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NEW THEORIES FOR SMECTIC AND NEMATIC LIQUID CRYSTALLINE POLYMERS

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Abstract A summary of results from new statistical-physics theories for both backbone and side-chain liquid crystalline polymers (LCPs) and for mixtures with LCPs is presented. Thermodynamic and molecular ordering properties (including odd-even effects) have been calculated as a function of pressure, density, temperature, and molecule chemical structures (including degree of polymerization and the following properties of the chemical structures of the repeat units: lengths and shapes, intra-chain rotation energies, dipole moments, site-site polarizabilities and Lennard-Jones potentials, etc.) in nematic and multiple smectic-A LC phases and in the isotropic liquid phase. These theories can also be applied to combined LCPs. Since these theories have no ad hoc or arbitrarily adjustable parameters, these theories have been used to design new LCPs and new solvents and to predict and explain properties.

INTRODUCTION

Liquid crystalline polymers (LCPs) are of considerable basic and applied interest (see Ref. 1). From a basic standpoint, LCPs in condensed phases constitute one of the most challenging many-body problems in physics--that is, the packing of many changing, very anisotropic shapes.

In backbone LCPs, the monomeric liquid-crystal (LC) structure is repeated many times to make the polymer chain or backbone. In side-chain LCPs, monomeric LC structures are attached as side chains to a non-LC polymer backbone (such as polyethylene), with the side chains resembling the teeth of a brush or comb. In combined LCPs, each molecule is a backbone LCP with LC side-chains.

Some backbone LCPs (such as Kevlar) have major uses as stronger, lighter-weight replacements for metals and other materials in various structural applications, such as body armor (football helmets, bulletproof vests, etc.) and auto and airplane parts. Uses of side-chain LCPs include electro-optic devices.

There are thousands of possible chemical structures in LCPs. A reasonably typical example of a monomeric LC structure that appears dp times to make a backbone LCP is

$$[\text{-O-}\phi\text{-N=N-}\phi\text{-O-}(\text{CH}_2)_y\text{-}]_{dp} \quad .$$

$$\underbrace{\leftarrow \qquad \rightarrow}_{\text{rigid section}} \; \underbrace{\leftarrow \qquad \rightarrow}_{\text{semiflexible section}}$$

ϕ indicates a <u>para</u>-substituted benzene ring. $y \sim 0$ to 20. dp is also the degree of polymerization. The side chains of side-chain LCPs are similar monomeric LC structures.

The overlap of π orbitals in the aromatic, double, and triple bonds in a rigid section leads to the rigidity of that section. The <u>n</u>-alkyl chain section is partially flexible (semiflexible) since there are one <u>trans</u> and two <u>gauche</u> rotational energy minima for a carbon-carbon bond between methylene or methyl units in a given chain section.

THEORY

In the theory of this paper, the chemical structure of each molecule is divided into a sequence of connected sites, where these sites correspond to small groups of atoms (such as benzene rings and methylene groups). We then use a localized mean-field (LMF) simple-cubic (SC) lattice theory to study the packing of the molecules in the system volume.

We use SC lattice theory since any orientation of a molecule or molecular part or bond can be decomposed into its <u>x</u>, <u>y</u>, and <u>z</u> components and mapped directly onto a SC lattice in a manner analogous to normal coordinate analysis in, for example, molecular spectroscopy. LMF means that there is a specific <u>average</u> neighborhood (of other molecular sites and empty space) in a given direction <u>k</u> around a given molecular site in a given local region in the system. These local regions are determined by the actual packing of the molecules in the system. This packing is done mathematically using lattice combinatorial statistics to determine the analytic partition function for the system. (The generalized combinatorics used in the theory of this paper have been found to be <u>quite</u> accurate when compared with

Monte Carlo computer simulations in at least one limiting case presently amenable to such simulations [see discussion in Ref. 2(a)].) Various continuum limits are taken in the theory of this paper.

