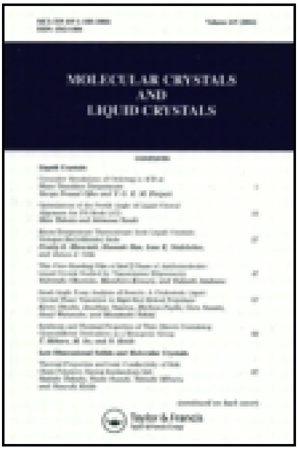

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# A Monte Carlo Simulation of Cyclic Polymeric Liquid Crystals

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# A MONTE CARLO SIMULATION OF CYCLIC POLYMERIC LIQUID CRYSTALS

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Abstract 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 to siloxane ring polymers and is simulated with two different mathematical models. In one model, the polymer molecules are represented as objects with disc-like symmetry, and columnar stacking of these molecules has been observed for simulations in two dimensions. In the other model the mesogenic moieties are represented individually by an anisotropic Lennard-Jones potential. The ring is represented solely as a constraint on the relative motions of the attached mesogens. If the ring-mesogen link is sufficiently flexible the mesogens are found to order at low temperatures.

## INTRODUCTION

New materials comprising polydimethylsiloxane rings with side-chain mesogenic moieties attached via ether linkages are currently being synthesized in the Chemistry Department of Sheffield City Polytechnic as part of a joint programme on novel polymeric liquid crystal systems. Ring sizes may be varied to generate conformations which will range between rigid and floppy, and the linkages themselves can be altered in length to show similar behaviour. An initial example of these materials and their general structure are shown in diagram 1.

The simulations described here attempt to identify those features which will be significant in generating liquid crystal structures. 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 conventional nematic phase. However, if the coupling is strong, the polymer ring will dominate the behaviour of these materials. For example, if the mesogens are rigidly attached to the rings in a splay conformation, discotic phases may be expected.

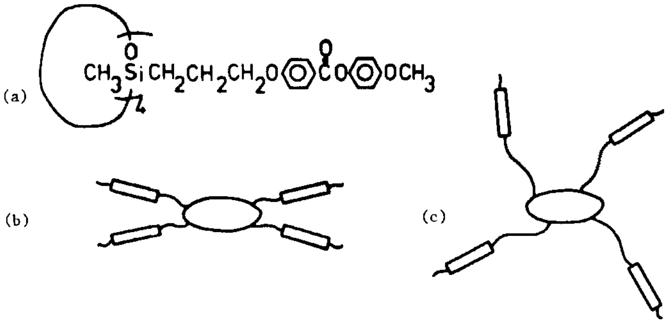


DIAGRAM 1. A cyclic compound under investigation (a). Schematic diagram of strong ring-mesogen coupling (b) and weak coupling (c).

The Metropolis[1] Monte Carlo technique was used to simulate these systems using two different mathematical models of the polymer molecules. The two models and the results of the simulations are described in separate sections below. These simulations were performed in the NVT ensemble in which each molecule was allowed free translational and rotational motion. The system was subject to periodic boundary conditions.

## SOFT DISC MODEL

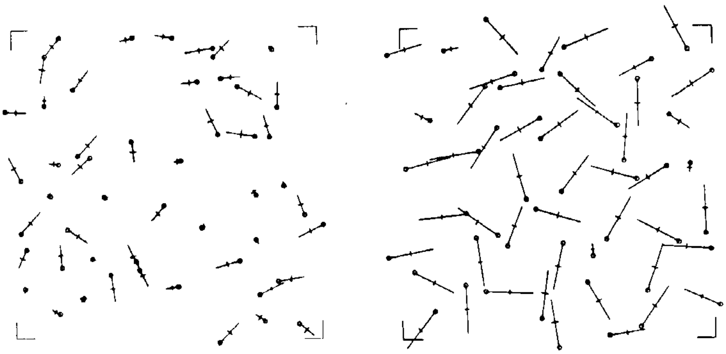
In the soft disc model, the polymer backbone was represented by a Lennard-Jones 12-6 potential whilst the average effect of the mesogenic moieties was approximated by a ring of softer potential which took the form of an $r^{-9}$ term. Hence, the interaction potential had the following form:-

$$U_{12} = 4\varepsilon \left[ \left(\frac{\sigma}{r_{12}}\right)^{12} + F(\theta_1,\theta_2)\left(\frac{\sigma}{r_{12}}\right)^{9} - \left(\frac{\sigma}{r_{12}}\right)^{6} \right] \qquad (1)$$

where the angles $\theta_1$ and $\theta_2$ are the angles made between the molecular axes and the molecular separation vector. The function $F(\theta_1,\theta_2)$ was expanded in spherical harmonics to second order and the coefficients were chosen to give a suitable disc shaped potential.

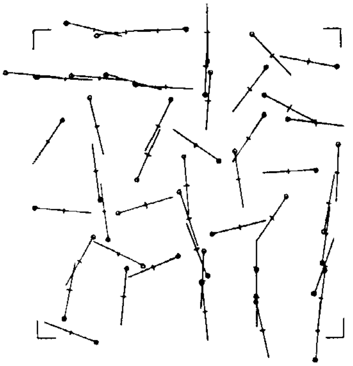
In this first simulation, the centres of the molecules were constrained to lie on a plane, whilst the molecules interacted with the full 3D potential (1). During the simulation, translational and rotational moves were attempted in alternation.

