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THEORETICAL PREDICTIONS FOR SIDE-CHAIN LIQUID-CRYSTAL POLYMERS AND COMPARISON TO EXPERIMENT

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ABSTRACT

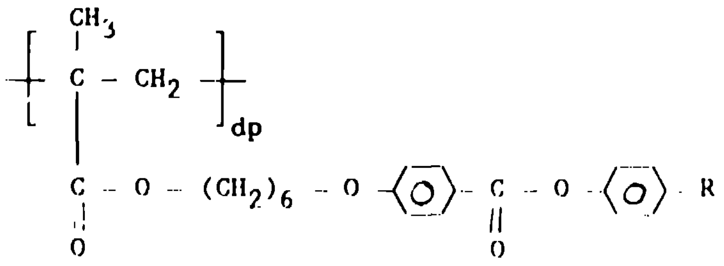
This paper presents results from a new unique microscopic molecular theory for side-chain liquid-crystalline polymers (LCPs) in the nematic (N) and multiple smectic-A (SA) LC phases and the isotropic (I) liquid phase. There are no ad hoc or arbitrarily adjustable parameters in this theory. The agreement between the theoretical and experimental values for various properties (including transition temperatures and quadratic characteristic radii) is very good (relative deviations between 0% and less than 6.2%). The theoretical results also show--for the first time--that the N and I phases for these LCPs involve the packing of plate-like sections of backbones and side chains and that the local bilayer SA phase involves packing of side-chains within a plate-like section. This type of packing is predicted to be typical for side-chain LCPs. This theory can predict--for the first time--whether the side chains of a molecule pack on the same or alternating opposite sides of the backbone and whether side chains on different molecules interdigitate (overlap) with each other.

INTRODUCTION

Uses of side-chain LCPs include electro-optic devices.

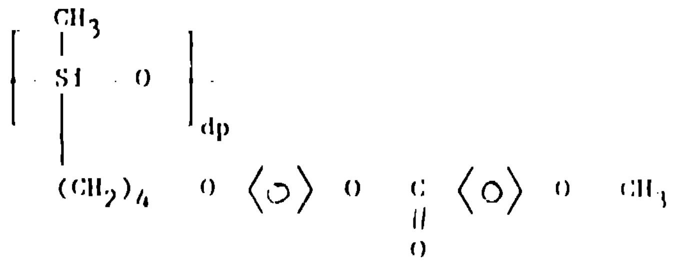
The side-chain LCPs studied in this paper have the following molecule chemical structures, where dp is the degree of polymerization:

PMA-R:



where R is $-OC_4H_9$, $-OCH_3$, or $-CN$.

$PMS-OCH_3$:



THEORY

Theory summary and theory equations

Due to length restrictions on this paper, the summary of the theory used in this paper and the equations of this theory are given in the companion paper[1] by this author in this same Proceedings volume.

Variables for the equations of this theory:

Terms not defined in this paper have been previously defined in the companion paper[1] by this author in this same Proceedings volume.

In addition to dp, the input variables for the molecule chemical structures in this theory are the following: ρ_k is the average density of the system (average fraction of lattice sites occupied by molecular segments) for k-type packing; $0 < \rho_k \leq 1$. v_{ok} is the volume of one lattice site (i.e., hard-repulsive volume of one molecular segment) for k-type packing. r_1 and f_1 are the number of rigid segments and semiflexible segments, respectively, in one repeat unit in the backbone of a molecule. $r_2 = r_3$ and $f_2 = f_3$ are the number of rigid segments and semiflexible segments, respectively, in each side chain of the molecule. E_g is the energy of a gauche rotational state (relative to the trans state) of a carbon-carbon bond between methylene groups in n-alkyl chains.

P_{2rk} is the average orientational order of the rigid sections of the molecule involved in k-type packing and is given by $P_{2rk} = \langle(3\cos^2\theta_k - 1)\rangle/2$, where θ_k is the angle between the long axis of the rigid section and the preferred axis of orientation for the rigid section; $0 < P_{2rk} \leq 1$. λ_k is the average fraction of one-dimensional positional alignment of the centers of mass of the molecule parts whose rigid-section long axes are oriented parallel to the preferred axis for orientation of the rigid sections in k-type packing; $0 < \lambda_k \leq 1$. (λ_k is thus a reduced ratio between the average layer thickness and the average effective molecule part length involved in positional ordering at a given T in a SA phase.)]

a_σ is the average separation distance between segment centers at the zero of energy in the Lennard-Jones (12,6) pair potential for any two segments in different molecules. ϵ_{cc1} and ϵ_{tt1} are the absolute values of the minimum of energy between two "core" segments and between two "tail" segments, respectively, in the Lennard-Jones (LJ) potential for backbones. "Tail" refers to the semiflexible segments and the two end rigid segments in a repeat unit, and "core" refers to the other rigid segments in a repeat unit. $\epsilon_{cc2} = \epsilon_{cc3}$ and $\epsilon_{tt1} = \epsilon_{tt2}$ are the absolute values of the minimum of energy between two "core" segments and between two "tail" segments, respectively, in the LJ potential for side chains.

