Supporting Information

Effect of Grafting Density on the Self-Assembly of Side-Chain Discotic

Liquid Crystalline Polymers with Triphenylene Discogens

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Simulation Method and Model Additional Information

As for the DPD method, the DPD system uses particles as the basic unit. The movement of all particles follows Newton's equation of motion,[1]

$$\frac{d\vec{r}_i}{dt} = \vec{v}_i, \quad \frac{d\vec{v}_i}{dt} = \frac{\vec{f}_i}{m_i}$$

where $\vec{r}_i$, $\vec{v}_i$, m_i and $\vec{f}_i$ denote the position, velocity, the force acting on the particle i and mass of it, respectively. And, the total force, is given by

$$\vec{f}_i = \sum_{j \neq i} (\vec{F}_{ij}^{C} + \vec{F}_{ij}^{D} + \vec{F}_{ij}^{R})$$

Where $\vec{f}_i$ consists of three parts, the conservative force $\vec{F}_{ij}^{C}$, the random force $\vec{F}_{ij}^{D}$, and the dissipative force $\vec{F}_{ij}^{R}$; each of them is pairwise interactions. And it only works on all particles within a certain cutoff radius r_C, beyond which the force is neglected. Here r_C is the only length scale in this system, and we considered it as the unit of length, i.e., $r_C = 1$. The conservation force is described as a kind of soft repulsive interaction acting along the centers of two particles：

$$\vec{F}_{ij}^{C} = a_{ij}\omega(r_{ij})\hat{r}_{ij}$$

Where a_{ij} represents the interaction parameter between particles i and j. The r-

dependent weight function $\omega(r_{ij})$ provides the range of interaction for DPD particles with a commonly used choice: $\omega(r_{ij}) = 1 - r_{ij}/r_C \ (r_{ij} \leq r_C)$, and $\omega(r_{ij}) = 0 (r_{ij} > r_C)$. $r_{ij} = |\vec{r}_{ij}|$, $\hat{r} = \vec{r}_{ij}/r_{ij}$, and $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$.

The dissipative force which is proportional to the relative velocity, $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$, is defined as

$$\vec{F}_{ij}^{D} = -\gamma \omega^{D}(r_{ij})(\hat{r}_{ij} \bullet \vec{v}_{ij})\hat{r}_{ij}$$

where γ serves as the friction coefficient to governing the magnitude of the dissipative force. And the random force acting as a heat source to equilibrate the thermal motion of unresolved scales is given by:

$$\vec{F}_{ij}^{R} = \sigma \omega^{R}(r_{ij})\theta_{ij}\hat{r}_{ij}$$

where σ is the noise amplitude controlling the intensity of the random force and θ_{ij} is a randomly fluctuating variable with Gaussian statistics: $\langle \theta_{ij}(t) \rangle = 0$ and $\langle \theta_{ij}(t)\theta_{kl}(t') \rangle = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t-t')$. The relationship between the two weight functions $\omega^{D}(r_{ij})$ and $\omega^{R}(r_{ij})$ is shown in the following equation: [2]

$$\omega^{D}(r_{ij}) = [\omega^{R}(r_{ij})]^2$$

As a simple choice, we set $\omega^{R}(r_{ij}) = \omega^{D}(r_{ij})$, i.e. $\omega^{R}(r_{ij})$ is the same function as in the conservative force. What is more, there is a relation between the two amplitude and $k_{B}T$:

$$\sigma^2 = 2\gamma k_{B}T$$

The combined effect of the dissipative and random force amounts to that of a thermostat.

