Computer simulations of a self-assembly of liquid crystalline dendrimers

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Abstract

A coarse-grained simulation model for a third generation liquid crystalline dendrimer (LCDr) is presented. It allows, for the first time, for a successful molecular simulation study of a relation between the shape of a polyphilic macromolecular mesogen and the symmetry of a macroscopic phase. The model dendrimer consists of a soft central sphere and 32 grafted chains each terminated by a mesogen group. The mesogenic pair interactions are modelled by the recently proposed soft core spherocylinder model of Lintuvuori and Wilson [J. Chem. Phys, 128, 044906, (2008)]. Coarse-grained (CG) molecular dynamics (MD) simulations are performed on a melt of 100 molecules in the anisotropic-isobaric ensemble. The model LCDr shows conformational bistability, with both rod-like and disc-like conformations stable at lower temperatures. Each conformation can be induced by an external aligning field of appropriate symmetry that acts on the mesogens (uniaxial for rod-like and planar for disc-like), leading to formation of a monodomain smectic A ($\mathrm{Sm_A}$) or a columnar (Col) phase, respectively. Both phases are stable for approximately the same temperature range and both exhibit a sharp transition to an isotropic cubic-like phase upon heating. We observe a very strong coupling between the conformation of the LCDr and the symmetry of a bulk phase, as suggested previously by theory. The study reveals rich potential in terms of the application of this form of CG modelling to the study of molecular self-assembly of liquid crystalline macromolecules.

Experimental background

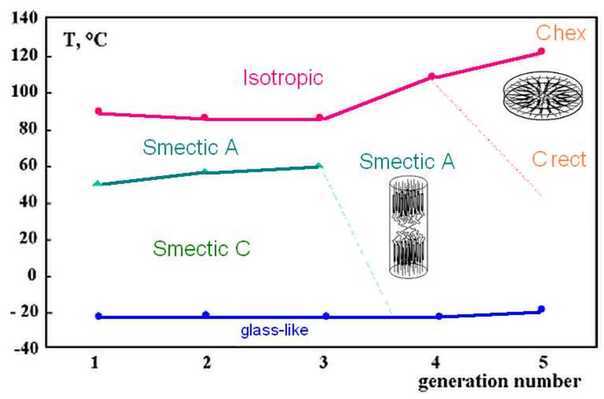

Fig.1. *Experimental phase diagram of the carbosilane LCDr depending on the generation number and temperature [S. Ponomarenko et al., Macromolecules, 33, 5549 (2000)].*

Important factors that shape up the phase diagram:

- generation number
- terminal spacer length
- packing density of LC groups on the surface

Model

Multiscale approach

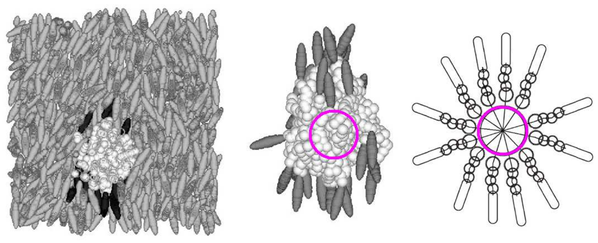

Fig.2. *The average shape of the LCDr in LC solvent has been studied first on atomic level by molecular dynamics simulations [M.R. Wilson, J. Ilnytskyi, L.M. Stimson, J. Chem. Phys. 119, 3509 (2003); Liq.Cryst. 33, 1167 (2006)] (left and central frame). This provided the basis for the CG model (right frame). In this study we use the model with an infinite core flexibility (free sliding chains on a core sphere.*

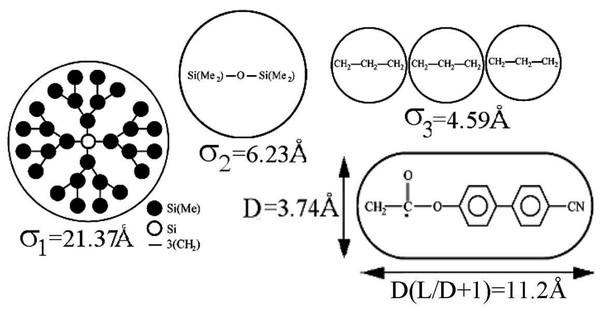

Fig.3. *The details of coarse graining procedure [Z. Hughes et al, Soft Matt. 1,436 (2005)].*