The partition function and the resulting equations for static thermodynamic and molecular ordering properties are functions of the pressure $\underline{P}$, temperature $\underline{T}$, density ρ, lengths and shapes of the rigid and semiflexible sections of the molecules, net energy difference E_g between *trans* and *gauche* states, dipole moments, site-site polarizabilities and Lennard-Jones (12,6) potentials, degree of polymerization, and orientational and one-dimensional (smectic-A) positional orderings of the different rigid and semiflexible parts of the molecules. The Lennard-Jones (LJ) potentials are used to calculate repulsions and London dispersion attractions between different molecular sites, and the dipole moments and polarizabilities are used to calculate dipole/dipole and dipole/induced dipole interactions between different molecular sites.

There are *no* ad hoc or arbitrarily adjustable parameters in this theory. All variables used in this theory are taken from experimental data for atoms or small groups of atoms or are calculated in the theory.

The theory used in this paper has been derived in detail elsewhere [Ref. 2(b)] and involves extension and refinement of earlier, very successful theories [Refs. 2(a) and 2(c)-2(g)] for LC monomers and their mixtures. Due to length constraints on this paper, we note only the *changes* made in this paper (to the LC monomer equations of these earlier papers) in order to treat backbone LCPs. (Somewhat analogous changes were made in order to treat side-chain LCPs and mixtures with LCPs in this paper.)

The equations in the theory of this paper for backbone LCPs are the same as the equations of Ref. 2(e), except for the following changes. [Variables not defined in this paper have been previously defined in Ref. 2(e).]

$(r - 1)$ in Eqs. (4), (5), and (10) of Ref. 2(e) has become $[r - (1/dp)]$ in this paper. Also, B_i in Eq. (13) of Ref. 2(e) has become $B_i - (1/dp) + x[2f(1 - P_{2i})/3)]$, where ν in Ref. 2(e) has become P_{2i} in this paper. Also, η and τ in Ref. 2(e) have become P_{2r} and P_{2f}, respectively, in this paper. (These symbol changes for ν, η, and τ are changes in the actual symbols, but *not* in the definitions of the variables for which these symbols stand.) $\underline{v}$ in Eq. (15) of

Ref. 2(e) has become $v = a^2((2a/dp) + v_o^{1/3}[m - (2/dp)]$. d_L in Eq. (16) in Ref. 2(e) has become $d_L = v_o^{1/3}(r + f[(1 + 2P_{2i})/3]) + [(a - v_o^{1/3})/dp]$.

The treatment of the flexibility of a semiflexible chain in Ref. 2(e) was significantly refined in Ref. 2(f): Thus, Eq. (14) of Ref. 2(e) is replaced in this paper by

$P_{2i} = \langle(3 \cos^2\psi - 1)\rangle/2 = 1 - 3u$, with $2u = 2\zeta_2$ for $f = 1$,
$2u = ((\Sigma_{j=1}^{2} Y_{1j}) + [(f - 2)/2][\Sigma_{j=1}^{2} Y_{2j}])/f$ for even $f \geq 2$,
$2u = ((\Sigma_{j=1}^{3} Y_{3j}) + [(f - 3)/2][\Sigma_{j=1}^{2} Y_{2j}])/f$ for odd $f \geq 2$,
$Y_{11} = 2(\zeta_1\zeta_2 + \zeta_2{}^2)/D_1$, $Y_{12} = 2(2\zeta_1\zeta_2 + \zeta_2{}^2)/D_1$,
$Y_{21} = Y_{22} = 2(\zeta_1{}^2 + 3\zeta_1\zeta_2 + 2\zeta_2{}^2)/D_2$,
$Y_{31} = 2(\zeta_1{}^2\zeta_2 + 3\zeta_1\zeta_2{}^2 + \zeta_2{}^3)/D_3$,
$Y_{32} = 2(2\zeta_1{}^2\zeta_2 + 4\zeta_1\zeta_2{}^2 + \zeta_2{}^3)/D_3$,
$Y_{33} = 6(\zeta_1{}^2\zeta_2 + \zeta_1\zeta_2{}^2)/D_3$,
$D_1 = \zeta_1{}^2 + 4\zeta_1\zeta_2 + 2\zeta_2{}^2$, $D_2 = 3\zeta_1{}^2 + 2(5\zeta_1\zeta_2 + 3\zeta_2{}^2$,
$D_3 = \zeta_1{}^3 + 2(3\zeta_1{}^2\zeta_2 + 4\zeta_1\zeta_2{}^2 + \zeta_2{}^3$,
$\zeta_1 = 1/(1 + 2\Lambda)$, $\zeta_2 = \Lambda/(1 + 2\Lambda)$, and $\Lambda = \exp[-E_g/(kT)]$.
In the limit $dp \rightarrow 1$, the equations here for backbone LCPs reduce to the equations of Refs. 2(e)-2(f) for LC monomers.