In the model (Fig. 1), all beads have the same size of r_C, except a bead of discotic core C represents a whole benzene ring with the size of $1.2 r_C$, and all of the beads have the same mass as $m=1$. Within triphenylene-based SDLCPs, neighboring beads

are bonded to each other by a harmonic spring force, $F = -k_s r$, where k_s is the spring constant. We set $k_s = 10.0$ for spacer, and tail chains, while setting $k_s = 100.0$ for discotic mesogenic core. And as for main chain, we set $k_s = 80$, and the elastic coefficient between the first and third beads of main chain $k_{13} = 0$, which reflects the rigidity of main chain. Meanwhile, to keep the discotic mesogen being rigid, a harmonic bending potential is also applied between beads C, which takes the form $U_\theta = 0.5 k_\theta (\theta - \theta_0)^2$, where θ and θ_0 are the current and specified angles formed by the adjacent bonds and k_θ is a stiffness constant. Besides, we use the Lennard-Jones potential to reflect $\pi - \pi$ interaction between discogens. Referring to the real system, the bead in the center of discogen only has interplay with the bead in the center of other adjacent discogens, and the peripheral three beads only have interplay with other adjacent peripheral beads. The time scale is set to $(mr_c^2/\varepsilon)^{1/2}$, and the energy scale is given by $k_B T = 1$, where k_B is the Boltzmann constant and T is the temperature. We use the modified velocity-Verlet algorithm with $\lambda = 0.65$ in integrating the equation of motion. What is more, we set time step $\Delta t = 0.03$ and the amplitude of random noise $\sigma = 3.0$ to avoid divergence of the simulation.
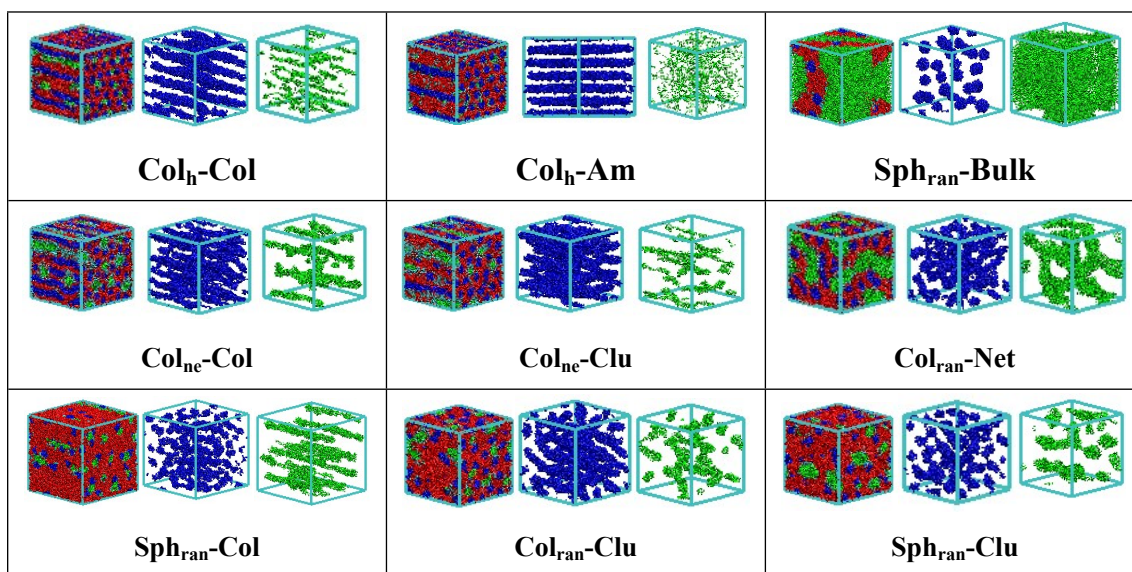
Nine phases of SDLCPs.

Col$_h$-Col	**Col$_h$-Am**	**Sph$_{ran}$-Bulk**
Col$_{ne}$-Col	**Col$_{ne}$-Clu**	**Col$_{ran}$-Net**
Sph$_{ran}$-Col	**Col$_{ran}$-Clu**	**Sph$_{ran}$-Clu**

Fig. S1 Representation of various phase self-assembled by SDLCPs under variant conditions: Col$_h$-Col, Col$_h$-Am, Sph$_{ran}$-Bulk, Col$_{ne}$-Col, Col$_{ne}$-Clu, Col$_{ran}$-Net, Sph$_{ran}$-Col, Col$_{ran}$-Clu, Sph$_{ran}$-Clu. The pictures of each phase are listed in order to show all the beads (left), only discotic mesogenic core beads (middle), and only polymer backbone beads (right).

