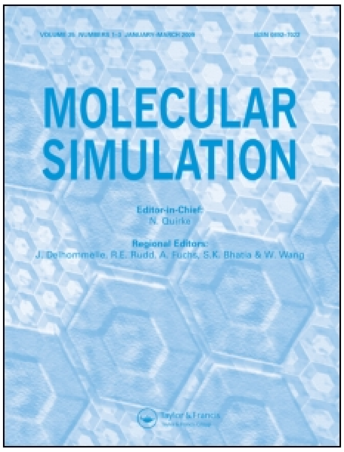


Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

A Monte Carlo Simulation of Nematic and Discotic Ordering in a Polymeric Liquid Crystal

D. R. R. Everitt[a]; C. M. Care[a]
[a] Department of Applied Physics, Sheffield City Polytechnic, Sheffield, UK

To cite this Article Everitt, D. R. R. and Care, C. M.(1990) 'A Monte Carlo Simulation of Nematic and Discotic Ordering in a Polymeric Liquid Crystal', Molecular Simulation, 5: 3, 167 — 173
To link to this Article: DOI: 10.1080/08927029008022128
URL: http://dx.doi.org/10.1080/08927029008022128

Molecular Simulation, 1990, Vol. 5, pp. 167–173
Reprints available directly from the publisher
Photocopying permitted by license only

A MONTE CARLO SIMULATION OF NEMATIC AND DISCOTIC ORDERING IN A POLYMERIC LIQUID CRYSTAL

D.R.R. EVERITT and C.M. CARE

Department of Applied Physics, Sheffield City Polytechnic, Pond Street,
Sheffield, S1 1WB, UK

(*Received November 1989, accepted December 1989*)

A cyclic polymeric liquid crystal system is simulated using the Metropolis Monte Carlo method in the NVT ensemble. The polymeric system consists of mesogenic moieties attached by alkyl chain spacers to siloxane ring polymers. In the model, the mesogenic moieties are represented individually by an anisotropic Lennard-Jones potential and the polymer ring is represented solely as a constraint on the relative motions of the attached mesogens. A transition from calamitic ordering to discotic ordering is observed as the ring-mesogen bond is varied from full flexible to rigid.

KEY WORDS: Liquid crystal, nematic, discotic, polymeric, Monte Carlo.

New materials comprising polydimethylsiloxane rings with side-chains mesogenic moieties attached via alkyl spacers are currently being synthesized [1], and it is hoped that these materials may be suitable for use in optical data storage devices [2]. A variety of ring sizes (4 to 7 repeating units) are being synthesized and the lengths of the spacer units varied to alter the coupling between the mesogens and the polymer backbone. An initial example of these materials and their general structure is shown in Figure 1.

The simulations described here attempt to identify those features of the molecular structure which will be significant in generating different liquid crystal phases. The behaviour of these materials will be strongly dependent upon the nature of the coupling between the mesogenic moieties and the polymer ring backbone. It is expected that weak coupling will result in a calamitic nematic phase [3] in which the rod-like mesogenic moieties tend to align. However, if the coupling is strong, the polymer ring will dominate the behaviour of these materials. For example, if the mesogens are rigidly attached in a planar splay conformation, discotic phases may be expected in which the normals of the ring planes tend to align.

The mesogenic moieties are represented individually by a modified Lennard-Jones 12–6 potential which contains an anisotropic term (Luckhurst [4]).

$$V = V_o + V_a \tag{1}$$

where V_o is the isotropic Lennard-Jones potential and V_a is the anisotropic term.

$$V_a = -4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} + \left(\frac{\sigma}{r}\right)^{6}\right] P_2(\cos\beta_{12}) \tag{2}$$