RESULTS AND DISCUSSION

This paper reports theoretical results calculated for backbone LCPs, side-chain LCPs, and mixtures with backbone LCPs.

THEORETICAL RESULTS FOR BACKBONE LCPS

Theoretical results for backbone LCPs are shown as a function of the degree of polymerization and as a function of the chemical structures of both the rigid section and the semiflexible section in the repeat unit.

Degree of Polymerization

Table I shows the effect of the degree of polymerization dp on some properties at the transition between the nematic (N) LC phase and the isotropic (I) liquid phase for a backbone LCP with the repeat unit $[-O-\phi-\phi-\phi-CH_2-(CH_2)_3-]_{dp}$. (N is the lower-T phase, and I phase is the higher-T phase.)

T_{N-I} is the transition temperature, and P_{2r} is the average orientational order for a rigid section of the LCP in the N phase at the transition. $P_{2r} = \langle(3\cos^2\theta_r - 1)\rangle/2$, where θ_r is the angle between the long axis of a rigid section and the preferred axis or orientation for this rigid section.

From experimental data for atoms or small groups of atoms, the input variables [for definitions, see Ref. 2(e)] for the repeat unit of this LCP were estimated [Ref. 2(b)] after the manner of Ref. 2(e) to be r = 5, f = 3, ϵ_{cc}/k = 290 K, ϵ_{tt}/k = 150 K, μ_D = 1.45 D, $\alpha_c' = 32\times10^{-24}$ cm^3, and $\alpha_t = 2\times10^{-24}$ cm^3. P = 1 atm. All calculations in this paper [as in Refs. 2(e)-2(f)] use E_g/k = 250 K.

TABLE I. Some transition properties vs. dp for a backbone LCP with N and I phases.

dp	T_{N-I} (K)	P_{2r}
1	311.7	0.6186
10	523.3	0.6945
10^2	562.7	0.7053
10^3	566.9	0.7065
10^4	567.4	0.7066
10^5	567.4	0.7066

In Table I, the transition properties increase as dp increases, with the value of a property tending to asymptote as dp → ~ 100. As might be expected, adding another repeat unit to the backbone makes less relative change in the length (and other properties) of the LCP as the length increases. The effects of polydispersity on system properties can be large for dp less than the asymptotic value, while polydispersities in the dp range greater than this asymptotic value have less effect on system properties.

Repeat-Unit Chemical Structures

Table II shows the effect of varying the repeat-unit chemical structure (specifically, the number $\underline{f}$ of methylene groups in a semiflexible chain) on some properties at the N-I transition for a backbone LCP with repeat unit $[\text{-O-}\phi\text{-}\phi\text{-}\phi\text{-CH}_2\text{-(CH}_2)_f\text{-}]_{100}$. The input variables for the calculations in Table II are as for Table I, except dp = 100 and $\underline{f}$ varies. P_{2f}, the average orientational order for a semiflexible chain section, is defined analogously to P_{2r}. Table II shows P_{2r} and P_{2f} in the $\underline{N}$ phase at the transition.

