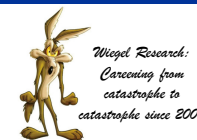


Supramolecular main-chain liquid crystalline polymers and networks with competitive hydrogen bonding: a study of rigid networking agents in systems with competitive hydrogen bonding



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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)

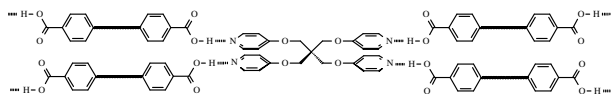
Molecular Self-assembly Through Hydrogen Bonding

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

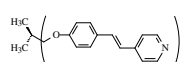
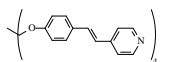
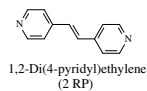
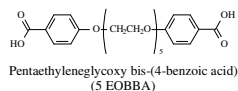


Mesogenic Networks

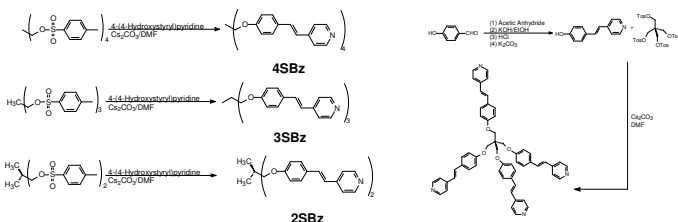
- Combine characteristic of networks and liquid crystals
- Couple physical deformations with liquid crystalline phase behavior
- Thermoreversibility through hydrogen bonding would introduce lability and the ability to reorganize to these characteristics



Materials Used



Synthetic Methodologies



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

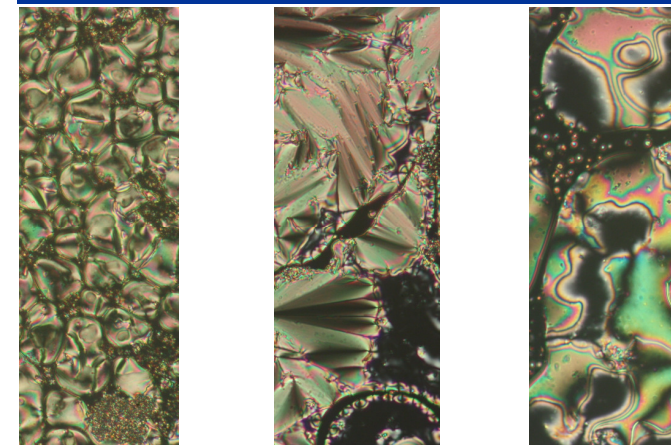
4EOBBA/2RP/nSBZ Networks

% 4SBZ	KI	KN	NI	IN	NS	SK	NK	IK
0	172.45	X	X	173.17	165.31	148.62	X	X
5	X	118.2	170.5	171.4	160.1	144.6	X	X
10	X	119.9	167.8	161.1	X	X	139.9	X
15	170.1	X	X	165.1	X	X	141.2	X
20	169.5	X	X	163.5	X	X	140.6	X
25	169.4	X	X	161.3	X	X	138.0	X
30	166.2	X	X	156.4	X	X	133.1	X
35	166.5	X	X	154.7	X	X	130.9	X
40	164.5	X	X	152.6	X	X	123.2	X
45	162	X	X	146.5	X	X	120.1	X
50	161.5	X	X	147.9	X	X	117.8	X
55	169.2	X	X	139.3	X	X	124.9	X
60	159.8	X	X	143.5	X	X	Vit	X
62.5	153.2	X	X	141.6	X	X	Vit	X
65	143.3	X	X	X	X	X	X	135.9
100	153.5	X	X	X	X	X	X	122.7

% 3SBZ	KI	IN	NS	SK	NK	KI
0	172.45	173.47	165.31	148.62	X	X
5	171.33	170.92	160.62	144.49	X	X
10	171.86	169.97	X	X	146.03	X
15	171.66	167.31	X	X	144.6	X
20	167.63	159.47	X	X	134.88	X
25	167.15	160.04	X	X	137.15	X
30	166.73	158.01	X	X	134.92	X
35	167.29	159.61	X	X	136.4	X
40	163.35	151.24	X	X	128.4	X
45	161.3	145.59	X	X	108.68	X
50	162.85	146.07	X	X	130.22	X
55	159.42	144.74	X	X	115.5	X
57.5	159.05	X	X	X	X	138.01
60	150.4	X	X	X	X	121.06
70	164.13	X	X	X	X	135.07
90	165.45	X	X	X	X	138.35
100	164.99	X	X	X	X	131.84

% 2SBz	KI	IN	NS	SK	NK	IK
0	172.45	174.43	166.67	152.36	X	X
5	173.71	175.83	166.6	150	X	X
10	172.1	171.44	161.17	145.87	X	X
15	169.85	168.34	155.57	141.07	X	X
20	169.31	166.48	X	X	139.27	X
30	168.05	161.59	X	X	133.72	X
40	163.69	154.06	X	X	122.2	X
45	153.92	145.39	X	X	111.54	X
50	153.82	144.37	X	X	111.52	X
57.5	155.4	138.36	X	X	115.37	X
60	154.59	X	X	X	X	119.76
65	155.04	X	X	X	X	118.44
70	151.54	X	X	X	X	117.63
100	165.28	X	X	X	X	142.68

Optical Images



Results/Observations

- The associative chain structures displayed mesogenic characteristics at loadings dependent on the functionality of the crosslinking agent
 - 4SBZ
 - Complexes displayed enantiotropic mesogenic phases in loadings up to and including 10%
 - Smectic phases were observed in the cooling cycle up to the same concentrations.
 - Above 10%, only monotropic (cooling) phases were observed up to 62.5% inclusion.
 - 3SBZ
 - Loadings of 3SBZ displayed monotropic phases in concentrations up to 55%
 - Smectic phases observed up to 5% loading.
 - 2SBZ
 - 2SBZ as disrupting agent nematic in loadings up to 57.5% (smectic phases observed up to 15%).

Conclusions

Supramolecular liquid crystalline networks and polymers have been synthesized with a flexible bisbenzoic acid group and two pyridyls:

- A small rigid bipyrindyl capable of forming a mesophase
- A series of rigid poly-pyridyls that serve as liquid crystalline disruptors.

It was found that the inclusion of the disruptor units varied according to the functionality-

- Tetra-functionalized species destroyed nematic phases at 62.5%,
- Tri at 55%
- Bi at 57.5% loadings.

These inclusion concentrations are markedly higher than those seen in analogous one-ring poly-pyridyl networking agents.

One supposition for this phenomenon is the increased rigidity of the nSBZ series is less disruptive to the overall formation of a mesophase.

Acknowledgements

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