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TITLE. PREDICTION AND DESIGN OF FIRST SUPER-STRONG MOSTLY-RIGID POLYMERS FROM VERY MOLECULAR THEORIES FOR SMECTIC AND NEMATIC POLYMERS

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PREDICTION AND DESIGN OF FIRST SUPER-STRONG MOSTLY-RIGID POLYMERS FROM VERY MOLECULAR THEORIES FOR SMECTIC AND NEMATIC POLYMERS

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ABSTRACT

This paper presents a new unique microscopic molecular theory for backbone liquid-crystalline polymers (LCPs), side-chain LCPs, and combined 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 thermodynamic and molecular ordering properties for existing LCPs is very good (relative deviations between 0% and less than 6.2%). This theory has been used by this author to predict and design (atom by atom, bond by bond) the first super-strong (SS) LCPs. This paper presents the design of SS mostly-rigid (MR) LCPs.

INTRODUCTION

Some relatively rigid solidified backbone LCPs (such as Kevlar) have major uses as stronger, lighter-weight replacements for metals, ceramics, and other materials in various structural applications, such as armor (bulletproof vests, football helmets, military tank armor, etc.) and auto and airplane parts (belted tire cord, airplane tail sections, etc.).

Solidified SS LCPs are designed to be the first polymers to have good compressive strengths, as well as to have tensile strengths and tensile moduli significantly greater than existing strong LCPs (such as Kevlar). SS LCPs are a class of specially-designed combined LCPs in which the backbones align with other backbones while the side chains of different molecules align with each other in interdigitated structures, leading to 3D LC ordering of the molecules. Thus, the key feature of this new class of LCPs is three-dimensional (3D) exceptional strength on a microscopic, molecular level (thus, on a macroscopic level), in contrast to present LCPs (such as Kevlar) with their 1D exceptional strength. While existing strong LCPs are limited in technical applications primarily to fibers in woven fabrics and composite matrices, SS LCPs can be used to make fibers, films, and bulk materials from the pure SS LCP (as well as from the SS LCP in a composite matrix).

The side chains of these SS LCPs are predicted to be soluble in most of the same solvents in which low-molecular-weight (LMW) LC molecules are soluble and thus, to increase the solubility of the whole molecule (including the backbone) in these solvents.

The chemical syntheses of several of these theoretically-designed SS LCPs are nearing completion at Los Alamos.[1,2]

THEORY

Theory summary, equations, and variables

The theory here is an extension and refinement of the highly successful theories presented by this author in Refs. 3-6 for backbone LCPs, side-chain LCPs, combined LCPs, LMW LC materials, and LC and LCP mixtures. (These latter theories in turn involved extension and refinement of even earlier highly successful theories presented by this author in Refs. 7-10 for LC materials.)

In the theory of this paper (as in Refs. 3-10), 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 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 in the *I* liquid phase, the *N* LC phase, and various SA LC phases.

As in Refs. 3-10, the theory here involves starting with a simple-cubic (SC) lattice theory and then taking various continuum limits. We start with a 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.

This decomposition and mapping onto a SC lattice allows us to treat--in a geometrically transparent and mathematically tractable manner--details of molecule chemical structure, including features that are essential in determining the LC ordering of real molecules. A significant number of these features (such as the flexibility of chains attached to rigid rodlike sections in LC phases) have not been amenable to treatment by continuum theories. The Gibbs free energy G of the system is minimized with respect to the individual x, y, and z components of the orientations of the long axes of the rigid rodlike sections of the molecules.

This theory is a localized-mean-field (LMF) theory.[3-10] LMF means that there is a specific *average* neighborhood (of other molecular sites and empty space) in a given direction i 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.

A rigid section is formed by a sequence of conjugated aromatic, double, and triple bonds in the molecule. The overlap of π orbitals in the aromatic, double, and triple bonds in the section leads to the rigidity of the section. A semiflexible section is usually formed by a *n*-alkyl chain section and is partially flexible (semiflexible) since it costs a finite (but easily achievable) energy to make rotations about any carbon-carbon bond between methylene units in a given chain section. The net energy difference between the one trans and either of the two gauche rotational energy minima is E_g, with the gauche states having the higher energy.

