Modeling of N_D and N_{Col} Phase Transitions in Discotic Side Chain Polymers by the Extended McMillan Theory

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*Received February 14, 2001
Revised Manuscript Received April 6, 2001*

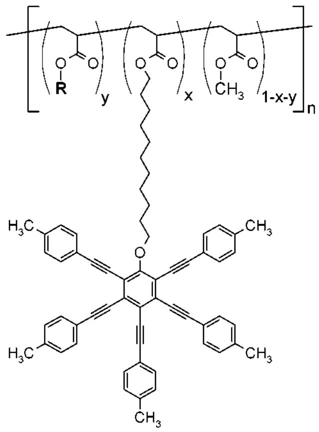
We have investigated the phase diagram of a series of liquid crystalline discotic side-chain acrylate polymers[1] bearing large disk-shaped 11-[pentakis(4-methylphenylethynyl)phenoxy]undecyl mesogens, see Figure 1. By comparing the various samples we find that a universal phase diagram can be constructed if the phase transitions are plotted as a function of the mesogen concentration [M], see Figure 2. The mesogen concentration is defined as the weight fraction of the rigid group in the liquid crystalline polymer. The phases that occur in these materials are the isotropic phase (I), at high temperatures, and two different nematic phases.

As shown in Figure 3, the nematic discotic phase only has orientational order of the discotic mesogens and the nematic columnar phase also has local columnar arrangement of the disks. At high mesogen concentrations both nematic phases are observed where the phase sequence is $N_{Col}-N_D-I$. At lower mesogen concentrations the N_D phase disappears giving rise to a $N_{Col}-I$ transition only. In our attempts to model the experimentally observed phase behavior we find that a simple mean-field model is particularly effective. The mean-field model we use is the McMillan model for smectic A phases,[2] extended for hexagonal columnar phases of discotic liquid crystals.[3] This model has been proposed for materials similar to ours.[4] But apart from the fitting of some homologous series,[5] no detailed analysis of the effectiveness of this model for describing discotic materials has been reported.

Here we show that McMillan theory, extended for discotic liquid crystals, quantitatively describes the phase diagram of our materials. We find that particularly simple scaling exponents can be used to describe the strength of the interaction terms as a function of mesogen concentration.

The synthesis of our discotic side chain polymers, Figure 1, has already been reported in detail.[1] Here, we will only discuss the extended McMillan model, comparing it with our phase diagram. Some aspects of our structural analysis of the phases can be found in a previous publication.[6]

The extended McMillan model for discotic liquid crystals, exhibiting a columnar and a nematic phase, is based on the use of the following mean-field potential of a test molecule at position **r** and oriented at angle θ with respect to the *z*-axis:



	R	x	y
1	CH_3	0.90	-
		0.64	-
		0.48	-
		0.31	-
2	C_5H_{11}	0.69	0.31
		0.41	0.43
		0.42	0.50
3	$C_{12}H_{25}$	0.61	0.11
		0.45	0.45
		0.33	0.42

Figure 1. Structure of our discotic side-chain acrylate polymers.

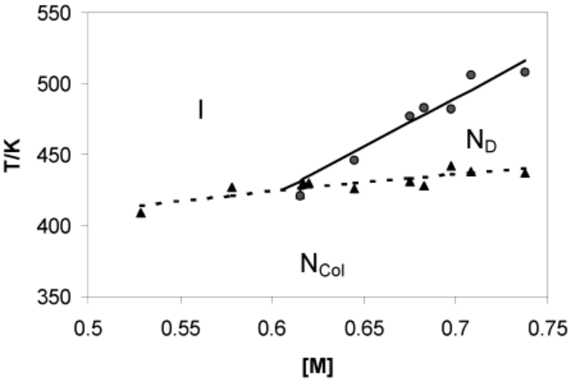


Figure 2. Phase diagram of our discotic SCLCP's versus monomer weight fraction [M]. Symbols indicate experimental data, drawn and dashed curves are from a fit to our model.

