A Coarse-Graining Approach to the Simulation of Macromolecular Liquid Crystals

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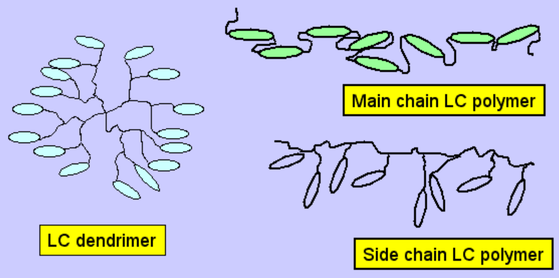
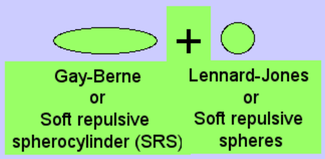
INTRODUCTION

•We have been developing coarse-grained simulation models capable of studying the molecular organisation in liquid crystal dendrimers and polymers, which exhibit microphase separation and nanoscale ordering.

•Model molecules are built from a combination of anisotropic and isotropic sites, linked together.

•Phase behaviour and molecular organisation is studied via constant *NpT* molecular dynamics simulation.





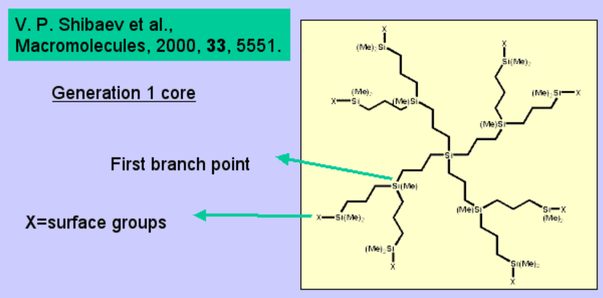
$$U = \sum_{i=1}^{N_{angle}} \frac{1}{2} k_i (\theta_1 - \theta_2)^2 + \sum_{i=1}^{N_{dihedral}} \sum_{n=0}^{n=5} C_n (\cos\phi_i)^n + \sum_{i=1}^{N_{LJ}} \sum_{j>i} U_{ij}^{LJ} + \sum_{i=1}^{N_{GB}} \sum_{j>i} U_{ij}^{GB} + \sum_{i=1}^{N_{LJ}} \sum_{j=1}^{N_{GB}} U_{ij}^{LJ/GB}$$

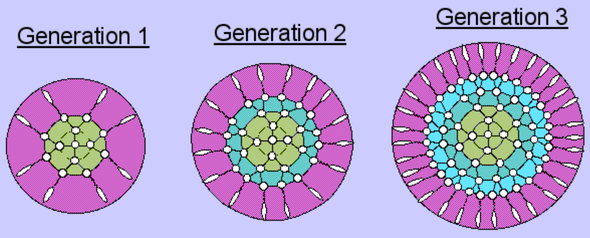
Bond angle bending | Dihedral angle twisting | Non-bonding interactions

and/or bond potential/SHAKE (+GB-angle) or FENE/soft-springs

CARBOSILANE LC DENDRIMERS

V. P. Shibaev et al., Macromolecules, 2000, **33**, 5551.

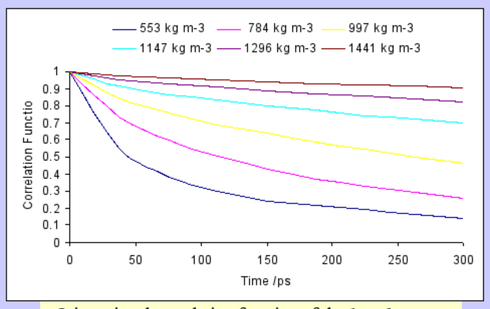




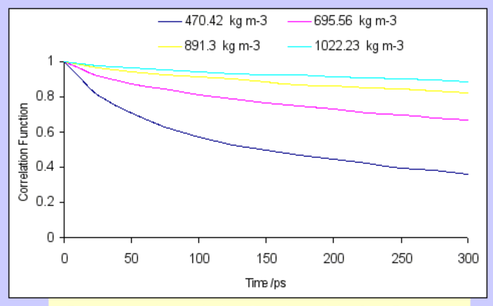
8 mesogens $C_{264}H_{404}O_{24}Si_{21}N_8$ 721 atoms

16 mesogens $C_{544}H_{844}O_{48}Si_{45}N_{16}$ 1497 atoms (x2.07)

32 mesogens $C_{1104}H_{1724}O_{96}Si_{93}N_{32}$ 3049 atoms (x2.04)



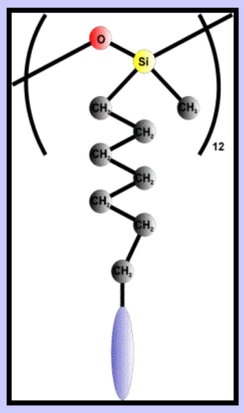
Orientational correlation function of the 1 to 6 system