The compositions of the local regions in this LMF theory are determined by how the molecules actually pack and interact with lowest 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 i 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, 1D positional alignment of the centers of mass of the rigid sections of the molecules, such that for oriented rigid sections, rigid sections tend to pack with other rigid sections (and associated semiflexible sections tend to pack with other semiflexible sections) as found in various SA phases]

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 (see discussion in Ref. 10).

Continuum limits are taken in this theory.[3-10] The thermodynamic limit is taken (that is, the number of lattice sites M in the system and the number of molecules N_m in the system each go to infinity), and thus the thermodynamic and molecular ordering variables in the system assume a continuum of allowed values.

The partition function Q and the resulting equations for static thermodynamic and molecular ordering properties are functions of P, T, and details of the molecule chemical structures (including bond lengths and angles, E_g, hydrogen bonds, dipole moments, site-site polarizabilities and Lennard-Jones (12,6) potentials, degree of polymerization dp, and orientational and 1D (SA) 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 taken from experimental data for atoms or small groups of atoms or are calculated in the theory.

The essence of this theory is that we take a test molecule with a given chemical structure and--given the orientations and positions of the different parts of $(N_m - 1)$ other molecules in the system (where $N_m \to \infty$) at a given P and 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 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 G for the system.

In practice, we determine the density ρ and the independent average orientational and positional order variables for the different parts of the molecules at a given P and T by simultaneously solving the PVT equation of state and the equations that minimize 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.

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.

Due to length restrictions on this paper, Appendix A of this paper presents the changes in the equations of the theory of this paper from the equations of earlier versions [3-10] of the theory, and the companion paper[11] by this author in this same Proceedings volume presents a listing of the actual values for the input variables for this theory used for an example LCP.

Test of theory for existing LCPs

The theory in this paper gives thermodynamic and molecular ordering results in very good agreement (relative deviations between 0% and less than 6.2%) with experimental data for existing LCPs. See the companion paper[11] by this author in this same Proceedings volume for a comparison of this theory with experiment for some existing side chain LCPs. See

Appendix B of this paper for a comparison of this theory with experiment for existing backbone LCPs.

PREDICTION AND DESIGN OF FIRST SS MR LCPS

SS LCPs (specially-designed combined LCPs) were first proposed[12] and designed by this author in 1983. At the request of the related chemical synthesis effort at Los Alamos, the author has delayed publication of the details (in this paper here) of the theoretical prediction and design of the SS MR LCPs until the first syntheses were close to completion. This author has mentioned the theoretical prediction and design of the first SS LCPs in an earlier publication.[5] In addition, the author has filed a patent application[13] on the details of the theoretical prediction and design of the first SS LCPs.

The prediction and design (atom by atom, bond by bond) of the molecule chemical structures of the first SS LCPs was accomplished using the theory presented by this author in this paper and earlier versions of this theory as presented by this author in other papers[3-10] dating back to 1983.

While the research groups of Ringsdorf[14] and of Arnold[15] have recently demonstrated the feasibility of chemically synthesizing combined LCPs, their LCPs do not have the correct features for SS LCPs (in particular, either the side chains are too widely spaced along the backbone, the side chains and backbones are too flexible, and/or the side chains are too short for these structures to be SS LCPs).

Essential general and specific features of SS MR LCPs

Physical interdigitation of side chains of SS MR LCPs

SS LCPs are a class of specially-designed combined LCPs in which the backbones align with other backbones, while the side chains of different molecules align with each other in physically interdigitated structures. See Fig. 1.

