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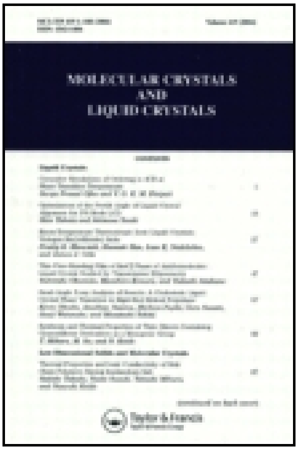

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New Theories for Smectic and Nematic Liquid Crystalline Polymers

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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

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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

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

$$\underleftrightarrow{\text{rigid section}} \quad \underleftrightarrow{\text{semiflexible section}}$$

ϕ indicates a para-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 n-alkyl chain section is partially flexible (semiflexible) since there are one trans and two gauche 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 study the multi-site packing and interactions of the molecules in the system volume V at given pressure P and temperature T, using an extension to LCPs (see Appendix) of the earlier, very successful localized mean-field (LMF) simple-cubic (SC) lattice theory of Refs. 2(a)-2(f) for LC monomers (specifically for low-molecular-weight multi-site molecules composed of rigid sections and semiflexible sections in the nematic and multiple smectic-A LC phases and in the isotropic liquid phase).

We use SC lattice theory since any orientation of a molecule or molecular part or bond can be decomposed into its x, y, and z 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 *average* neighborhood (of other molecu-

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lar sites and empty space) in a given direction $\underline{k}$ around a given molecular site in a given local region in the system. These local regions can have more than a random probability to contain specific parts of the molecules, such as rigid sections or semiflexible sections [Ref. 2(a)]. The compositions of these local regions are determined by how the molecules actually pack and interact with lowest Gibbs free energy $\underline{G}$. The local regions are defined such that there are no edge effects (i.e., continuity of the individual molecules and of the density ρ is preserved from one region to another). The fact that the packing can be different for different directions $\underline{k}$ allows us to treat partial orientational ordering along a preferred axis. And, the treatment of local regions allows us to deal with partial positional ordering [for example, one-dimensional (1D) positional alignment of the centers of mass of the rigid sections of the molecules, such that for oriented rigid sections, rigid sections pack with other rigid sections (and associated semiflexible sections pack with other semiflexible sections)].

The molecular 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 quite accurate when compared with Monte Carlo computer simulations in at least one limiting case presently amenable to such simulations [Ref. 2(a)].) Various contiuum 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 $\underline{P}$, $\underline{T}$, 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 1D (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 sites. Each interaction in the theory here depends explicitly on the intramolecular and intermolecular orientational and positional ordering of the specific molecular sites involved in the interaction.

There are no ad hoc or arbitrarily adjustable parameters in this theory. All variables used in this theory are

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taken from experimental data for atoms or small groups of atoms or are calculated in the theory. Further details of these variables for specific molecule chemical structures are discussed later as these structures are introduced.

The essence of this lattice theory is that we take a test molecule with a given chemical structure and--given the orientations and positions of the different parts of $\underline{N}$ (where $N \to \infty$) other molecules in the system at a given $\underline{P}$ and $\underline{T}$--we (1) count the number of ways that this test molecule (with its set of different chain rotational states) can be packed in the system $\underline{V}$ and (2) sum up the site-site intermolecular interaction energies and the energies of the chain rotational minima. (1) and (2) together give us the partition function for the system. In general, (1) gives us the entropy and PV effects, and (2) gives us the energy; thus, we obtain $\underline{G}$ for the system. In practice, we determine the ρ and the independent average orientational and positional order variables for the different parts of the molecules at a given $\underline{P}$ and $\underline{T}$ by simultaneously solving the PVT equation of state and the equations that minimize $\underline{G}$ with respect to these average orientational and positional order variables. (These equations are derived thermodynamically from the partition function.) The dependent average order variables and the other thermodynamic properties of the system are then calculated. (The reader interested in the actual equations of the theory of this paper is referred to the Appendix.)

Some of the competing interactions explicitly calculated in this theory are packing of rigid vs. semiflexible sections, entropic effects (disorder from different chain rotations and different ways to pack the molecules) vs. energetic effects (energies of different chain rotational minima and of attractive and soft repulsive forces), and repulsive forces vs. attractive forces. The ρ and the orientational and positional orderings are coupled through the intramolecular and intermolecular packing and interactions of the different parts of the molecules. (Both the coupled interactions and the competing interactions are discussed in more detail with regard to different phases and molecule chemical structures in the next sections.)