Orientational correlation function of the 1 to 8 system

SIDE-CHAIN LIQUID CRYSTAL POLYMER

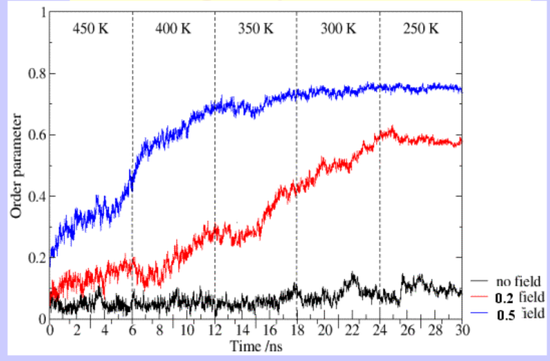
Side Chain LCP based on LC functionalised polydimethylsiloxane



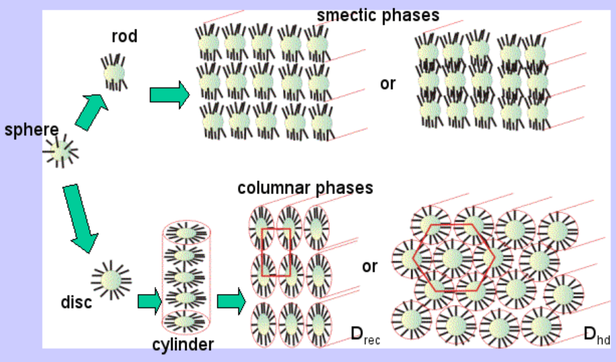
- LJ united atoms for O, Si, CH_3/CH_2
- Gay-Berne mesogens
- 64 molecule melt
- free rotation for Si-O-Si-O,
- standard CH_2-CH_2 -CH_2 -CH_2 torsion,
- SHAKE, standard K_b, θ^o
- *NpT* molecular dynamics @ 1 atm
- Large system size & long annealation required
- Cooling through from 500 K to 250 K with and without magnetic field

$E = -\nu \langle P2(\cos\theta) \rangle$

Ordering of System Over Time



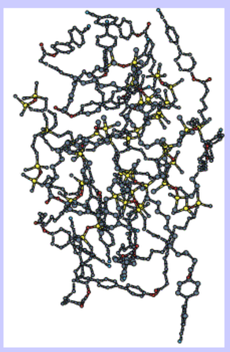
Bulk phases predicted from X-ray studies



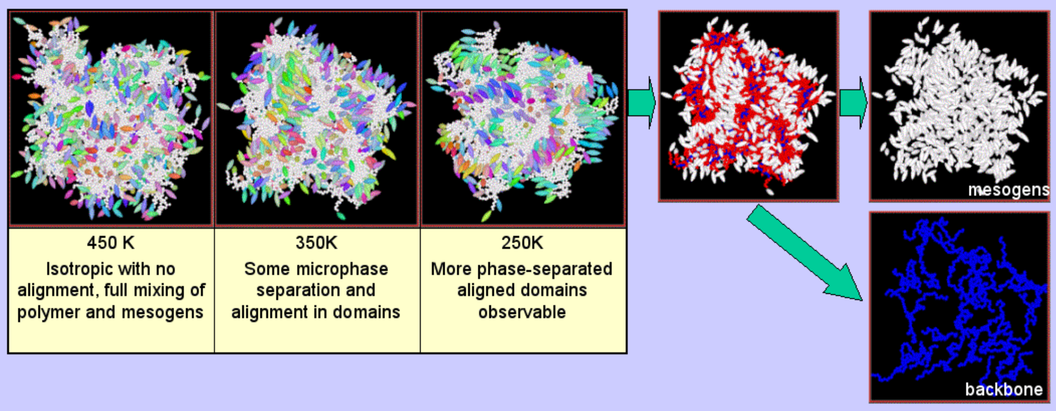
Evidence from X-ray studies of Rob Richardson, Bristol

Gas Phase Studies

- 3049 atoms
- OPLS All-Atom force field
- Monte Carlo simulations
- Extract conformational info
- Mean field to mimic surrounding molecules
- See alignment of mesogenic groups
- Use results to design coarse-grained model



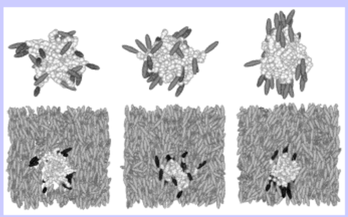
SCLCP cooled without field



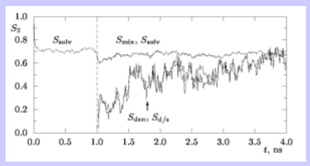
450 K	350K	250K
Isotropic with no alignment, full mixing of polymer and mesogens	Some microphase separation and alignment in domains	More phase-separated aligned domains observable