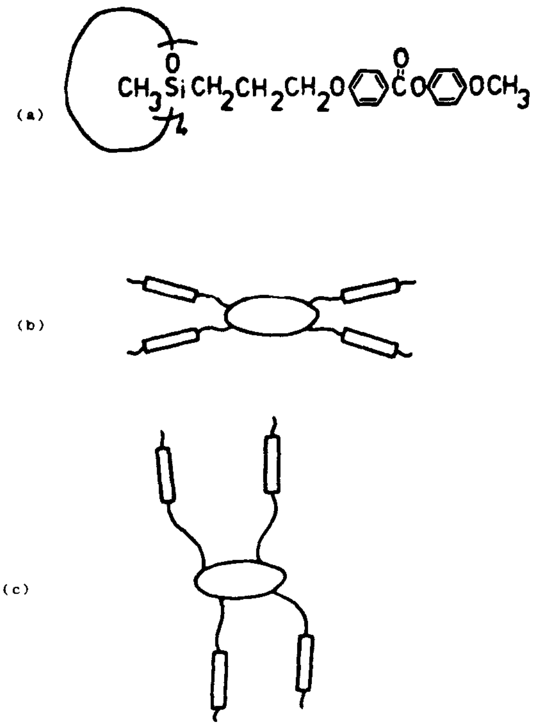


Figure 1 A cyclic compound under investigation (a). Schematic diagram of strong ring-mesogen coupling (b), and weak coupling (c).

The cyclic polymer backbones are represented simply as a constraint on the relative motions of the attached mesogens. The backbones are taken to have a planar ring conformation with the mesogens attached equidistant around the ring, as shown in Figure 2. The strength of the coupling between a ring and the attached mesogens is represented as a restriction on the orientation which the mesogens can have with respect to the ring axes. This potential and its associated constraints are clearly only a first approximation but it is hoped that it contains the essential features of the true inter-molecular potential.

The simulations were performed with a mesogen anisotropy of $\lambda = 0.15$. Preliminary calculations were also performed with a higher anisotropy, but it was found that the degree of order obtained was persistent up to high temperatures, in agreement with the results obtained by Luckhurst [4] for monomeric systems.

The Metropolis [5] Monte Carlo technique was used to simulate a system of one hundred mesogens attached four to a ring. The simulations were performed in the NVT ensemble and each molecule was allowed free translational and rotational motion in 3D. The system was subject to the usual periodic boundary conditions.

The structure of the molecules allowed for just three types of Monte Carlo move: ring translations, where the attached mesogens were moved by the same translational increment in order to maintain their relative positions; ring rotations, where the

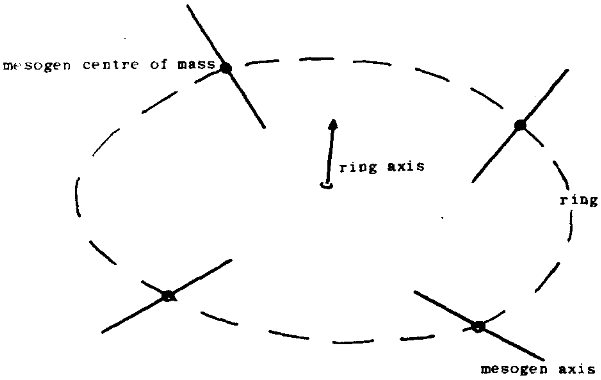


Figure 2 Schematic representation of the model.

ring-mesogen entity was rotated as a rigid body; mesogen rotations, where an individual mesogen was rotated with respect to the ring.

Two order parameters were obtained, one based on the unique symmetry axes of the individual mesogens and the other based on the unique symmetry axes of the rings.

The conventional order parameter for a uniaxial phase is

$$S = \langle P_2(\cos\beta_i)\rangle \tag{9}$$

where β_i is the angle between a mesogen symmetry axis and the director of the system.

In the simulations, the following tensor order parameter was calculated [6]:

$$S = \begin{bmatrix} \langle x_i x_i\rangle & \langle x_i y_i\rangle & \langle x_i z_i\rangle \\ \langle y_i x_i\rangle & \langle y_i y_i\rangle & \langle y_i z_i\rangle \\ \langle z_i x_i\rangle & \langle z_i y_i\rangle & \langle z_i z_i\rangle \end{bmatrix}$$

where x_i is the x component of the direction cosine of the ith mesogen axis and $\langle\ldots\rangle$ represents the average over all molecules as well as Monte Carlo configurations. This tensor is diagonalised to yield three eigenvalues. In the uniaxial case, one of these (λ_1) is different from the other two (λ_2, λ_3) which should be equal. The uniaxial order parameter is then obtained by the substitution of λ_1 for $\langle\cos^2\beta_i\rangle$ in equation (3). Owing to the limited number of molecules in our system, complete uniaxial ordering was never obtained and the order parameters presented correspond to the configuration average of the eigenvalue most different from the other two.