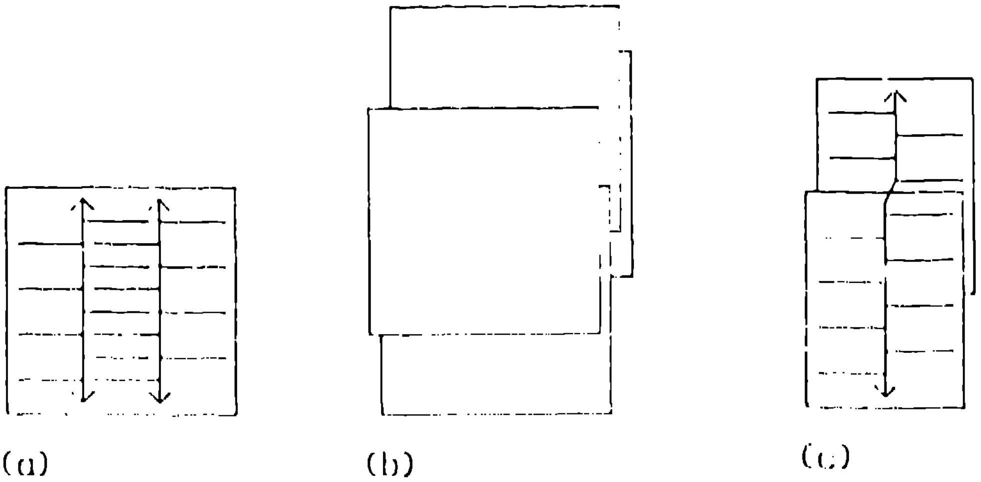


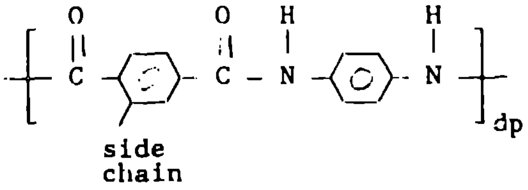
FIGURE 1. Schematic diagram for SS MR LCPs illustrating (a) the tendency of the backbones and side chains to pack in a plane; (b) the orientational alignment of these planes, such that the backbones in one plane align with backbones in other planes and similarly for side chains; and (c) one sub-molecular strip of a molecule packing in one plane, and another sub-molecular strip packing in an adjacent parallel plane. (The arrows indicate the continuation of the backbones.)

Molecule chemical structures for SS MR LCPs

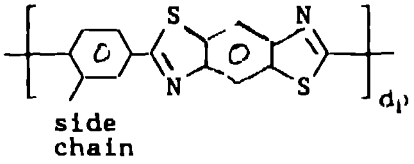
Here are some molecule chemical structures for some of the theoretically-designed SS MR LCPs studied in this paper:

Backbones:

Kevlar-type: b-Kev-1:

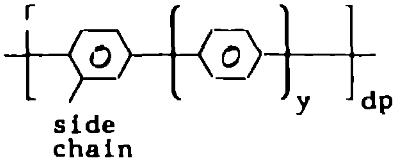


PBT-type: b-PBT:



The backbone b-PBO (i.e., the PBO-type backbone) is obtained by substituting -O- for each -S- in b-PBT.

Phenyl-type: b-Ph-y-1:

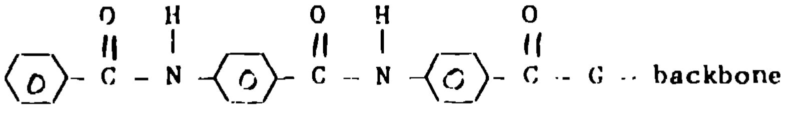


y: 1,2

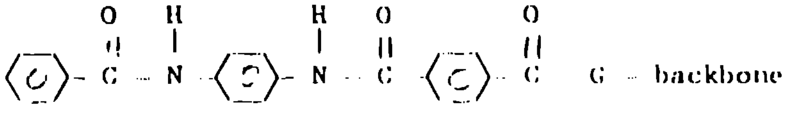
Side Chains:

Kevlar-like:

s-Kev-1:

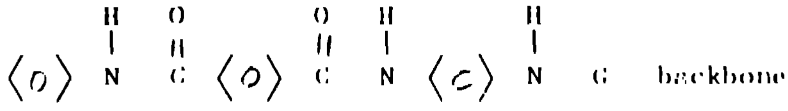


s-Kev-2:



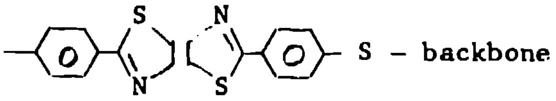
where here G = -O-, -NH-, or $-CH_2-$.