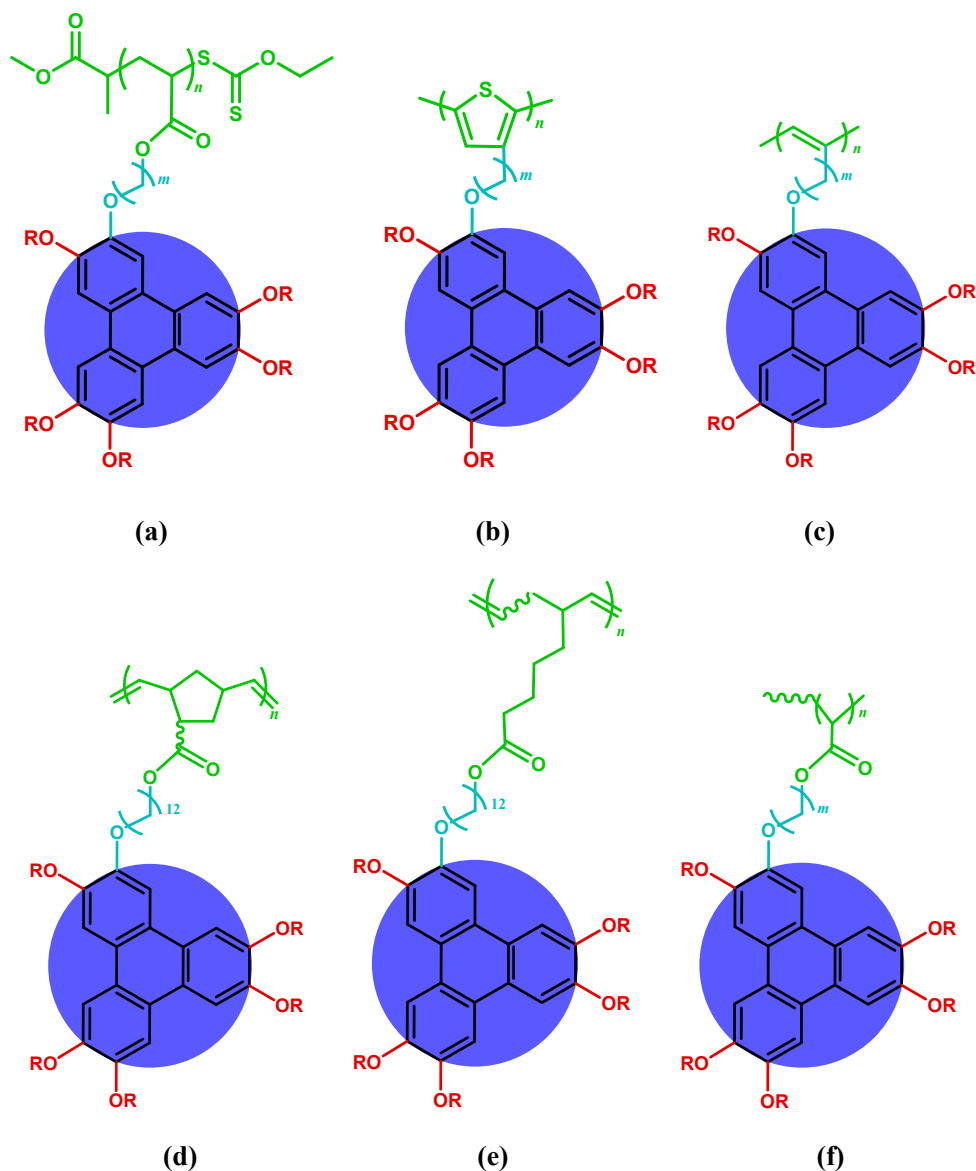**Several SDLCPs with different main chain**

Fig. S2 Several kinds of triphenylene-based side-chain discotic liquid crystalline polymers (SDLCPs) with different polymer backbone of (a) polyacrylate,[3] (b) polythiophene,[4] (c) polyacetylene,[5] (d) polynorbornene,[6] (e) polycyclobutadiene,[6] (f) polymethylene.[7]

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