The simulations started from a random configuration at high temperature and as the temperature was reduced, the final configuration at each temperature became the initial configuration for the new temperature. At each temperature the first half of the data points were discarded to allow for thermalisation. The total number of attempted moves is given on the figures.

The reduced temperatures and volume are defined as:

$$T^* = k_B T/\varepsilon \qquad V^* = V(\sigma^3 N_{\text{mesogens}})^{-1}$$

The simulation programmes were written in Pascal and run on the CRAY X-MP/48 at the Rutherford Appleton Laboratory, England.

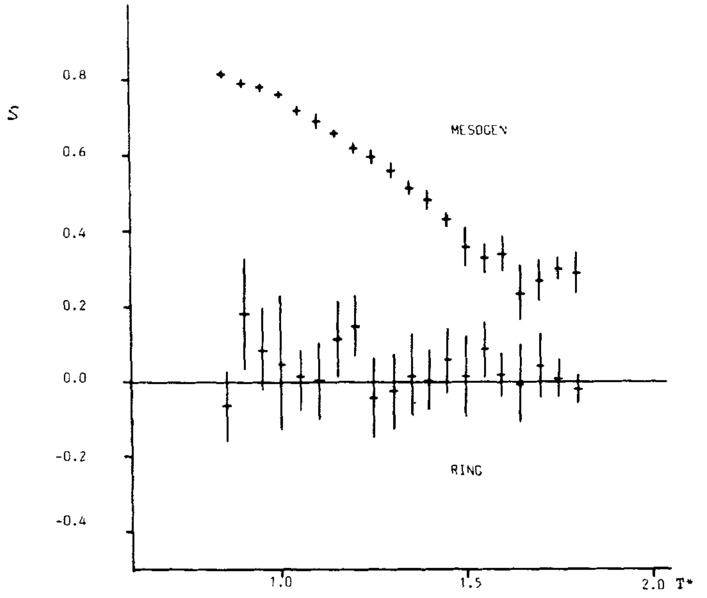


Figure 3 Ring and mesogen order parameters as a function of reduced temperature for fully flexible coupling. Each data point represents 6 × 10^6 attempted moves and the error bars indicate one standard deviation fluctuation. V* = 1.20 Ring radius = 0.7σ.

The mesogen and ring order parameters plotted in Figure 3 were obtained from simulations in which the coupling between the mesogens and the rings was fully flexible. A transition in the mesogen order is observed at a reduced temperature of approximately $T^* = 1.4$. Weak mesogen ordering ($S = 0.3$) is observed at high temperature and high mesogen ordering ($S = 0.8$) is observed at low temperature. The finite values of the mesogen order parameter at high temperature result in most part from the close packing and enhanced alignment of the mesogens attached to the same ring. The system of rings remains disordered throughout the temperature range with a low order parameter fluctuating about $S = 0.0$. The contrast between the strong ordering of the mesogens and the disorder of the rings at low temperature can clearly be seen from the configuration represented in Figure 4 which was obtained at a reduced temperature of $T^* = 0.95$.

A series of simulations was also carried out in which the ring-mesogen coupling was kept rigid with the mesogens on a ring fixed in a splay conformation coplanar with the ring. The order parameters obtained from these simulations are plotted in Figure 5. A sharp transition in the ring order parameter is observed at a reduced temperature of $T^* = 0.95$. Low ring order parameters of about $S = 0.15$ are observed at high temperatures whilst at low temperatures the rings are highly ordered with order parameters of about $S = 0.96$. Owing to the fixed relationship between the rings and the attached mesogens, the mesogen order parameters are simply a multiple of -0.5 times the values of the ring order parameters for all temperatures. The negative order parameters correspond to the tendency for the unique axes of the mesogens to lie in a plane perpendicular to their director. Shorter preliminary simulations indicate that there may be some hysteresis in the transition in the ring order parameter. The