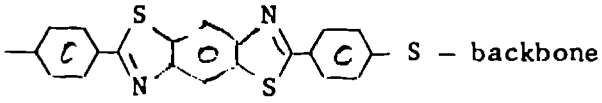
s-Kev-3:

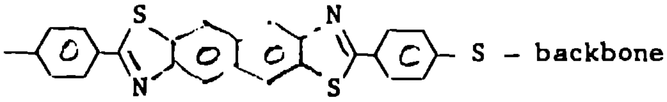


where here G = nothing, -O-, $-\overset{O}{\overset{\|}{C}}-$, or $-CH_2-$.

PBT-like:

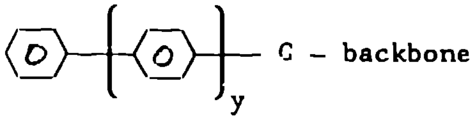
s-PBT-0: 

s-PBT-1: 

s-PBT-2: 

The PBO-like side chains s-PBO-0, s-PBO-1, and s-PBO-2 are obtained by substituting -O- for each -S- in s-PBT-0, s-PBT-1, and s-PBT-2, respectively.

Phenyl-like:

s-Ph-y: 

where here G = -O-, -S-, or $-CH_2-$.

For best mechanical properties (especially tensile strength and modulus), the average degree of polymerization dp should be at least 10 or more and preferably 50 to 100 or more. As with existing backbone LCPs (see, for example, Table I in Ref. 3 and Table I in Ref. 4), the orientational ordering of the backbone (thus, tensile strength and modulus) of SS MR LCPs increases as dp increases, reaching the asymptotic region around dp = 1000. The asymptotic region is being rapidly approached with dp values as small as 100 or even 10.

Enhanced molecular ordering and mechanical properties for SS MR LCPs

For several examples of theoretically-designed SS MR LCPs, Tables I and II show that the orientational ordering of the backbones and the side chains, respectively, of the SS MR LCP molecules is increased over the orientational ordering of existing backbone LCPs. Thus, in addition to good compressive strength, these SS MR LCPs will also have greater tensile strength and modulus than present backbone LCPs. (For the SS MR LCPs in Tables I and II, the abbreviations for the backbone structure and for the side-chain structure are given before and after the slash, respectively.)

In Table I, $P_2 = \langle 3 \cos^2\theta - 1\rangle/2$, where θ is the angle between the long axis of the backbone repeat unit and the preferred axis of orientation for the backbone repeat unit. P_2 can vary from 0 to 1, with 0 indicating no order and 1 indicating full order. In Table II, P_2 is the arithmetic average of (1) P_2 for the packing of the side chains of a molecule with the non interdigitated side chains of other molecules and (2) P_2 for the packing of the side chains of a molecule with side chains in the same molecule or with the interdigitating side chains of other molecules. P_2

for the side chains is defined relative to the preferred axis of ordering for the side chains, which is more or less perpendicular to the preferred axis of ordering for the backbones of these SS MR LCPs.

TABLE I. P_2 at *T* = 300 K, 450 K, and 600 K for the *backbones* of some theoretically-designed SS MR LCPs and for some existing strong backbone LCPs at P = 1 atm. dp = 1000.

molecule	300 K	450 K	600 K
Existing strong backbone LCPs:			
Kevlar	0.95619	0.89206	0.81439
PBO	0.97329	0.92349	0.85935
SS MR LCPs:			
b-Kev-1 / s-Kev-1 [NH]	0.99918	0.99696	0.99404
b-Kev-1 / s-PBT-0	1.00000	1.00000	1.00000
b-PBO / s-PBO-1	1.00000	1.00000	1.00000

TABLE II. P_2 at *T* = 300 K, 450 K, and 600 K for the *side chains* of some theoretically-designed SS MR LCPs at P = 1 atm. dp = 1000.

molecule	300 K	450 K	600 K
b-Kev-1 / s-Kev-1 [NH]	0.63227	0.61398	0.60474
b-Kev-1 / s-PBT-0	0.50663	0.50662	0.50662
b-PBO / s-PBO-1	0.50794	0.50792	0.50791

The P_2 values in Tables I and II constitute upper bounds (i.e., maximum values) possible for specific molecules at given *T*. The better the processing of the LCP, then the closer one comes to achieving these P_2 values. Relatively small changes in P_2 are accompanied by much larger changes in other properties (including thermodynamic as well as mechanical properties). (This point is illustrated for backbone LCPs in, for example, Table I of Ref. 3 and Table I of Ref. 4.)