Dendrimer in Nematic Solvent

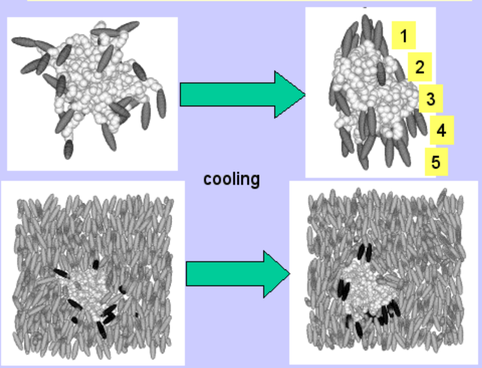
Structure Change
- Dendrimer structure distorts so that mesogens align with solvent



Order Parameter
•Solvent uncompromised
•Dendritic mesogen becomes nematic over 4 ns

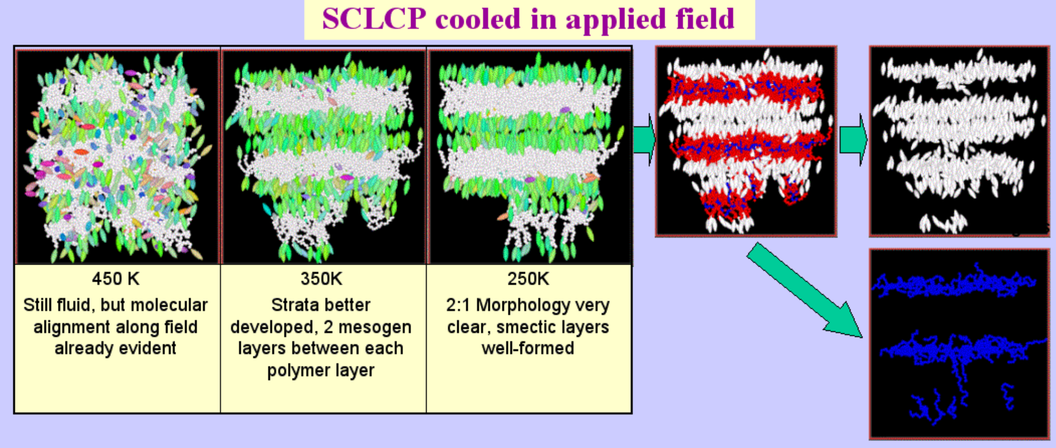


Dendrimer in Smectic Solvent



Dendrimer mesogens spread over 5 smectic layers

SCLCP cooled in applied field



Coarse grained simulation of the bulk phase

•Coarse grained model is used for bulk phases

•Central sphere used for dendrimer core, small spheres used to coarse-grain chains and mesogens coarse-grained to spherocylinders

•The bulk phase consists of 100 dendrimer molecules

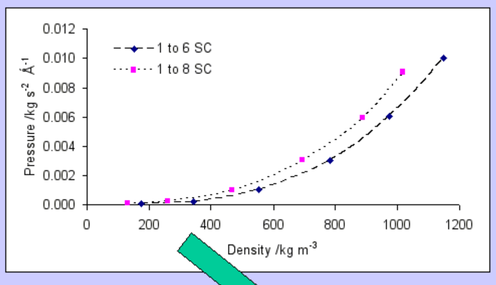
•The system starts with the molecules on lattice points in the gas phase

•The pressure is then increased slowly. At each density the system is allowed to equilibrate

•The initial model had spherocylinders with an aspect ratio of 1 to 6. This model didn't form mesophases

•This model didn't form mesophases so the aspect ratio was increased to 1 to 8

Coarse grained model



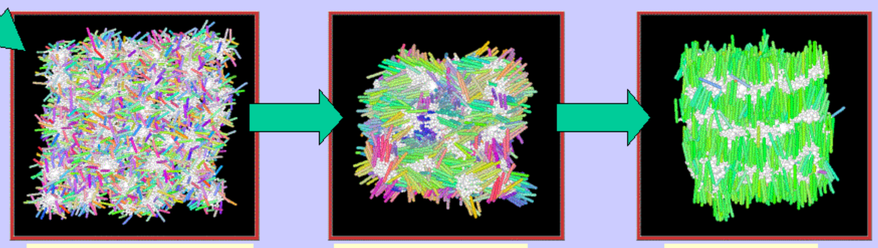
•The increase in length helped the formation of liquid crystalline phase

•However the increased spherocylinder length does mean the reorientational movement of the system is decreased

•The reorientational motion of the system was measured using the correlation function of the rate of decay of the mesogens

•The decay of the correlation function for the 1 to 8 spherocylinders is much slower

Spontaneous microphase separation occurs at higher densities leading to a stable smectic-A phase



Bulk phase at low pressure | Microphase seperation | Smectic-A phase

Radial distribution functions, *g(r)*

• 450 K systems are isotropic with no differences from field

• low T alignment to Sm_A in field

•If *g(r)* is resolved parallel and perpendicular to the director we see the onset of microphase separation and smectic layer formation.

•For the smaller applied field the mesogens remain nematic within the layers.