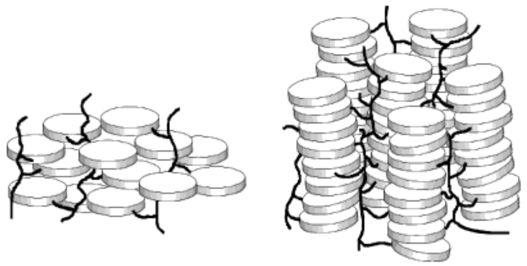


Figure 3. Schematic structure of the (a) N_D and (b) N_{Col} phase.

$$U = -V_0\{S + \alpha\sigma[\cos(\mathbf{A}\cdot\mathbf{r}) + \cos(\mathbf{B}\cdot\mathbf{r}) + \cos(\mathbf{C}\cdot\mathbf{r})]\}P_2(\cos\theta)$$

Here the parameter V_0 represents the absolute strength of the potential and serves to fix the absolute temperature scale. The $P_2(\cos\theta)$ term describes the dependence of the potential on the mesogen orientation with respect to the director. The parameter α determines the relative contribution of the columnar potential. The columnar phase is described by a superposition of three density waves with the primitive vectors **A**, **B**, and **C** with $\mathbf{A} = (4\pi/\sqrt{3}d)\mathbf{j}$, $\mathbf{B} = (4\pi/\sqrt{3}d)(\sqrt{3}\mathbf{i}/2 - \mathbf{j}/2)$, $\mathbf{C} = \mathbf{A} + \mathbf{B}$ in which **i** and **j** are the unit vectors along the *x*- and *y*-axis and *d* is the lattice constant.

It is noted that the polymers described here do not exhibit a columnar hexagonal phase, but rather a nematic columnar phase. However, because of the high organization of the N_{Col} phase found in these materials, we can assume that locally the columnar order

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[1] Kouwer, P. H. J.; Gast, J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *in Mol. Cryst. Liq. Cryst.* In press.

[2] McMillan, W. L. *Phys. Rev. A* **1971**, *4*, 1238.

[3] Feldkamp, G. E.; Handschy, M. A.; Clark, N. A. *Phys. Lett.* **1981**, *85A*, 359−362

[4] Ebert, M.; Frick, G.; Baehr, C.; Wendorff, J. H.; Wüstefeld, R.; Ringsdorf, H. *Liq. Cryst.* **1992**, *11*, 293−309.

[5] (a) Ghose, D.; Bose, T. R.; Mukherjee, C. D.; Roy, M. K.; Saha, M. *Mol. Cryst. Liq. Cryst.* **1986**, *138*, 379−392. (b) Chandrasekhar, S. *Philos. Trans. R. Soc.* **1983**, *A309*, 93.

[6] Kouwer, P. H. J.; Jager, W. F.; Mijs, W. J.; Picken, S. J. *Macromolecules* **2000**, *33*, 4336−4342.

10.1021/ja015672j CCC: $20.00

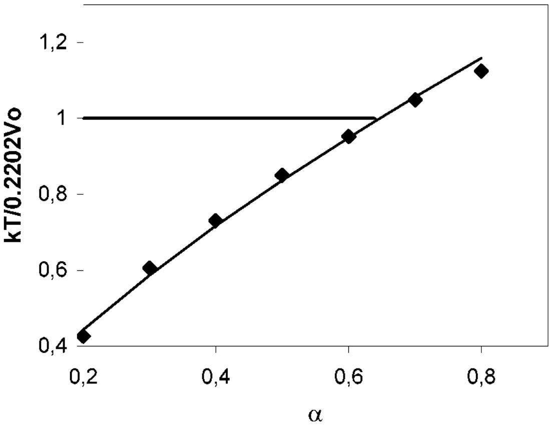

Figure 4. Phase diagram from the extended McMillan theory; symbols are the exact result, the drawn curve corresponds to the power law fit to $\kappa\alpha^{0.69}$, with $\kappa = 0.30$.

is well established, hence deviations from the hexagonal arrangement are small and the use of this theory is permitted.

The order parameters S and σ respectively describe the orientational order and positional order, via

$$S = \langle P_2(\cos\theta)\rangle$$

$$\sigma = \langle\{\cos(\mathbf{A}\cdot\mathbf{r}) + \cos(\mathbf{B}\cdot\mathbf{r}) + \cos(\mathbf{C}\cdot\mathbf{r})\}P_2(\cos\theta)\rangle$$

In this case the averaging process for calculating the order parameters as indicated by the brackets involves integration over both the angle θ and the position coordinates x and y.