TABLE II. Some transition properties vs. $\underline{f}$ for a backbone LCP with $\underline{N}$ and $\underline{I}$ phases.

f	T_{N-I} (K)	P_{2r}	P_{2f}
4	545.5	0.6931	0.04142
5	490.7	0.6727	0.02863
6	501.7	0.6692	0.04151
7	480.5	0.6582	0.03080
8	501.9	0.6585	0.03948

As seen in Table II, there is an odd-even alternation in the magnitudes of the transition properties as the number of methylene groups in the semiflexible chain section varies from odd to even. The relative effect is larger in P_{2f} than in P_{2r} since the semiflexible chain section is the origin of the odd-even effect. P_{2r} is approximately an order of magnitude larger than P_{2f}, since the rigid rodlike sections prefer to orient much more than the semiflexible chain sections. However, because the rigid and semiflexible sections are physically attached to each other in the backbone, P_{2r} has a smaller relative odd-even effect, and

P_{2f} is larger than zero.

Comparing Tables II and III shows the effect of varying the chemical structures of both the rigid section and the semiflexible section in the repeat unit of a backbone LCP. Table III addresses the relative stabilities of the SA1, SAd, *N*, and *I* phases. SA1 and SAd refer to smectic-A phases with total and partial one-dimensional positional order, respectively, of the molecules. In the SA1 phase, rigid sections pack with other rigid sections, and semiflexible sections with other semiflexible sections). In the SAd phase, molecular sections *tend* to pack with other like sections.

In particular, Table III shows the effect of varying *f* on the SA1-SAd, SAd-N, and N-I transition *T* for a backbone LCP with repeat unit of $[-CH_2-\phi-\phi-CH_2-(CH_2)_f-]_{100}$. The input variables for the calculations in Table III are as in Table II, except $r = 4$, $\epsilon_{cc}/k = 300$ K, $\mu_D = 0$, $\alpha'_c = 24\times10^{-24}$ cm^3. The calculations in Table III were not pursued below $T = 100$ K.

TABLE III. Some transition *T* vs. *f* for a backbone LCP with *I*, *N*, and multiple SA phases.

f	$T_{SA1-SAd}$ (K)	T_{SAd-N} (K)	T_{N-I} (K)
20		412.0	633.4
21	123.2	434.0	647.5
22		482.1	671.0
23	168.2	499.4	684.4
24	203.4	543.1	706.3
25	264.8	557.3	718.8

As seen in Tables II and III, shorter rigid sections and longer semiflexible sections are required in order to have stable multiple SA phases at higher temperatures. This trend is consistent with both experimental and theoretical results [see discussions in Refs. 2(c)-2(d)] for monomeric LCs. For the rigid section in the repeat unit of Table III, the SAd phase first appears to become stable at $T > 100$ K for $f \sim 10$ [see Ref. 2(b)].

THEORETICAL RESULTS FOR SIDE-CHAIN LCPS

Ref. 2(b) shows in detail the effect of backbone and side-chain chemical structures of a side-chain LCP on the transition of the side chains from packing in a monolayer SA (i.e., a SA1 phase) to packing in a bilayer SA phase (i.e., a SA2 phase). In the monolayer SA1 phase, the side chains on a molecule interdigitate with (i.e., pack between) the side chains of other molecules. In the SA2 phase, the side chains on a molecule pack only with neighboring side chains on the same molecule. The SA1 phase is the lower-$\underline{T}$ phase and the SA2 phase is the higher-$\underline{T}$ phase.

In general, energy favors the SA1 phase, and entropy favors the SA2 phase. That is, the side chains are closer to each other in the SA1 phase (interdigitated phase) and have more favorable attractive energies than in the SA2 phase (non-interdigitated phase). [This statement is true for the SA1 phase if the backbone chemical structure has been chosen such that the side-chains are far enough apart so that they do not experience the strongly repulsive parts of their potentials when they are interdigitated in a SA1 phase.] In the SA2 phase, the side chains are farther from each other and thus have more entropy (disorder) than in the SA1 phase. As discussed in detail in Ref. 2(b), the relative stabilities of the SA1 and SA2 phases are a very sensitive function of the specific chemical structures of the backbone and the side chains of side-chain LCPs and of how the flexibility, packing, and intermolecular forces of these structures change as a function of $\underline{T}$ and ρ.