RESULTS AND DISCUSSION

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

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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 ($\underline{N}$) LC phase and the isotropic ($\underline{I}$) liquid phase for a backbone LCP with the structure of $[-O-\phi-\phi-\phi-CH_2-(CH_2)_3-]_{dp}$. ($\underline{N}$ is the lower-$\underline{T}$ phase, and $\underline{I}$ is the higher-$\underline{T}$ phase.)

T_{N-I} is the transition $\underline{T}$, and P_{2r} is the average orientational order for a rigid section of the LCP in the $\underline{N}$ 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 orientation axis for this rigid section.

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

From experimental data (Ref. 3) for atoms or small chemical groups (such as benzene rings, methylene groups, etc.), the input variables for the repeat unit of this LCP are chosen as in Ref. 2(d) to be $E_g/k = 250$ K, $r = 5$, $f = 3$, $v_o = 2.98\times10^{-23}$ cm^3, $\epsilon_{cc}/k = 290$ K, $\epsilon_{tt}/k = 150$ K, $a_\sigma = 4\times10^{-8}$ cm, $\mu_D = 1.45$ D, $\alpha_c' = 32\times10^{-24}$ cm^3, and $\alpha_t = 2\times10^{-24}$ cm^3. These variables are the numbers of rigid ($\underline{r}$)

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and semiflexible (f) segments (sites) per repeat unit, the average volume (v_o) of a lattice site, the average LJ ϵ/k between rigid sites (ϵ_{cc}/k) and between semiflexible sites (ϵ_{tt}/k), the average separation distance (a_σ) between centers of first-neighbor intermolecular sites at the zero of energy in a LJ potential, the dipole moment μ_D for a repeat unit, and the polarizabilities for the rigid section (α_c') and for a semiflexible site (α_t). (k is the Boltzmann constant.) The above variables for a LCP are calculated as in Ref. 2(d) by summing and/or averaging over experimental values (Ref. 3) of these variables for the different atoms and chemical groups in the rigid and semiflexible sections and sites in the repeat unit of the LCP. The sums and/or averages are made as indicated in the definitions of the LCP input variables given above. P = 1 atm. $\epsilon_{ct} = (\epsilon_{cc}\epsilon_{tt})^{1/2}$.

The transition properties in Table I increase as dp increases, with the value of a property tending to asymptote as dp → ~ 100. It makes sense that 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 f of methylene groups in a semiflexible chain) on some properties at the N-I transition for a backbone LCP with a structure of $[\text{-O-}\phi\text{-}\phi\text{-}\phi\text{-CH}_2\text{-(CH}_2)_f\text{-}]_{100}$. The input variables for the calculations in Table II are as for Table I, except dp = 100 and 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 N phase at T_{N-I}.

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 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

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backbone, P_{2r} has a smaller relative odd-even effect, and P_{2f} is larger than zero.

TABLE II. Some transition properties vs. f for a backbone LCP with N and 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

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 1D positional order, respectively, of the molecules. The smectic-A order variable λ is the average fraction of 1D positional alignment of the centers of mass of oriented rigid sections, such that (for oriented rigid sections) rigid sections pack with other rigid sections (and the associated semiflexible sections pack with other semiflexible sections); $\lambda = 1$ and $0 < \lambda \leq 1$ in the SA1 and SAd phases, respectively [Refs. 2(a)-2(d)]. $\lambda = 0$ in N and I phases.

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 the structure 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. Calculations in Table III were not pursued below T = 100 K. For the the LCP structure of Table III, the SAd phase becomes stable at T > 100 K for $f \geq 13$.

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.

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This trend is consistent with both experimental and theoretical results [Refs. 2(b)-2(c)] for monomeric LCs. The N phase is stabilized by positional disorder (entropy); and the SA phases are stabilized by more efficient packing (the semiflexible sections bend and twist well around each other, but do not pack as well with the oriented rigid sections), especially at the larger ρ seen at lower T. Table III illustrates the point that dipolar forces are not required for stable SA phases.

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

THEORETICAL RESULTS FOR SIDE-CHAIN LCPS

We summarize theoretical results for the effects 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-T phase, and the SA2 phase is the higher-T phase. (For the side chains in the theory of this paper, $\lambda = 1$ in the SA1 and SA2 phases.)