Solving the McMillan model involves finding self-consistent solutions for the orientational and positional order parameters. The stable solution corresponds to the lowest free energy, using:

$$F = U - TS \propto \frac{1}{2}(S^2 + \alpha\sigma^2) - \frac{k_BT}{V_0}\log(Z)$$

where Z is the partition function given by:

$$Z = \frac{2}{\sqrt{3}d^2}\int\int dx\, dy \int_0^{\pi} d(\cos\theta) e^{-U(x,y,\theta)/k_BT}$$

The phase diagram resulting from McMillan theory is shown in Figure 4 as a function of the scaled temperature and the interaction parameter α.

Note that for high values of α we find a nematic columnar to isotropic transition and lower α values yield the $N_{Col}-N_D-I$ sequence.

To fit our experimental data we have to determine the dependence of the model parameters V_0 and α on the mesogen concentration [M]. To this end we will assume that the transition temperatures T_{NI} and T_{Col} show a power-law dependence on [M]. Using a simple scaling analysis that correlates the transition temperatures with V_0 and α, a system of equations is obtained:

$$T_{NI} = A[M]^{\gamma} = 695[M]^{0.98}$$

$$T_{Col} = B[M]^{\delta} = 465[M]^{0.18}$$

The numbers given are obtained from fitting the power-law expressions to the experimental data. Because $k_BT_{NI}/V_0 = 0.2202$ in the theory, we find that V_0 is a nearly linear function of [M], i.e., $V_0 \propto A[M]$. From fitting a power law to McMillan theory we find that k_BT_{Col}/V_0 scales as $\alpha^{0.69}$ for a reasonable range of α values. This fit is shown in Figure 4 together with the exact values of T_{Col}/V_0 versus α. Combining the various power-law expressions then leads to the following relation for the scaling behavior of α as a function of [M] (using $T_{NI} = A[M]^{\gamma}$ and the power-law $\alpha = c_2[M]^{\epsilon}$):

$$B[M]^{\delta} = T_{Col} = T_{NI}\kappa\alpha^{0.69} = A[M]^{\gamma}\,\kappa(c_2[M]^{\epsilon})^{0.69}$$

Solving for ϵ we find $\delta = \gamma + 0.69\epsilon$ and thus $\epsilon = (\delta - \gamma)/0.69 = (0.18 - 0.98)/0.69 = -1.16$. Now the mean-field potential can be written as a function of [M]:

$$U = -V_0\{S + \alpha\sigma f(\mathbf{r})\}P_2(\cos\theta)$$

$$= -k_Bc_1[M]^{0.98}\left\{S + \frac{c_2}{[M]^{1.16}}\sigma f(\mathbf{r})\right\}P_2(\cos\theta)$$

where $f(\mathbf{r}) = [\cos(\mathbf{A}\cdot\mathbf{r}) + \cos(\mathbf{B}\cdot\mathbf{r}) + \cos(\mathbf{C}\cdot\mathbf{r})]$ and c_1 and c_2 are constants: $c_1 = A/0.2202 = 3156$ K and $c_2 = (B/\kappa A)^{1/0.69} = 3.2$.

In conclusion, we have described the phase diagram of a series of discotic liquid crystalline side chain polymers, using the McMillan theory, extended for columnar phases of discotic liquid crystals. We find that the strength of the potential V_0 shows a linear dependence on the mesogen concentration. Due to opposing effects, a higher concentration of mesogens and a weaker aromatic−aliphatic phase separation process, the net strength of the columnar interaction αV_0 is almost independent of [M]. Taking $\gamma = 1$ and $\epsilon = -1.16$ results in the drawn curves for T_{NI} and T_{Col} shown in Figure 2. From this we conclude that extended McMillan theory can give a very satisfactory description of the effect of mesogen concentration [M] on the various nematic phases occurring in our discotic side chain polymers.

Acknowledgment. We thank Ben Norder for technical assistance and Jeroen Gast for synthesis of some of the discotic side chain polymers.

JA015672J