For the SS MR LCP b-Kev-1 / s-Kev-1 [NH] at T = 450 K, the theory of this paper calculates the following increases--over Kevlar values--for mechanical properties: 25 GPa for tensile strength, 1539 GPa for tensile modulus, and 25 GPa for compressive strength. [These increases in mechanical properties constitute upper bounds (i.e., maximum values) possible at T = 450 K. The better the processing of the LCP, then the closer one comes to achieving these values.] For comparison, here are the experimental ranges[16] of "as-processed" values for the backbone LCPs Kevlar, PBT, and PBO: 3.5 to 5.8 GPa for tensile strength, 130 to 365 GPa for tensile modulus, and 0.40 to 0.48 GPa for compressive strength.

Rigid sections, including lengths

The repeat unit of the backbone and each side chain should be essentially rigid except for the connecting group between the backbone and each side chain. For best compressive strength, the side chain should in general be at least about 15 A long. Slightly shorter side chains are acceptable if they contain strong dipolar groups and/or strong hydrogen-bonding groups. In theory, the longer the side chain, then the better the compressive strength could potentially be. However, in practice, the lengths of side chains longer than about 50 to 60 A will be harder to orient under dynamic processing conditions.

For an example theoretically-designed SS MR LCP b-Ph-2-1 / s-Ph-y [CH_2], Table III shows that the average orientational ordering values P_2 for the backbones and for the side chains increase as the length of the rigid section in the side chain increases. For the molecule backbone and side chains in Table III, the backbone repeat unit b-Ph-2-1 has a calculated length of 12.96 A; and the side chain s-Ph-2 [CH_2] has a calculated length of 15.83 A, with each additional phenyl group in the side chain adding 4.32 A to the calculated length of s-Ph-2 [CH_2].

TABLE III. P_2 values vs. side-chain y at T = 450 K for the backbones and for the side chains of b-Ph-2-1 / s-Ph-y [CH_2] at P = 1 atm. dp = 1000.

side-chain y	back P_2	side P_2
2	0.97013	0.54482
3	0.99554	0.58945
4	0.99939	0.63884

For comparison, here are calculated lengths for the backbone repeat units and side chains in these other theoretically-designed SS LCPs in Tables I and II: 12.74 A for b-Kev-1, and 12.28 A for b-PBO. 20.74 A for s-Kev-1 [NH], 14.89 A for s-PBT-0, and 16.45 A for s-PBO-1.

Spacing distance between side chains along backbone

The spacing distance between the side chains along the backbone is a *critical* factor in determining compressive strength in SS LCPs. For best compressive strength, the spacing between two side chains along the backbone of a molecule should be such that the side chain of another molecule can interdigitate between (i.e., pack between) these two side chains with separation distances of about 4 to 5 A between the centers of directly adjacent interdigitated side chains. This conclusion is based on the following:

The spacing between adjacent backbones in backbone LCPs (and between adjacent molecules in low-molecular-weight LC molecules) is about 4 to 5 A. a^* = 4.5 A is the approximate average separation distance between centers of nearest-neighbor molecule segments at the minimum (thus, at the maximum attractive dispersion interactions) in the Lennard-Jones (12,6) potential energy and is calculated from a value of a_σ = 4 A, which (see the companion paper[11] by this author in this same Proceedings volume) is an approximate average value appropriate for methane or benzene molecules,[17] which are reasonable approximations for the chemical species in typical LC molecules.)

For separation distances between the centers of adjacent interdigitated side chains greater than about 4.5 A, the orientational alignment of the side chains (and thus, compressive strength of the LCP) will decrease as these separation distances increase. If the spacing between centers of adjacent side chains becomes too large along the backbone, the side chains will decrease the orientational ordering of the backbones (and thus the tensile strength and tensile modulus), and there will also be no significant increase in compressive strength as compared to the backbone LCPs.

There can be more than one side chain per backbone repeat unit, as long as the spacing distance meets the above requirements.

