Discotic Liquid Crystals and Polymers
In Cylindrical Confinement:
Supramolecular Architecture of LC Nanorods and nanotubes

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Motivation

Relevance: two-dimensional LC nanostructures are potential components of miniaturized devices with specific electronic properties


Dependence of mesophase texture on:

>> Interfacial energies
>> Diameter
>> Curvature

(>> Doping)
Specific motivation

Polymer dispersion controls optoelectronic properties
Mesophase Formation in 2D Geometric Confinement

Strategy:

Preparation of nanostructures by

Electrospinning

1. Variation of the polymer matrix

Wetting of ordered porous templates

1. Dispersed/nondispersed system

2. Modification of pore diameter $>>$ diameter $>>$ curvature

3. Modification of pore walls $>>$ Interfacial energies

4. Doping of the LC phase

Simulation of structure formation
Discotic Model System: Ada-PBT

Discotic liquid crystal of the triphenylene type: Ada-PBT

Spontaneous formation of columns
Columns form hexagonal superstructures

High charge carrier mobility along long axis of columns
Performance depends on degree of order

Dominant Reflections

(100) – intercolumnar distance
$2\Theta \sim 5^\circ$, very strong

(001) – intracolumnar distance
$2\Theta \sim 25^\circ$, weak
Linear PDLC systems:

>> nanofibers

Electrospinning

Coelectrospinning
Amorphous polymers
Polymethylmethacrylate (PMMA)
Polystyrene (PS)
- transparent
Electrospun PDLC fibers

REM studies
Electrospun PDLC fibers

Electron microscopical studies
(Rutheniumtetroxide stained)
Electrospun PDLC fibers

Molecular dispersion in fibers during electrospinning - kinetic effect

Phase separation and coarsening at elevated temperatures

>> Pronounced LC-Phase after annealing
>> No columnar orientation along fiber axis

Core shell structures yet not consistently
Method: Template wetting

- Melting the discotic onto the surface of ordered porous alumina
- Discotic LC infiltrates the template as an isotropic liquid
- Rapid quenching to glassy state
Highly Ordered Templates

Order by self-assembly; sharp pore size distribution
(H. Masuda, K. Fukuda, Science 1995, 268, 1466)

Pore diameters: 25 to 400 nm; pore depth: 100 μm

Laterally extended membranes having aligned pores
Ada-PBT/PMMA

50 nm pore diameter  >> nanorods

400 nm pore diameter  >> nanotubes

(Rutheniumtetroxide stained); $M_w$(PMMA): $\sim 250.000$ g/mol
Triphenylene (Ada-PBT)

complete filling of the pores
no defects

>> Nanorods
Ada-PBT Nanorods: Structure Model

Planar core phase, columns grow along long axes of template pores

⇒ potential nanocables

Homeotropic anchoring at pore walls. Homeotropic shell at the LC/wall interface surrounds planar core phase

XRD: $\Theta/2\Theta$ scans

XRD on *aligned* Ada-PBT nanorods:

Intensity of inter-columnar (100) peak originates from homeotropic phase

Intensity of intra-columnar (001) peak originates from planar phase

inter-columnar (100) peak $d = 1.6$ nm

intra-columnar (001) peak $d = 0.35$ nm
Ada-PBT nanorods: intra-columnar (001) peak with strongly enhanced relative intensity

Isotropic bulk Ada-PBT

Pore diameter: 400 nm

Ada-PBT nanorods: intracolumnar (001) peak with strongly enhanced relative intensity

Dominant planar orientation (columns parallel to long axes of template pores)!

Uniaxial orientation of the columns along the pore axis
Modification of pore walls

Templates have pore walls consisting of alumina

>> polar surface

How does non-polar surface modification influence texture of mesophase?
Coating of pore walls with PPX

**Evaporation** 200°C  
**Pyrolysis** 600-700°C  
**Deposition** <30°C

Chemical vapour deposition of PPX

Infiltration of Ada-PBT into PPX-coated templates

**Poly(paraxylylene):**

- non-polar; high chemical and mechanical stability;
- very good insulator
XRD: $\Theta/2\Theta$ scans

XRD on *aligned* Ada-PBT nanorods:

- Intensity of inter-columnar (100) peak originates from homeotropic phase
- Intensity of intra-columnar (001) peak originates from planar phase
$\Theta/2\Theta$ scans of aligned AdaPBT nanorod in PPX pores

Non-modified pore walls:
- Planar texture
  - 400 nm
  - 35 nm

Non-polar pore walls modified with PPX:
- No texture; bulk-like pattern

>> No texture; bulk-like pattern
Doping of mesophase

Dopants incorporated into Ada-PBT columns


**Model dopants**: nitrofluorenone derivatives
**Selected mixing ratio**: 80 mol-% Ada-PBT, 20 mol-% dopant
Dopants: nitrofluorenone derivatives

2,4,5,7-Tetranitro-9-fluorenone

2,4,7-Trinitro-9-fluorenone

2,7-Dinitro-9-fluorenone

2-Nitro-9-fluorenone

Systematic variation of the substitution pattern
Θ/2Θ-Scans on aligned, doped Ada-PBT Nanorods - 400 nm

In contrast to pure Ada-PBT nanorods: no dominance of intra-columnar (001) reflection!

Growth of planar core phase disturbed!

Planar texture suppressed
Θ/2Θ-Scans on aligned, doped Ada-PBT Nanorods - 35 nm

In contrast to pure Ada-PBT nanorods: planar texture less pronounced! Exception in nanorods with Dinitrofluorenon:
XRD: Texture analysis

$\Psi$-scans represent orientation distributions of (100) and (001) lattice planes with respect to template surface $\Theta$ and $2\Theta$ adjusted to corresponding peak maxima.
Ψ–scan (100) - 400 and 35 nm pores

Ψ-Scans of inter-columnar (100) peaks (homeotropic phase):

- **pure Ada-PBT**: no significant difference between 400 and 35 nm pores
- **400 nm**: slight lower degree of orientational order in case of doped Ada-PBT
- **35 nm**: no significant difference between pure Ada-PBT and doped nanorods
**Ψ–scan (001) - 400 and 35 nm**

**Ψ-Scans of intra-columnar (001) peaks (planar phase):**

- **pure Ada-PBT:** slightly lower orientational order in 35 nm pores
- **400 nm:** doping leads to decrease in orientational order depending on the substitution pattern
- **35 nm:** much lower influence of dopants on orientational order
Outlook I: MD-simulations

Simulation of ~14,000 molecules

>> Simulations of molecular shape rather than atomic detail

>> Neglecting adamantanoyle substituent

Cylindric cell, 20x molecular diameter

Molecule/molecule interaction:
Angular dependent Gay Berne potential with Bates Luckhurst extension

Favouring homeotropic anchoring on walls
Neglecting surface curvature in exploratory simulations

Results of exploratory MD runs

>> formation of a hexagonal columnar core

>> good agreement with the previous experimental results structure model

future simulations will focus on varying curvature and surface interaction
Conclusions:

Polar pore walls: pronounced planar texture.
Non-polar pore walls: no apparent texture

Doping of the Ada-PBT nanorods suppresses planar texture in 400-nm pores, but not in 35-nm pores

Future work will focus on the influence of the thermal history on the mesophase formation

Morphology design by molecular dynamics simulations (MD)

>> Set of parameters can be systematically varied
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