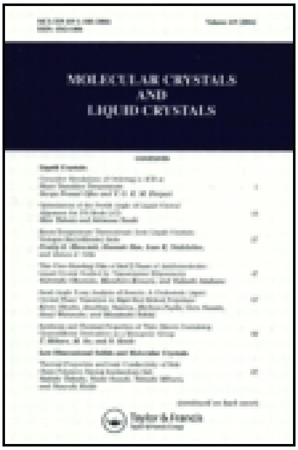

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A Mean-Field Theory of Nematic Ring Polymers

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A Mean-Field Theory of Nematic Ring Polymers

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A mean-field calculation is presented for cyclic polymers with attached rod like mesogenic side groups. The mean-field includes energy contributions for ring-ring, rod-rod and ring-rod interactions. The uniaxial solution for this model yields two ordered phases: a conventional calamitic nematic phase in which the rods tend to align parallel and a discotic nematic phase in which it is the rings that tend to align parallel. These phases are shown to be dependent upon the relative strengths of the three energy contributions, the number of mesogens per ring and temperature. In certain cases polymorphism is observed with an isotropic phase cooling to the nematic discotic phase and then on further cooling to the calamitic nematic phase.

INTRODUCTION

The classic mean field treatment of the nematic phase is that developed by Maier and Saupe[1] in the late 1950s. Their work predicted a first order phase change from nematic at low temperatures to isotropic at high temperatures for rod-like molecules. This type of calculation has also been applied to a variety of liquid crystal systems including binary mixtures of rods and plates[2,3] and several polymer liquid crystal systems.[4,5,6] Of particular interest to us is the work of Wang and Warner[6] in which the unaxial phases of comb-like liquid crystal polymers are explored. Nematic phases were found in which either the polymer backbones or the rod-like side groups or both together exhibited positive ordering.

We wish to apply the mean field approach to the study of comb-like liquid crystal oligomers in which the oligomer backbone is cyclic, providing a ring like structure. An example of such a material is a cyclic poly(dimethysiloxane) backbone with rod-like mesogenic side groups attached via alkyl spacer units. The chemical formula of one of the materials is shown in Figure 1 together with a schematic diagram of its structure. A variety of ring sizes has been synthesized[7,8] and the lengths of the spacer units varied to alter the coupling between the backbone and the mesogenic units.

The aim of the calculations presented here is to identify those features of the molecules which are significant in the formation of different liquid crystal phases

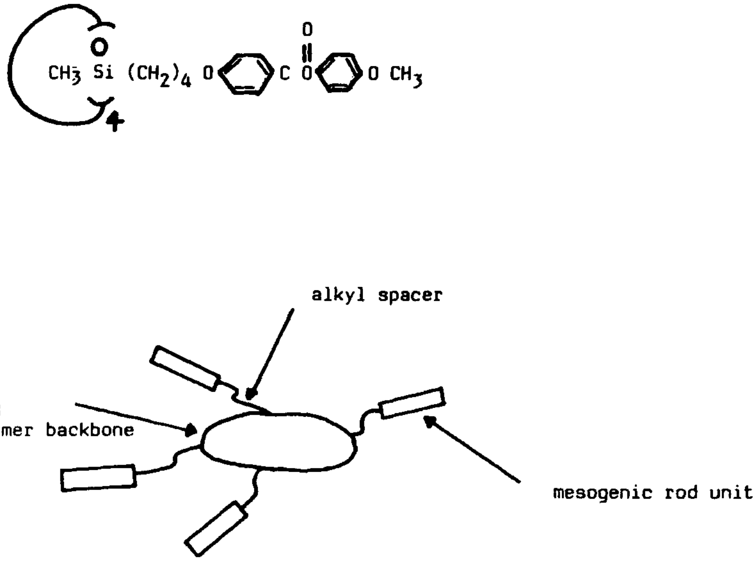

FIGURE 1 The chemical structcure of a cyclic compound under investigation.