$\mu_{D\|1}$ and $\mu_{D\|2} = \mu_{D\|3}$ are the net longitudinal dipole moments for the repeat unit for the backbone and for each side chain, respectively. $\mu_{D\perp1}$

(where $i = 1,2,\ldots$) and $\mu_{D\perp 2i} = \mu_{D\perp 3i}$ (where $i = 1,2,\ldots$) are the individual transverse dipole moments for the repeat unit of the backbone and for each side chain, respectively. α_{c1} and α_{t1} are the average polarizabilities for a core segment and a tail segment, respectively, in a repeat unit of the backbone. $\alpha_{c2} = \alpha_{c3}$ and $\alpha_{t2} = \alpha_{t3}$ are the average polarizabilities for a core segment and a tail segment, respectively, in each side chain.

$a_{//hk}$ is the average separation distance between segment centers at the zero of energy in the pair potential for hydrogen bonding between any two segments in different molecules involved in $\underline{k}$-type packing. [Here, we use a LJ (12,6) potential, which is different from the LJ potentials used above for London dispersion forces.] ϵ_{cch1} is the absolute value of the minimum of energy for hydrogen bonding between two "core" segments in the backbones. ϵ_{cch2} and ϵ_{cch3} are the absolute values of the minimum of energy for hydrogen bonding between two "core" segments in the side chains for 2-type packing and 3-type packing, respectively.

Values of r_k and f_k are calculated by summing up the lengths of the rigid and semiflexible sections using average bond lengths (for example, C=N) from experimental data[2] and using average bond angles (for example, 120° for angles involving an sp^2-bonded carbon) and then dividing by the length of one segment (here, one methylene segment). Here for an example side-chain LCP PMA-OC_4H_9, the length of one methylene segment is also the same as $a_w = 1.27$ A, the separation distance[3] between adjacent carbons in the all-trans conformation of a $\underline{n}$-alkyl chain.

For PMA-OC_4H_9, for Ω_1 and E_{I1}, $r_1 = 2$ and $f_1 = 0$ (since we want to look at the orientational ordering of the bond between the two segments in the backbone repeat unit). For a', $r_1 = 1$ and $f_1 = 1$, since the two segments in the backbone repeat unit are semiflexible methylene units. $r_2 = r_3 = 12.2$ and $f_2 = f_3 = 12$. $E_g/k_B = 250$ K from experimental data for n-alkyl chains.[4] (k_B is the Boltzmann constant.) $a_{//} = 4$ A, an approximate average value appropriate for methane or benzene molecules,[5] which are reasonable approximations for the chemical species in typical LC molecules.

Values for ϵ for LJ (12,6) potentials for different chemical groups (such as benzene rings and methylene groups) are taken or estimated from experimental data in Ref. 5. Values of ϵ_{cck} and ϵ_{ttk} are then calculated by summing up these ϵ and dividing by the number of segments involved. For PMA-OC_4H_9, $\epsilon_{cc1}/k_B = \epsilon_{tt1}/k_B = 120$ K, $\epsilon_{cc2}/k_B = \epsilon_{cc3}/k_B = 145$ K, and $\epsilon_{tt2}/k_B = \epsilon_{tt3}/k_B = 116$ K.

Values of $\mu_{D\parallel k}$, $\mu_{D\perp ki}$ ($i = 1,2,\ldots$), α_{ck}, and α_{tk} are taken or estimated from experimental bond and group dipole moments[6(a),7] and polarizabilities.[6(b)] $\mu_{D\|k}$ is calculated by summing up the longitudinal bond and group dipole moments. α_{ck} and α_{tk} are calculated by summing up the polarizabilities for the different bonds and dividing by the number of segments involved. For PMA-OC_4H_9, $\mu_{D\|1} = \mu_{D\perp 1i} = 0$ (with $i = 1,2,\ldots$). For $k = 2$ and $\overset{\sigma}{k} = 3$, $\mu_{D\|k} = 0$ and $\mu_{D\perp k1} = \mu_{D\perp k2} = 2.5$ D. $\alpha_{c1} = \alpha_{t1} = 13\times10^{-25}$ cm^3. $\alpha_{c2} = \alpha_{c3} = 25\times10^{-25}$ cm^3, and $\alpha_{t2} = \alpha_{r3} = 18\times10^{-25}$ cm^3.

There is no hydrogen bonding in PMA-OC_4H_9. For molecules that do have hydrogen bonding, ϵ_{cchk} can be calculated by summing up all of the ϵ_h for all the hydrogen bonds (in the rigid section) in the molecule part with k-type packing and dividing by the number of segments involved in the rigid section of the molecule part. $a_{\sigma hk}$ can be calculated by taking an average of the $a_{\sigma h}$ for all the hydrogen bonds (in the rigid section) in the molecule part with k-type packing. Values for ϵ_h and $\alpha^*_h = \alpha_{\sigma h}/2^{1/6}$ can be taken or estimated from experimental data in, for example, Ref. 8.