Potentials:

$$V_{ij}^{\mathrm{sp-sp}} = \begin{cases} U_{\max}^{\mathrm{sp-sp}}(1-r_{ij}^*)^2, & r_{ij}^* < 1 \\ 0, & r_{ij}^* \geq 1, \end{cases}$$

$$V_{ij}^{\mathrm{sc-sc}} = \begin{cases} U_{\max}^{\mathrm{sc-sc}}(1-d_{ij}^*)^2, & d_{ij}^* < 1 \\ U_{\max}^{\mathrm{sc-sc}}(1-d_{ij}^*)^2 - U_{attr}^*(\hat{r}_{ij},\hat{e}_i,\hat{e}_j)(1-d_{ij}^*)^4 + \epsilon^*, & 1 \leq d_{ij}^* < d_c^* \\ 0, & d_{ij}^* > d_c^*, \end{cases}$$

$$U_{\mathrm{attr}}^*(\hat{r}_{ij},\hat{e}_i,\hat{e}_j) = U_{\mathrm{attr}}^* - \left[5\epsilon_1 P_2(\hat{e}_i\cdot\hat{e}_j) + 5\epsilon_2(P_2(\hat{r}_{ij}\cdot\hat{e}_i) + P_2(\hat{r}_{ij}\cdot\hat{e}_j)\right].$$

$$V_{ij}^{\mathrm{sp-sc}} = \begin{cases} U_{\max}^{\mathrm{sp-sc}}(1-d_{ij}^*)^2, & d_{ij}^* < 1 \\ 0, & d_{ij}^* \geq 1, \end{cases}$$

where $r_{ij}^* = r_{ij}/\sigma_{ij}$, $\sigma_{ij} = (\sigma_i+\sigma_j)/2$, $d_{ij}^* = d_{ij}/D$, $d_{ij}^* = d_{ij}/\sigma_{ij}$, $\sigma_{ij} = (\sigma_i + D)/2$, $U_{\max}^{\mathrm{sp-sc}} = U_{\max}^{\mathrm{sp-sp}}$

Details of the simulations:
$N = 100$ LCDr molecules in the melt, coarse-grained molecular dynamics, $NP_{xx}P_{yy}P_{zz}T$ ensemble, $\Delta t = 20\,\mathrm{fs}$

Field-assisted self-assembly

Extra energy term to describe reorientation of LC groups:

$$U_{\mathrm{rot}} = -F\cos^2(\theta_i),$$

where $F > 0$ imposes uniaxial alignment and $F > 0$ imposes planar one (in planes perpendicular to the field direction), reduced field constant f, $F = f\cdot 10^{-20}$J.

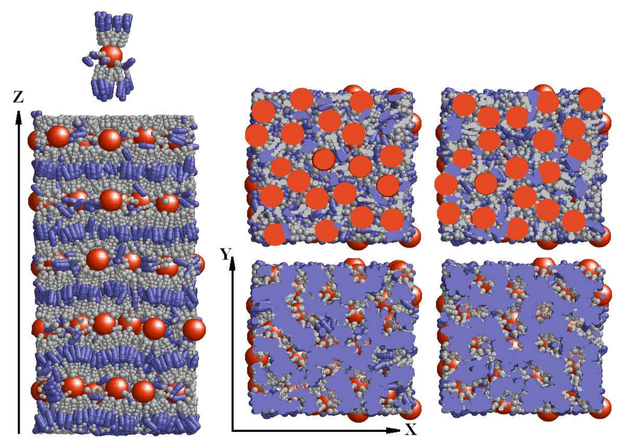

Fig.4. *The $\mathrm{Sm_A}$ phase induced by the uniaxial field ($f = 2$) subsequently equilibrated at $T = 470\,K$ with no field. Typical molecular conformation is shown above lamellar structure (left frame). 2D cuts of layers are shown in the right frame.*

Metric properties and nematic order along the field:
Gyration tensor:

$$G_{\alpha\beta}^{[k]} = \frac{1}{N^{[k]}}\sum_{i=1}^{N^{[k]}}(r_{i,\alpha}^{[k]} - R_\alpha^{[k]})(r_{i,\beta}^{[k]} - R_\beta^{[k]}), \quad \vec{R}^{[k]} = \frac{1}{N^{[k]}}\sum_{i=1}^{N^{[k]}}\vec{r_i^{[k]}},$$

asphericity $a = [G_{zz} - \frac{1}{2}(G_{xx}+G_{yy})]R_g^{-2}$, nematic order along the field $S_z = \langle P_2(e_i^z)\rangle$.