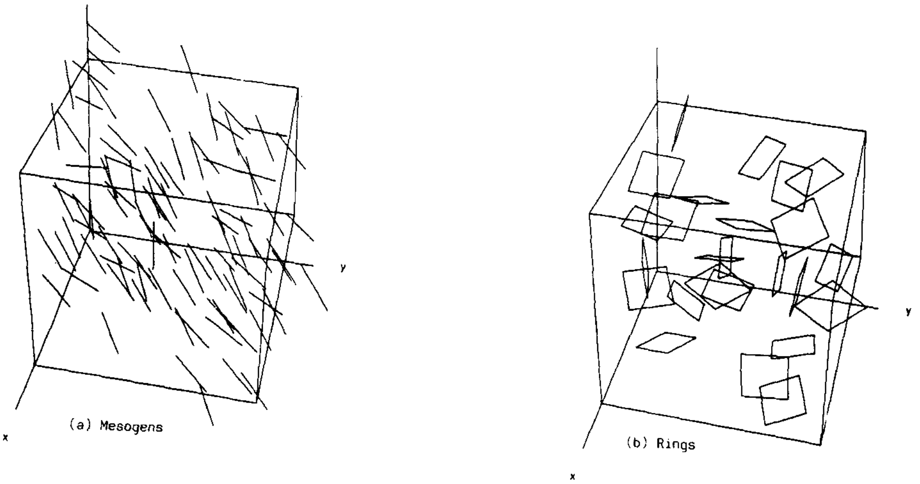


Figure 4 Calamitic order. The final configuration obtained from the simulation of rings and mesogens with fully flexible coupling at a reduced-temperature of T* = 0.95. The rings are represented by squares whose corners correspond to the points of attachment of the mesogens.

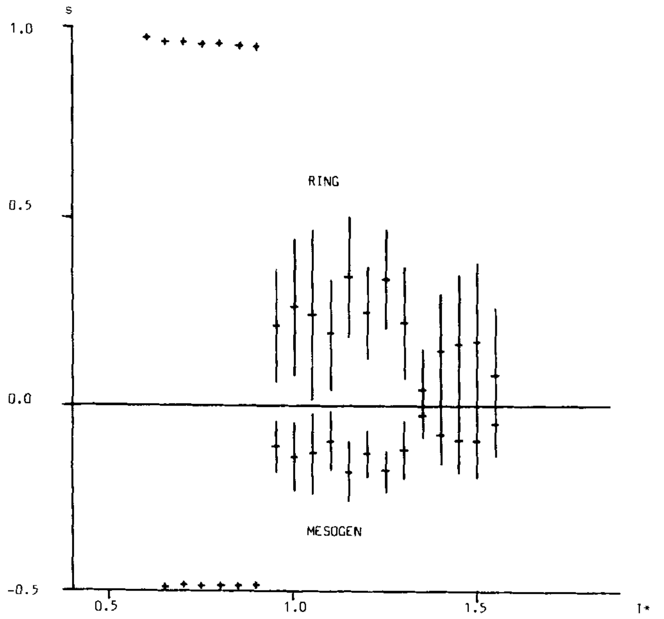
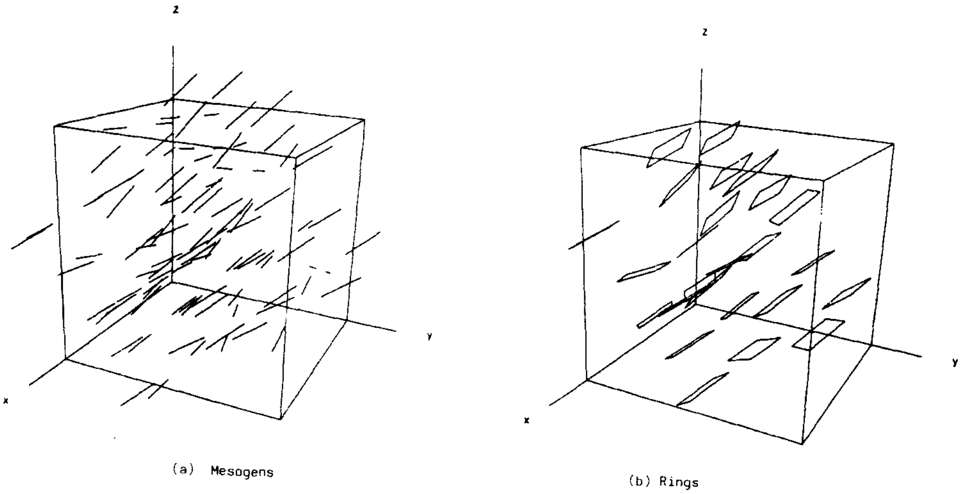