COMPARISON OF THEORY WITH EXPERIMENT

Tables I and II compare theoretical results of this paper with experimental results[9-12] for T_{NI} and T_{SN}, where T_{NI} and T_{SN} are phase transition temperatures involving the N and smectic (S) LC phases and the I liquid phase. The relative deviations between the theoretical results and the experimental results in Table I and II are less than 6.2% and 5.8%, respectively.

TABLE I. Theoretical and experimental T_{NI} in K at P = 1 atm.

molecule	dp	theor. T_{NI}	exper. T_{NI}	exper. ref.
PMA-OC_4H_9	654	376	381, 388	9, 10
PMA-OCH_3	767	394	383	11
PMA-CN	36	380	381	12
PMS-OCH_3	80	400	377	11

TABLE II. Theoretical and experimental T_{SN} in K at P = 1 atm.

molecule	dp	theor. T_{SN}	exper. T_{SN}	exper. ref.
PMA-OC_4H_9	654	369	365, 383	9, 10
PMA-CN	36	346	365	12
PMS-OCH_3	80	367	347	11

The theoretical calculations show, for the first time, that the N and I phases for these LCPs involve the packing of plate like sections of backbones and side chains. See Fig. 1(b). The theoretical results also show, for the first time, that the particular S phase for these LCPs is a local smectic-A2 (SA2) phase which involves the packing of side chains within a plate-like section. See Fig. 1(a). This SA2 phase is a bilayer smectic phase where the side chains of a molecule pack on opposite (alternating) sides of the backbone and do not interdigitate with side chains on other molecules. These theoretical results are consistent with the experimental data (see especially, Ref. 12).

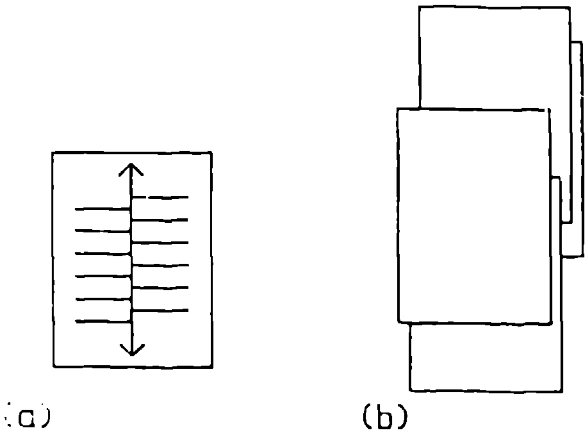


FIGURE 1. Schematic diagram illustrating (a) the tendency of the backbones and side chains to pack in a plane; and (b) the orientational alignment of these planes, such that the backbones in one plane align with backbones in other planes and similarly for side chains. (The arrows indicate the continuation of the backbones.)

Tables III and IV compare theoretical results of this paper with experimental (neutron scattering) values[11] for the the quadratic characteristic perpendicular radii $R_{\perp}$ (describing the conformation of the backbone) and $R_{\parallel}$ (describing the conformation of the side chains) when the long axes of the side chains are aligned (oriented) parallel to an applied magnetic field in the N LC phase. Table III presents the change in $R_{\parallel}$ as a function of varying dp. In Table III, the physically reasonable assumption has been made that the length of the terminal n-alkyl group in the side chains of the PMA-O-alkyl molecules does not significantly affect the conformations of the backbone. In Table III, the theoretical results are the same as the experimental results.

TABLE III. Theoretical and experimental $\Delta R_{\perp}/\Delta dp$ [i.e., change in $R_{\perp}$ (in Å) vs. change in dp] in the N LC phase at P = 1 atm.

molecule	dp	theor.	exper.	exper. ref.
PMA-O-alkyl	654, 767	0.2	0.2	11
PMS-OCH_3	35, 80	0.2	0.2	11

TABLE IV. Theoretical and experimental $R_{\perp}$ and $R_{\parallel}$ (both in Å) in the N LC phase at P = 1 atm.

molecule	dp	R	theor. R	exper. R	exper. ref.
PMA CN	36	$R_{\parallel}$	26.1	26.5	11
PMS OCH_3	35	$R_{\perp}$	15	15	11

Table IV presents comparisons of $R_{\parallel}$ and $R_{\perp}$. The relative deviations between the theory and experiment in Table IV are 2% or less.

In the theory of this paper, $R\perp$ and $R\|$ are calculated from the actual calculated lengths (along the long axes) of the backbones and side chains, respectively, of the side-chain LCPs; the calculated separation distances between the ends of the backbones and the side chains, respectively; and the well-known relation $L^2 = 12R^2$ (see, for example, Ref. 13), where L is the actual length (along the long axis) of the molecule part and R is the radius of the molecule part. We should note that for backbones and side chains with semiflexible sections (as is the case in the side-chain LCPs in Tables III and IV) the actual calculated lengths are shorter--in LC phases and in the *I* phase--than the fully extended (all-trans) lengths.

ACKNOWLEDGMENTS

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