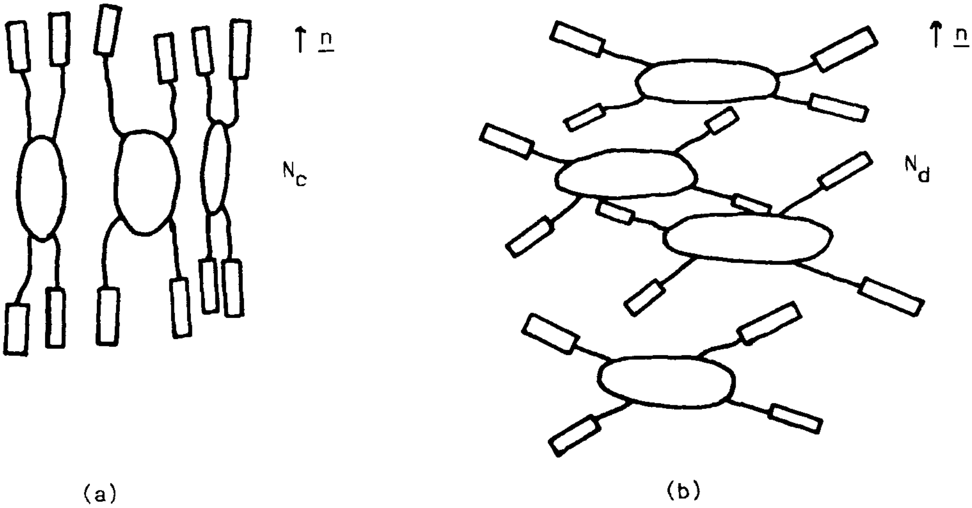

FIGURE 2 A diagrammatic representation of (a) the calamitic nematic phase (N_c) and (b) the discotic nematic phase (N_d) for the cyclic oligomers. *n* indicates the director of the phase.

and in this paper we only consider uniaxial solutions. We use the usual second rank order parameter to quantify the ordering of the two components. For the rod-like mesogens the order is given by

$$\langle P_2\rangle_m = 1/2\,\langle 3\cos^2\theta_m - 1\rangle$$

where $\langle\ \rangle$ denotes a thermal average and θ_m is the angle between a mesogen and the unique director of the phase. The order of the rings, $\langle P_2\rangle_r$, is defined similarly in terms of the angles, θ_r, between the ring normals and the same director. Two possible ordered, uniaxial phases for these oligomers are shown diagramatically in Figure 2. In the calamitic nematic (N_c) phase the mesogens tend to align parallel to the director and the ring normals tend to lie in the plane perpendicular to the director, whilst in the discotic nematic (N_d) phase it is the rings that tend to align parallel and the mesogens which are perpendicular to the director. The formation of these phases may depend upon the strength of the coupling between the ring backbones and the attached mesogenic rods. Where the coupling is weak, the rod-rod interactions will dominate and a calamitic nematic phase may be expected. However, where the coupling is strong with the rods perpendicular to the ring normals, the resultant star shaped molecules may form a discotic nematic phase. Modelling using the Metropolis Monte Carlo technique[9,10] in which these two extremes have been explored, has indicated the formation of both N_c and N_d phases. It is the aim of the mean field calculations to examine further the behaviour of this type of molecule and in particular explore the region between the two extremes in which there is a coupling of variable strength between a rod and its ring backbone.

THE MODEL

We consider a system of rigid ring polymers each with *n* rod-like mesogens attached by flexible spacer units and consider only uniaxial phases. We assume that each mesogen moves in a Maier-Saupe potential of the form.

$$V_m(\cos\theta_m) = -V_o(\langle P_2\rangle_m - \lambda_c\langle P_2\rangle_r)\, P_2(\cos_m)$$

where θ_m is the angle between the mesogen length and the unique director in the system and P_2 is the second order Legendre Polynomial. The first term in this equation is a standard Maier-Saupe term and represents the drive towards parallel ordering which is caused by the steric and long-range forces between the mesogens. The second term represents a coupling between a ring and its attached mesogens which arises from the spacer unit. The strength of the coupling is determined by the positive dimensionless parameter λ_c which is the ratio of the coupling potential and the mesogen-mesogen potential. We assume that the molecules are such that as the coupling strength is increased the molecules will adopt conformations in which the rods and the ring normals tend to be mutually perpendicular.

The polymer rings are assumed to experience a mean field potential of the form

$$V_r(\cos\theta_r) = -V_o\lambda_c(\lambda_r\langle P_2\rangle_r - n\langle P_2\rangle_m)\, P_2(\cos\theta_r)$$

where θ_r is the angle between the ring normal and the unique director in the system. The first term is a Maier-Saupe potential which will tend to induce parallel ordering of the polymer ring backbones. The mesogenic ordering of small chain cyclic poly(dimethylsiloxane) molecules has not been reported and so the polymer rings are assumed not to have any intrinsic drive towards parallel order. However, we envisage that if the mesogenic rods attached to a ring are forced to adopt a planar splay conformation perpendicular to the ring normal then the resultant rigid molecules will be approximately disc shaped and will tend to align with their normals parallel owing to local packing effects. We account for this induced steric interaction by scaling the ring-ring interaction by λ_c. The parameter λ_r is a positive dimensionless constant which determines the strength of the ring-ring interaction. The second term in the ring potential is a ring mesogen coupling term which is scaled by the number, n, of mesogens attached to each ring.