Diagram 2 shows typical configurations for a simulation of fifty molecules. At low density, it can be seen that the molecules have random orientations with



(a) T* = 0.44, ρ* = 0.11

(b) T* = 0.44, ρ* = 0.31



(c) T* = 0.44, ρ* = 0.44

$T^* = K_B T/\varepsilon$

$\rho^* = N\sigma^2/\text{Area}$

The projections of the symmetry axes of the discs on the plane are represented by the lengths of the lines, with the attached circles indicating the upper end of the axes.

DIAGRAM 2. Typical configurations from the soft disc model. The temperature was reduced in 10 decrements from a random configuration at high temperature with 100 000 attempted moves per temperature. The simulations were performed with 50 particles confined to a plane. Increasing order is observed as the density is increased.

respect to the plane. However, at high density, it is found that the symmetry axes of the molecules lie in the plane and there is evidence of columnar stacking. This stacking is not uniform throughout the plane and domains of different orientation are observed. This ordered phase is destroyed at high temperatures.

## MULTI-MESOGEN RING MODEL

In this more detailed model, the mesogenic moieties were represented individually by a modified Lennard-Jones 12-6 potential which contained an anisotropic term (Luckhurst[2]):-

$$U = U_o + U_a \tag{2}$$

where $U_o$ is the isotropic Lennard-Jones potential and $U_a$ is the anisotropic term:-

$$U_a = -4\lambda \left[ \left(\frac{\sigma}{r}\right)^{12} + \left(\frac{\sigma}{r}\right)^{6} \right] P_2(\cos\beta_{12}) \tag{3}$$

The ring was represented solely as a constraint on the relative positions of the attached mesogens, and the coupling between the ring and the mesogens was represented as a restriction on the orientations which mesogens could have with respect to the ring axes. This 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 ring-mesogen entity was rotated as a rigid body; mesogen rotations, where an individual mesogen was rotated with respect to the ring. This model was not chosen to be a specific representation of the actual polymers being synthesized, but rather to allow investigation of the general relationships between the strength of ring-mesogen coupling and liquid-crystalline ordering.

The results shown in diagram 3 were obtained using a system of forty mesogens. Each ring had four mesogens attached and was allowed complete translational freedom in 3D, with no restriction on the orientation of a mesogen with respect to its ring. Two order parameters were obtained, one based on the symmetry axes of the

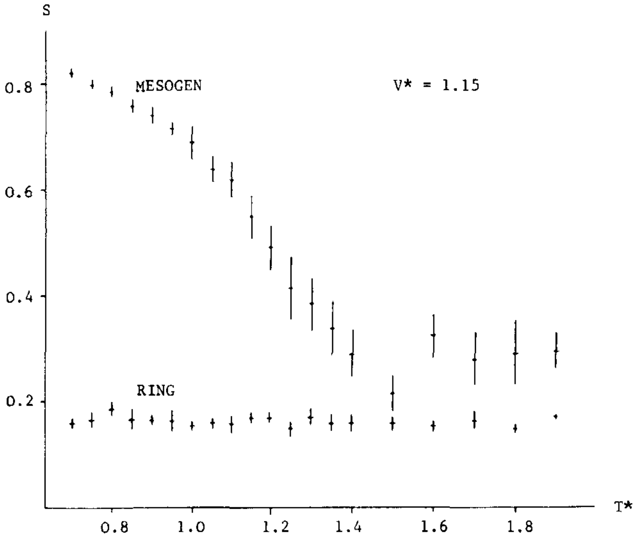


DIAGRAM 3. Ring and mesogen order parameters as a function of reduced temperature for the multi-mesogen ring model. The reduced temperature and volume are defined as:-

$T^* = K_B T/\varepsilon \qquad V^* = V/\sigma N_{mesogens}$

Each data point represents 300 000 attempted moves and the error bars indicate one standard deviation fluctuation.

individual mesogens and the other based on the symmetry axes of the rings. In each case the order parameter was of the usual form:-

$$s = \langle P_2(\cos\beta_i)\rangle \qquad (4)$$

where $\beta_i$ is the angle made between a mesogen symmetry axis and the director of the system.

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. A transition occurs at a reduced temperature of approximately $T^* = 1.4$. Weak mesogen ordering ($S = 0.3$) is observed at high temperature and strong mesogen ordering ($S = 0.8$) at low temperature. Further extended simulations are being carried out to determine if the relatively large value of S at high temperature is a consequence of the polymeric nature of the system, the limited system size, or the short run lengths used in these preliminary studies. No transition was observed in the ring order parameter for this weak coupling. The above simulation was performed with a mesogen anisotropy parameter of $\lambda = 0.15$. A simulation was also performed for $\lambda = 0.25$ but it was found that the degree of order obtained persisted up to high temperatures. These results are consistent with Luckhurst's[2].

## CONCLUSION

Columnar stacking of the disc-like objects in the soft-disc model has been observed at low temperatures and high densities. This is consistent with a discotic phase.

The multi-mesogen model has shown a nematic-isotropic transition for weak coupling. This latter result is consistent with observations of other side chain polymeric liquid crystals (Engel at al[3]). Further detailed investigations of the multi-mesogen model are being undertaken to investigate the importance of ring size, number of mesogens per ring and ring-mesogen flexibility. It is hoped to characterise the transformation from nematic mesogen behaviour to a discotic ring behaviour.

## ACKNOWLEDGEMENTS

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