For best uniformity in compressive strength, the side chains should be spaced as <u>regularly</u> as their points of attachment to the backbone allow, in order to promote regular interdigitation of the side chains on different molecules (thus promoting <u>uniform</u> compressive strengths on the sub-molecule level).

<u>Side chain interdigitation in sub-molecular strips and on one or both sides of the backbone</u>

The side chains of one molecule can interdigitate with the side chains of a second molecule for a length (sub-molecular strip) along the backbone, then interdigitate with the side chains of a third backbone for another sub-molecular strip, and so forth. The interdigitation of one molecule with the side chains of several other molecules leads to an <u>effective long-range</u> three-dimensional ordering of the side chains and thus to effective good long-range three-dimensional compressive strength in the LCP system. See Fig. 2(a).

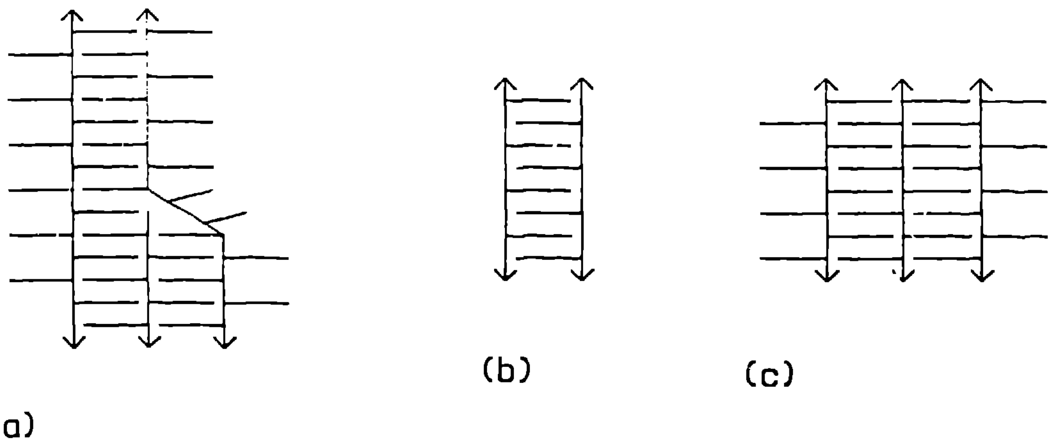


FIGURE 2. Schematic diagrams illustrating side-chain interdigitation (a) with several different molecules in different sub-molecular strips, (b) on one side of a backbone, and (c) on alternating opposite sides of a backbone.

For the calculations reported in Tables I-III in this paper, the side chains of a molecule interdigitate on one (i.e., the same) side of the backbone with the side chains of a neighboring molecule for the following SS MR LCPs: b-Kev-1 / s-Kev-1 [NH] and b-Ph-2-1 / s-Ph-y [CH_2] (where $y \geq 2$). See Fig. 2(b). The side chains of a molecule interdigitate on alternating sides of the backbone with the side chains of neighboring molecules for the following SS MR LCPs: b-Kev-1 / s-PBT-0 and b-PBO / s-PBO-1. See Fig. 2(c).

In all the calculations reported in this paper for these SS MR LCP cules, the side chains pack in a local interdigitated smectic-A1 (SA1) e; this is a SA phase in which the side chains are virtually fully digitated and in which there is virtually complete local one-dimensional positional order of the side chains one with another.

<u>Symmetry of functional groups and directional forces in side chains</u>

In general, the side chains should be as symmetrical as possible with regard to the sequences of functional chemical groups from one end of the side chain to the other end (for example, -A-B-C-D-C-B-A), in order to obtain maximum overlap (penetration) of interdigitated side chains (thus, maximized alignment of side chains and therefore, maximized compressive strength of the LCP). This requirement for symmetry can be relaxed if the there are stronger forces (such as stronger dipolar and/or hydrogen-bonding forces) between the side chains when they are interdigitated than when they are not.

It is easier to align the backbones and side chains in an electric or magnetic field if the the backbones and side chains do not both have longitudinal dipolar forces (i.e., dipolar forces parallel to the long axes of the backbones or of the side chains) or do not both have transverse dipolar forces and/or hydrogen bonding. Alignment in such fields is easiest if the backbone has only longitudinal dipolar forces while the side chains have only transverse dipolar forces and/or hydrogen bonding--or vice versa--such that the backbones and side chains can be correctly aligned at the same time by one uniaxial field.