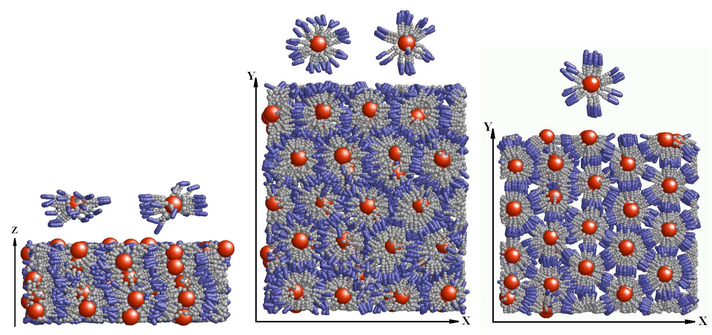

Fig.5. *Col phase (at $T = 490\,K$) and frozen Col phase (at $T = 350\,K$). The arrangement of LCDrs into columns are seen in the left frame, hexagonal arrangement of columns is seen in the middle frame, molecular conformations are shown above each snapshot. Frozen Col phase has highly ordered structure with the LCDrs adopting a hexamer-like conformation (right frame).*

Synchronicity in changes of macromolecules asphericity and bulk nematic order:

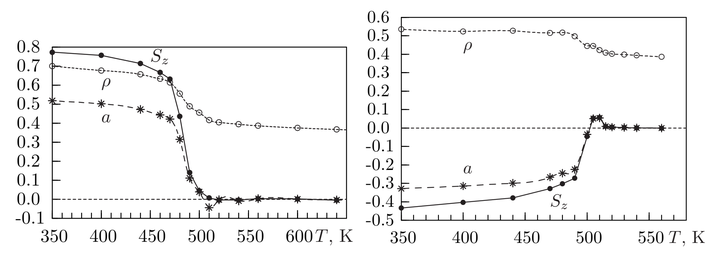

Fig.5. *Synchronicity in the changes of molecular asphericity a, density ρ and nematic order parameter S_z at the $\mathrm{Sm_A}$ -I (left frame) and Col-I (right frame) phase transitions.*

Spontaneous self-assembly

The mixture of both phases ($\mathrm{Sm_A}$ and Col) is observed at both slow cooling down and slow compression of the isotropic phase with no field applied.

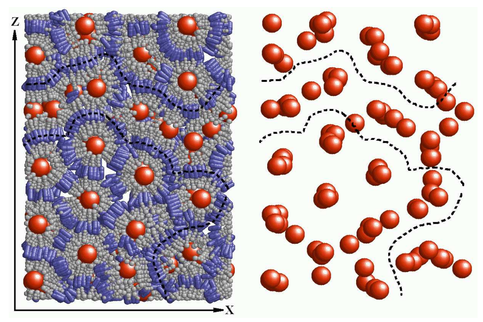

Fig.6. *All particles (left frame) and dendritic cores only (right frame) for the spontaneously assembled mixture of $\mathrm{Sm_A}$ and Col phases. This phase is obtained by isobaric ($P = 50\,\mathrm{atm}$) cooling of an isotropic phase from $520\,K$ down to $400\,K$ at a rate $12\,K/\,\mathrm{ns}$ (for $10\,\mathrm{ns}$) and then keeping the constant temperature at $400\,K$ (for another $15\,\mathrm{ns}$). Approximate domain boundaries are shown by dotted contours.*

Conclusions:

- Succesfull simulation of macromolecular self-assembly;
- Supports experimentally observed shape-phase relation;
- The model with an infinite flexibility of internal core leads to conformational bistability of LCDr and, as the result, bulk phase bistability;
- The need to generalise a model via finite flexibility of the core, varying spacer length, fine parametrisation of the potential.

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