We are only interested in oligomers with a small number of repeat units and so do not consider the drive towards maximal chain entropy which would be more appropriate for long chain polymers. Also we do not consider the interaction between rods and rings other than via the attachment spacer as it is thought that rod-ring interactions are likely to be a second order influence on the formation of ordered phases.

The above potentials define the nature of the molecules with three independent parameters λ_r, λ_c, and n. These together with T^* determine the phase of the material where T^* is a reduced temperature defined by

$$T^* = \frac{K_B T}{V_o}$$

From these two potentials the following self consistent equations may be written:

$$\langle P_2\rangle_m = \frac{\int_0^1 P_2(\cos\theta_m)\exp(-V_m(\cos\theta_m)/k_B T)\, d\cos\theta_m}{\int_0^1 \exp(-V_m(\cos\theta_m)/k_B T)\, d\cos\theta_m}$$

and

$$\langle P\rangle_r = \frac{\int_0^1 P_2(\cos\theta_r)\exp(-V_r(\cos\theta_r)/k_B T)\, d\cos\theta_r}{\int_0^1 \exp(-V_r(\cos\theta_r)/k_B T)\, d\cos\theta_r}$$

These equations were solved numerically for $\langle P_2\rangle_r$ for selected values of λ_c, λ_r, n and T^*. In the regions of interest to us we found three solutions at low temperature: an N_C phase, an N_D phase and an isotropic phase. At these temperatures the equilibrium phase of the system was taken as that with the lowest total free energy, F_{TOT}, whilst at high temperatures the isotropic was the only solution.

The entropic contribution to the free energy was obtained from the partition

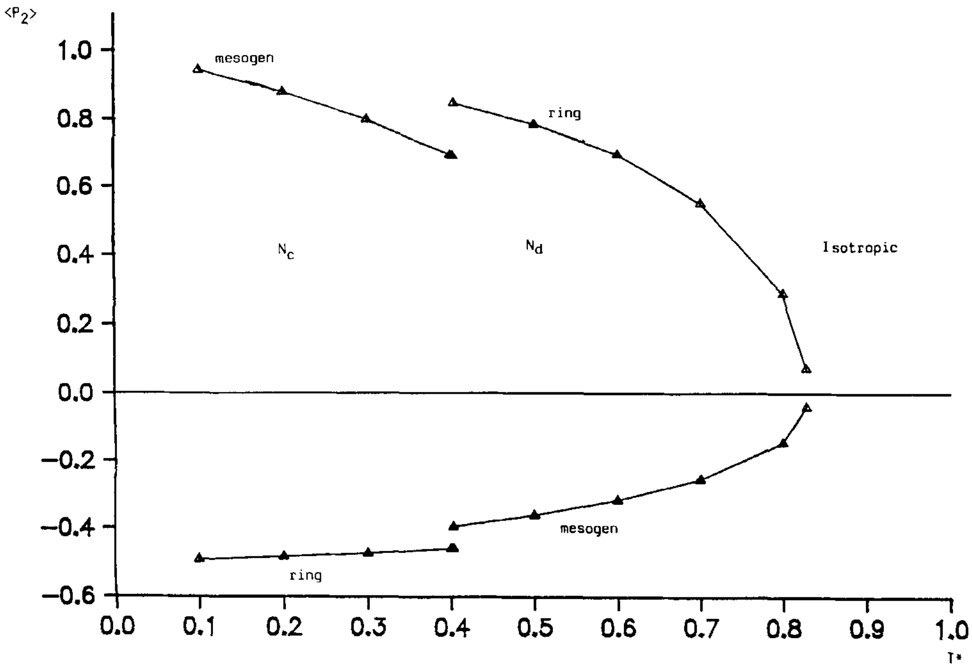

FIGURE 3 The equilibrium value of $\langle P_2 \rangle$ for the rings and the mesogens as function of temperature for $\lambda_r = 0$, $\lambda_c = 1.8$ and $n = 4$.

functions (Z_m and Z_r) for the mesogen and ring components:

$$Z_m = \int_0^1 \exp(-V_m(\cos_m)/k_B T)\, d\cos\theta_m$$

$$Z_r = \int_0^1 \exp(-V_r(\cos_r)/k_B T)\, d\cos\theta_r$$

The free energy terms for a mesogen and a ring are then

$$F_m = -k_B T \ln Z_m - 1/2\, \langle V_m \rangle$$

and

$$F_r = -k_B T \ln Z_r - 1/2\, \langle V_r \rangle$$

We define the total free energy F_{TOT} to be

$$F_{TOT} = nF_m + F_r$$

The results obtained were in agreement with Maier-Saupe in the limit $\lambda_c \rightarrow o$.

