the flexibility possessed in 4EOBSB
•Increased flexibility allows for the chains to realign and maintain mesogenicity by overcoming localized structural defects and disruptive agents.

Acknowledgements

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