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. A theoretical result here is that 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 $\underline{P}$.

THEORETICAL RESULTS FOR MIXTURES WITH LCPS

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

Another calculated theoretical result is that 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 [Ref. 2(f)]. The coexistence curves for the mixtures here are not straight lines in reduced $\underline{T}$ vs. x_2 phase space, but rather are curved in a concave-downward (i.e., concave toward lower-$\underline{T}$) manner.

Another theoretical result here is 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 here are larger (as might be expected with polymeric LC systems) than are the curvatures of the coexistence curves for monomeric LC systems.

Another theoretical result here is that less of a polymeric non-LC solute (than of a monomeric non-LC solute)

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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 of 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 arbitrarily adjustable parameters in these theories. To emphasize the predictive ability of these LCP theories, the molecule 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 quantitatively). [A detailed comparison of some results for existing LCP systems calculated using the LCP theories of this paper with experimental results for these systems will be published later.]

The theories for LCPs in this paper have also been extended to study combined LCPs. [For experimental examples of combined LCPs, see Ref. 4 and references therein.] The theories of this paper are in the process of being extended to treat mixtures with side-chain and combined LCPs. The theories of this paper have been used to design (atom-by-atom, bond-by-bond) new LCPs and new solvents for LCPs.

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APPENDIX: THEORY EQUATIONS

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

(r - 1) in Eqs. (4), (5), and (10) of Ref. 2(d) has become [r - (1/dp)] in this paper. Also, B_i in Eq. (13) of Ref. 2(d) has become $B_i = (1/dp) + x[2f(1 - P_{2i})/3)]$, where ν in Ref. 2(d) has become P_{2i} in this paper. Also, η and τ in Ref. 2(d) 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.) v in Eq. (15) of Ref. 2(d) has become $v = a^2\{(2a/dp) + v_o^{1/3}[m - (2/dp)]\}$. d_L in Eq. (16) in Ref. 2(d) 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(d) was significantly refined in Ref. 2(e): Thus, Eq. (14) of Ref. 2(d) is replaced in this paper by

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$$P_{2i} = \langle (3\cos^2\psi - 1)\rangle/2 = 1 - 3u, \text{ with } 2u = 2\zeta_2 \text{ for } f = 1,$$

$$2u = \{(\Sigma_{j=1}^{2} Y_{1j}) + [(f - 2)/2][\Sigma_{j=1}^{2} Y_{2j}]\}/f \text{ for even } f \geq 2,$$

$$2u = \{(\Sigma_{j=1}^{3} Y_{3j}) + [(f - 3)/2][\Sigma_{j=1}^{2} Y_{2j}]\}/f \text{ for odd } f \geq 2,$$

$$Y_{11} = 2(\zeta_1\zeta_2 + \zeta_2^2)/D_1, \quad Y_{12} = 2(2\zeta_1\zeta_2 + \zeta_2^2)/D_1,$$

$$Y_{21} = Y_{22} = 2(\zeta_1^2 + 3\zeta_1\zeta_2 + 2\zeta_2^2)/D_2,$$

$$Y_{31} = 2(\zeta_1^2\zeta_2 + 3\zeta_1\zeta_2^2 + \zeta_2^3)/D_3,$$

$$Y_{32} = 2(2\zeta_1^2\zeta_2 + 4\zeta_1\zeta_2^2 + \zeta_2^3)/D_3,$$

$$Y_{33} = 6(\zeta_1^2\zeta_2 + \zeta_1\zeta_2^2)/D_3,$$

$$D_1 = \zeta_1^2 + 4\zeta_1\zeta_2 + 2\zeta_2^2, \quad D_2 = 3\zeta_1^2 + 2(5\zeta_1\zeta_2 + 3\zeta_2^2),$$

$$D_3 = \zeta_1^3 + 2(3\zeta_1^2\zeta_2 + 4\zeta_1\zeta_2^2 + \zeta_2^3),$$

$$\zeta_1 = 1/(1 + 2\Lambda), \quad \zeta_2 = \Lambda/(1 + 2\Lambda), \text{ and } \Lambda = \exp[-E_g/(kT)].$$

In the limit dp → 1, the equations here for backbone LCPs reduce to the equations of Refs. 2(d)-2(e) for LC monomers.

(Somewhat analogous changes were made to treat side-chain LCPs and mixtures with LCPs in this paper.)