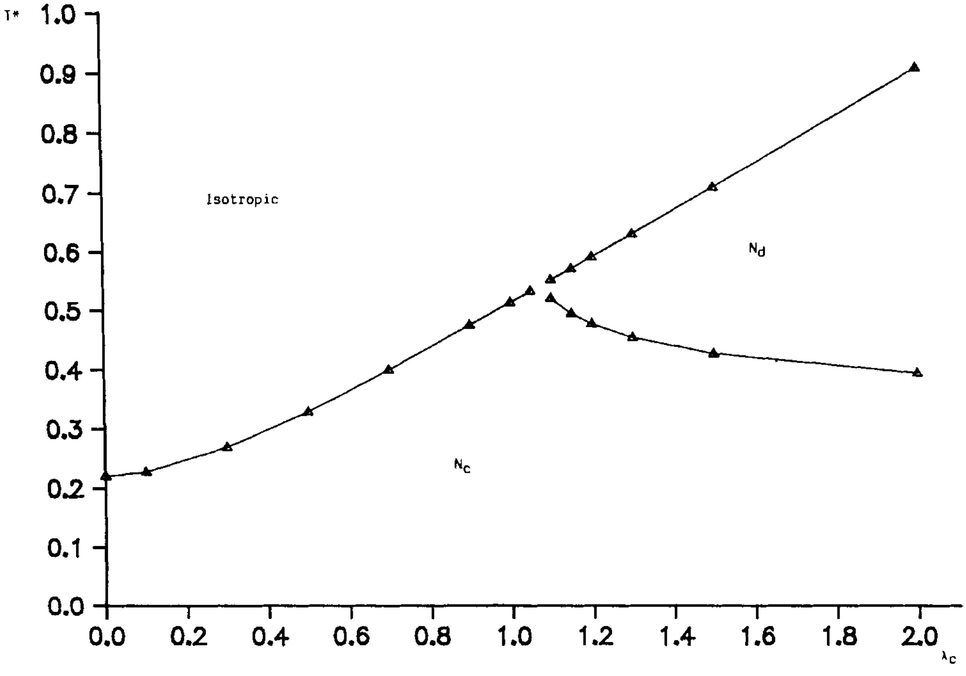

FIGURE 4 The phase diagram for $\lambda_r = 0$, $n = 4$.

Extrapolation of the numerical results to $T^* = 0$ are also in agreement with the expected values.

RESULTS

Solutions to the model are presented for those values of n, λ_c and λ_r which might be expected to provide the best comparison with actual liquid crystal polymers and the Monte Carlo model. The mean field model was solved for values of $n = 4$ and $n = 6$, while for the Monte Carlo work $n = 4$ was used and polymers have been synthesized with a range of repeat units from 4 to 7. As already discussed, we would expect the ring-ring interaction to result from steric interactions and to be comparatively small, and so we arbitrarily restrict λ_r to take values between 0 and 2.

The ring-ring interaction is also scaled by λ_c, and so for nonzero λ_r we may expect the model to correspond to the real polymers more successfully for low values of λ_c.

Figure 3 shows the ring and mesogen order parameters as functions of reduced temperature for $\lambda_r = 0$, $\lambda_c = 1.8$ and $n = 4$. A transition from a strongly ordered calamitic nematic phase ($\langle P_2\rangle_m = 0.69$) at low temperature to a strongly ordered discotic nematic phase ($\langle\langle P_2\rangle\rangle_r = 0.85$) at high temperature is observed at a reduced temperature of $T^* = 0.403$, with an associated increase in entropy of 10.6 $J\ K^{-1}\text{mol}^{-1}$. A further transition from a weakly ordered discotic nematic phase