THEORETICAL RESULTS FOR MIXTURES WITH LCPS

Ref. 2(b) shows in detail theoretical results calculated for binary mixtures of a backbone LCP (component 1) and a second component (which may be either LC or non-LC in its pure state and either polymeric or monomeric) at the N-I transition. Since this transition is a (weakly) first-order transition, there is a two-phase region (i.e., a range of mole fraction x_2 of component 2 in which both phases ($\underline{N}$ and $\underline{I}$) coexist simultaneously). x_{2N} and x_{2I} are the mole fractions of component 2 in the coexisting $\underline{N}$

and I phases, respectively, at a given reduced T given by $T/(T_{N-I})_1$, where $(T_{N-I})_1$ is the N-I transition T for pure component 1.

As shown in Ref. 2(b), a non-LC solute tends to disrupt the orientational ordering of the backbone LCP, thus lowering the T_{N-I} of the mixture. This result is consistent with the results for monomeric LC systems [see Ref. 2(g)]. The coexistence curves for the mixtures in Ref. 2(b) are not straight lines in reduced T vs. x_2 phase space, but rather are curved in a concave-downward (i.e., concave toward lower-T) manner.

Ref. 2(b) shows that steric repulsions are sufficient to generate the curvatures of these coexistence curves; attractive forces (including dipolar forces) are not required. The curvatures of the coexistence curves for the systems in Ref. 2(b) are larger (as might be expected with polymeric LC systems) than are the curvatures of the coexistence curves seen in the results in Ref. 2(g) for monomeric LC systems.

Ref. 2(b) shows that less of a polymeric non-LC solute (than of a monomeric non-LC solute) is required to lower the T_{N-I} of the mixture. That is, for a given mole fraction x_2, the long chains of the polymeric non-LC solute are more effective in disrupting the orientational ordering of the backbone LCP than are the much shorter chains of the monomeric non-LC solute.

CONCLUDING REMARKS

This paper has presented a summary of some results (especially general trends) calculated using new theories for backbone LCPs, for side-chain LCPs, and for mixtures with backbone LCPs. (These theories for LCPs are extensions and refinements of earlier, very successful theories for monomeric LCs.)

These new LCP theories predict and explain thermodynamic and molecular ordering properties of these systems as a function of the different features of the molecule chemical structures and their packing. There are no ad hoc or arbitraily adjustable parameters in these theories. To emphasize the predictive ability of these LCP theories, the molcule chemical structures chosen for study in this paper have not yet (to the author's knowledge) been synthesized.

While constraints on the length of this paper prohibit a detailed comparison of results calculated from the LCP theories of this paper and experimental results, we do note that the trends calculated for LCPs in this paper are physically reasonable and are in agreement with available experimental data. Furthermore, a comparison of the magnitudes of various thermodynamic and molecular ordering properties calculated for the LCP systems of this paper with the magnitudes of these properties for existing LCP systems indicates that the calculated results in this paper can be expected to be rather accurate qualitatively and semiquantitatively (in some cases, also probably quantitatively). [See Ref. 2(b) for a detailed comparison of some results for existing LCP systems calculated using the LCP theories of this paper with experimental results for these systems.]

The theories for LCPs in this paper have also been extended [see Ref. 2(b)] to study combined LCPs. [For experimental examples of combined LCPs, see Ref. 3 and references therein.] The theories of this paper are in the process of being extended to treat mixtures with side-chain and combined LCPs.

These theories of this paper have been used to design (atom-by-atom, bond-by-bond) new LCPs and new solvents for LCPs [see Ref. 2(b)].

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