

Supramolecular liquid crystalline polymers and networks: incorporating flexible networking agents in mesophase formation and stability



Wiegand Research:
Catastrophe from
catastrophe

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Background

Liquid Crystals

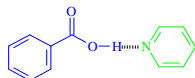
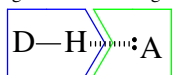
• Materials that exhibit long-range and limited short-range directional ordering in a fluid state.

• Composed of mesogens (shaped molecules) and flexible spacers

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

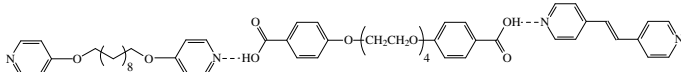
Molecular Self-assembly Through Hydrogen Bonding

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

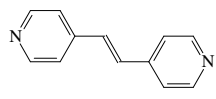


Mesogenic Networks

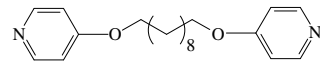
- Combine characteristic of networks and liquid crystals
- Couple physical deformations with liquid crystalline phase behavior
- Thermoreversibility through hydrogen bonding would introduce lability and the ability to reorganize to maximize these characteristics



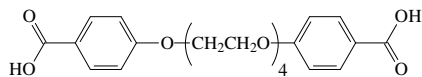
Materials Used



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

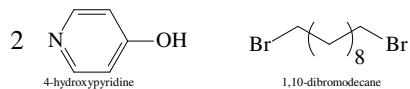


1,10-bis(4-pyridyl)decane
10BPD

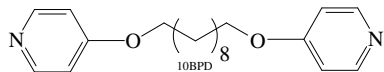


Tetraethyleneglycoxy bis(4-benzoic acid)
4EOBBA

Synthetic Methodologies



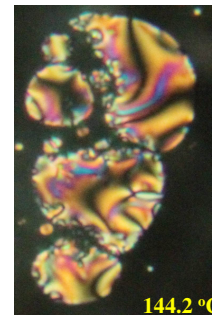
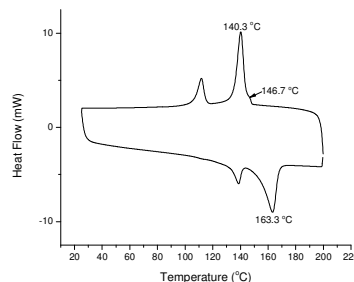
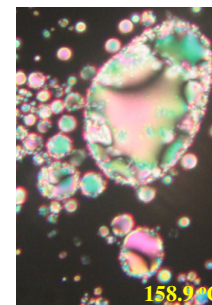
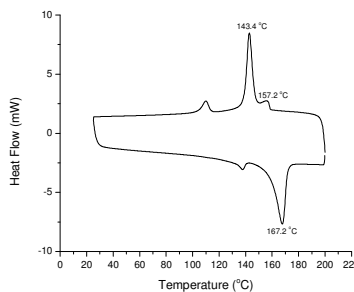
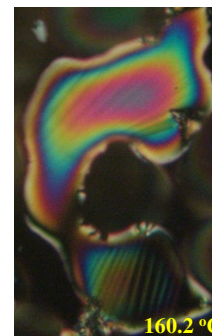
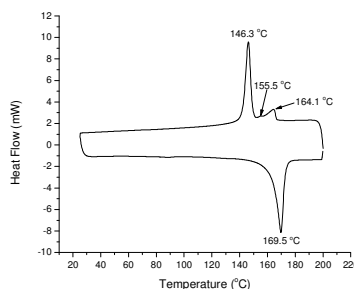
Cs_2CO_3 DMF



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:2RP/10BPD Networks



4EOBBA:2RP/10BPD Networks

4EOBBA:2RP/10BPD						
10BPD	KI	IN	NS	SK	NK	IK
0%	172.5	173.5	165.3	148.6	X	X
5%	170.0	170.8	162.7	147.6	X	X
10%	169.5	164.1	155.5	146.3	X	X
15%	167.8	160.6	151.9*	145.3	X	X
20%	167.2	157.4	X	X	143.4	X
25%	163.1	149.2	X	X	140.4	X
30%	163.3	146.7	X	X	140.3	X
40%	162.1	145.1	X	X	139.4	X
45%	153.1	X	X	X	X	122.7
50%	153.5	X	X	X	X	125.6
55%	153.4	X	X	X	X	126.4
100%	143.1	X	X	X	X	119.5

Results/Observations

General Observations:

- Nematic monotropic phases (cooling)
- Observed in all systems, smectic until 15% loading of disruptor
- Almost all samples display a decreasing melting with increasing loading

Specific Observations:

- 10BPD competitor for hydrogen bonds in systems
- Liquid crystal characteristics disappeared between 45 and 50% loadings
- Linear Polymers still maintained
- Overall decrease in transition temperatures throughout systems

Conclusions

- A series of novel liquid crystalline supramolecular linear polymers formed through hydrogen bonds have been synthesized.
- Polymers display monotropic nematic character at high concentrations of disrupting acceptors
- Decreasing mesogenicity with increasing loading concentrations of the non-liquid crystalline component could be a function of decreasing melting temperatures of the disrupting agent.
- Loadings in systems are markedly higher than those seen utilizing a smaller, crosslinking poly-pyridyl (tetrafunctional 25%).
- Increased tolerance for disruptive agents can be attributed to the flexibility possessed in 10BPD
- Increased flexibility allows for the chains to realign and maintain mesogenicity by overcoming localized structural defects and disruptive agents.

Acknowledgements

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