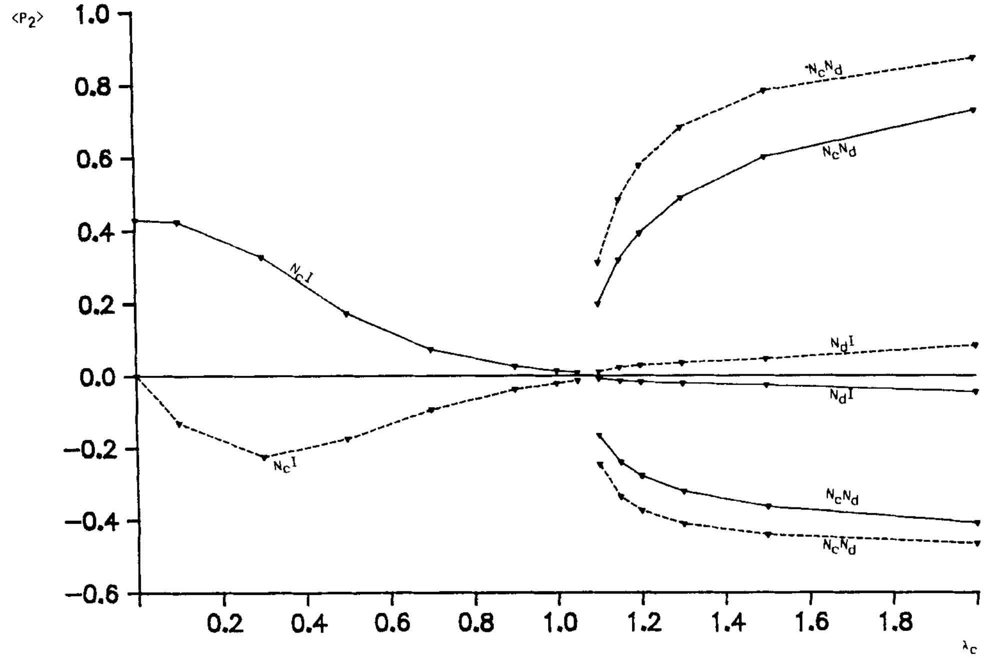

FIGURE 5 The spontaneous order parameters at transitions for $\lambda_r = 0$, $n = 4$. The phase transitions are labelled, for example, N_cI = calamitic nematic to isotropic. The solid line represents mesogen order and the broken line, ring order.

($\langle P_2\rangle_r = 0.07$) to isotropic is observed at $T^* = 0.828$, with an increase in entropy of $0.25\ J\ K^{-1}\mathrm{mol}^{-1}$. Figure 4 shows the overall phase behaviour as a function of λ_c for the model with $\lambda_r = 0$. For values of λ_c below a particular value only a single transition from calamitic nematic to isotropic is observed. For $\lambda_c = 0$ the transition from calamitic nematic to isotropic occurs at a reduced temperature of $T^* = 0.220$, in agreement with the Maier-Saupe results. The model exhibits an isotropic phase at high temperature and a calamitic nematic phase at low temperature. If $\lambda_r = 0$ and λ_c is greater than a specific value, a N_d phase exists between the isotropic and N_c phase. This specific value of λ_c corresponds to a 'triple point' at which the three phases co-exist in equilibrium.

The spontaneous order parameters at the phase transitions are given as a function of λ_c in Figure 5. The spontaneous order in every case is seen to weaken dramatically in the region close to the triple point.

It is especially interesting to note the formation of a discotic nematic phase in the absence of specific ring-ring interactions. Analysis of the numerical data indicates that the ring based ordering results from the forces between the attached mesogens and the increased entropic contribution to the free energy over the more ordered calamitic nematic phase.

Our Monte Carlo calculations also show the existence of a discotic nematic phase in the case of strong coupling. However only the two extremes of coupling have been explored in the Monte Carlo simulations; fully rigid with the mesogens in a planar splay conformation and fully flexible. Calamitic nematic ordering is observed