Figure 5 Ring and mesogen order parameters as a function of temperature. Rigid coupling with mesogens attached in planar splay conformations. Each data point represents 4 × 10^6 attempted moves and the error bars indicate one standard deviation fluctuation. V* = 1.25. Ring radius = 0.7σ.



(a) Mesogens

(b) Rings

Figure 6 Discotic order. The final configuration obtained from the simulation of rings and mesogens with rigid planar splay coupling at a reduced temperature T* = 0.95. The rings are represented by squares whose corners correspond to the points of attachment of the mesogens.

positive ordering of the rings and the negative ordering of the mesogens can be seen from the configuration presented in Figure 6 which was obtained at a reduced temperature of $T^* = 0.85$.

When the ring-mesogen coupling is flexible, the system is observed to be mesogen driven, resulting in a calamitic ordered phase below the transition temperature. This behaviour is consistent with the observations of other side-chain polymeric liquid-crystals (Engel *et al.* [7]). When the mesogens are rigidly attached to the rings in planar splay conformations the system is observed to be ring driven, resulting in a discotic phase at low temperatures (Chandrasekhar [8]). Further investigations of this model are being undertaken both by Monte Carlo simulation and mean field approximation [9] to investigate the nature of the transitions for intermediate ring-mesogen flexibilities and also the importance of the ring size.

Acknowledgements

We should like to acknowledge the support of the National Advisory Body and the Science and Engineering Research Council. (Grant Ref GR/E/70733).

References

[1] Private Communication. S. Cockett, D. Simmonds and K. Dodgson, Department of Chemistry, Sheffield City Polytechnic.

[2] J. Pinsl, C. Brauchle and F.H. Kreuzer, "Liquid Crystalline Polysiloxanes for Optical Write-Once Storage", *Journal of Molecular Electronics*, **3**, 9–13 (1987).

[3] D.R.R. Everitt, C.M. Care and R.M. Wood, "A Monte Carlo Simulation of Cyclic Polymeric Liquid Crystals", *Mol. Cryst. Liq. Cryst.*, **153**, 55–62 (1987).

[4] G.R. Luckhurst and S. Ramano, *Proc. R. Soc. London*, "Computer Simulation Studies of Anisotropic Systems IV. The Effect of Translational Freedom", **A373**, 111–130 (1980).

[5] N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth and A.H. Teller, "Equation of State Calculations by Fast Computing Machines", *J. Chem. Phys.*, **21(6)**, 1087–1092 (1953).
[6] I. Ono and K. Ito, "Monte Carlo Simulations and Pair Approximations on the Phase Transition of the Restricted Orientation Lattice Model for Liquid Crystals". *J. Phys. C. Solid State Phys.*, **15**, 4417–4430 (1982).
[7] M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H. Schmidt and P. Tschirner, "Synthesis, Structure and Properties of Liquid Crystalline Polymers", *Pure & Applied Chem.*, **57(7)**, 1009–1014 (1985).
[8] S. Chandrasekhar, *Phil. Trans. R. Soc. London*, "Liquid Crystals of Disc-like Molecules", **A309**, 93–103 (1983).
[9] D.R.R. Everitt, C.M. Care and R.M. Wood, "A mean field theory of nematic ring polymers", Molec. Cryst, Liq. Cryst. (1990), to be published.