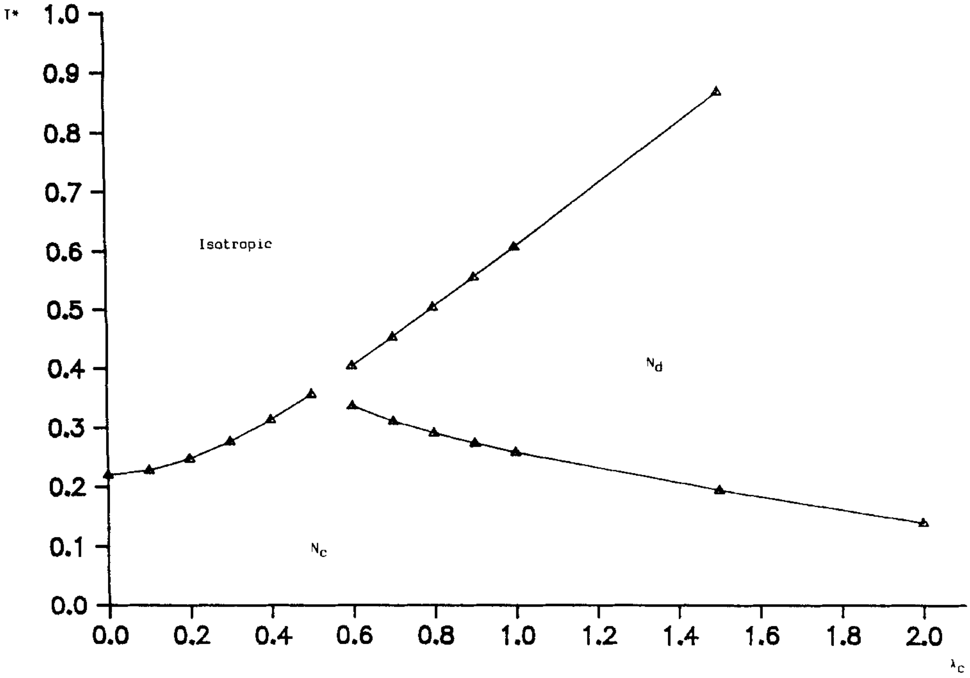

FIGURE 6 The phase diagram for $\lambda_r = 1.0$, $n = 4$.

TABLE I

Values of T^* and λ_c at the triple point for a range of n, λ_r

n	λ_r	T^*_{triple}	λ_c, triple
4	2.0	.31	.34
4	1.0	.37	.53
4	0.5	.42	.69
4	0.0	.54	1.07
6	0.0	.44	.67

in the flexible case and discotic ordering in the rigid case. However, in the rigid case the lack of flexibility precluded the formation of a calamitic nematic phase and thus the polymorphism exhibited by the mean field model has not yet been observed in the Monte Carlo model.

The phases of the model when $\lambda_r = 1$ are shown in Figure 6. The main effect of introducing a finite ring-ring interaction is to enlarge the discotic region at the expense of the calamitic and isotropic phases. Thus for $\lambda_r = 1$ both the reduced temperature, and coupling strength decrease at the triple point.

For non-zero λ_r the calamitic phase is not the only equilibrium solution at $T^* = 0$. For values of the coupling strength greater than $\lambda_c = n/\lambda_r$ the discotic phase is favoured. Hence, for large λ_c only the discotic and isotropic phases are observed, in agreement with the Monte Carlo results.

The values of coupling strength and reduced temperature at the triple point for various λ_r are given in Table I. The stronger the ring-ring coupling the more dominant the N_d phase becomes, with associated decreases of λ_c and T^* at the triple point. Also given are the triple point values for $n = 6$. Again, the discotic phase dominates at the expense of both the isotropic and calamitic phases as the number of mesogens attached to a ring is increased. However in real materials increasing the number of mesogens necessitates an increase in ring size which may give rise to a decrease in ring rigidity. In the model presented no account is taken of such a decrease in ring rigidity.

CONCLUSION

The phase behaviour of liquid crystal cyclic polymers is the result of a variety of influences owing to the composite nature of the molecules, and as such is generally more complicated than the phase behaviour of low molecular weight liquid crystals. We have presented a mean field model which predicts both calamitic and discotic liquid crystal phases for small ring, cyclic polymers with side-chain mesogens. A discotic nematic phase is shown to result from the long-range interactions of splay clusters of rod-like mesogens in the absence of specific ring-ring interactions.

We have also shown the transition from a calamitic nematic phase to a discotic nematic phase as a result of a change in temperature in the cases where the ring-mesogen coupling energy is substantial. It may be possible to synthesize molecules which show this polymorphism, but it should first be noted that our results are restricted to uniaxial phases and that biaxial phases may, in fact, be preferentially formed by simple side-chain ring polymers.

In our model, the specific phase behaviour was shown to be dependent upon the relative strengths of the various component interactions. However, the form of the phase diagram was not greatly affected by a change in the number of repeat units in a ring or the strength of the ring-ring interaction for the range of values investigated. The effect of increasing the ring-ring interaction or increasing the number of rods per ring was in each case to enhance discotic tendencies.

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