Attachment of side chains to backbone

The side chain needs to be attached to the backbone such that there is no steric hinderance [i.e., the side chain can be fitted (packed) into the backbone chemical structure at that point]. For backbones containing benzene rings, there is in general less chance of steric hinderance if a side chain is attached to a side of a benzene ring rather than to smaller groups located between these rings in the backbone.

Processing the SS MR LCP is easiest if the functional chemical group (in the side chain) connecting the side chain to the backbone is a relatively small group and is connected by only a single bond to the backbone and by only a single bond to the rest of the side chain. The small size of this group and the semiflexibility of these single-bond connections will allow the side chain to fold down somewhat--with minimum steric hinderance-- parallel to the backbone (after the manner of spokes or ribs of an umbrella) when linear processing (such as flow through a pipe) of the SS MR LCP is required. See Fig. 3(a).

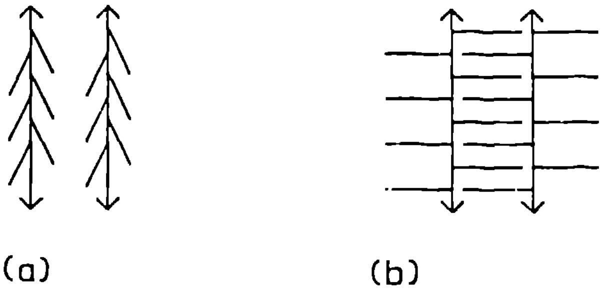

(a)
(b)

FIGURE 3. Schematic diagrams showing (a) the side chains folded down somewhat in linear processing and (b) the side chains folded back out after processing.

After linear processing is completed, then the side chains can be then be folded out from the backbone so as to pack more or less perpendicularly to the backbone such that the LCP molecules align in the three dimensions (i.e., backbones align parallel to one dimension and the side chains align in the other two dimensions) as required for super-strong mechanical properties. See Fig. 3(b).

Good connecting groups include -O-, -S-, -NH-, and $-CH_2-$.

Other Chemical Structures for SS LCPs

This paper has presented SS MR LCPs whose backbones and side chains contain chemical structures that are primarily variations on (1) chemical structures in the backbone LCPs Kevlar, PBT, and PBO; and (2) phenyl structures. It is also possible to design SS LCP molecules whose backbones and side chains contain chemical structures that (1) are primarily variations on chemical structures in other backbone LCPs (such as polyacetylenes, polyazobenzenes, polyazoxybenzenes, polyethers, polyesters, etc.) and (2) contain short semiflexible sections. Calculations for SS LCPs containing these types of chemical structures are reported by this author in later papers.

Processing of these SS MR LCPs

It is predicted here that existing processing techniques (particularly solution) can be used to process the theoretically-designed SS MR LCPs presented in this paper here. Both unaxial techniques (such as linear flow; uniaxial mechanical stretching; spinning; application of uniaxial electric or magnetic fields to align dipoles, etc.; and extrusion through a uniaxial orifice) and multiaxial techniques (such as biaxial mechanical stretching, as of a film; and application of electric or magnetic fields to alternate axes of the sample) exist. More development and extension of existing processing technologies (especially multiaxial processing methods) could be done to make these technologies even more effective for the SS MR LCPs here.

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APPENDIX A: THEORY EQUATIONS

Due to length restrictions on this paper, we present here only the changes in the theory of this paper from earlier versions [3-10] of the theory. The equations in this paper are the same as in earlier papers [3,6], except for the following changes. (Variables not defined in this paper have been previously defined in Ref. 3 and 6.) Here, $\Omega = \Pi_k \Omega_k$ and $E_I = \Sigma_k E_{Ik}$, where here $k = 1$ refers to the packing and interactions of the backbones, $k = 2$ refers to the packing and interactions of a plate-like section of the side chains of a molecule with the plate-like sections of the side chains of other molecules, and $k = 3$ refers to the packing and interactions of the side-chains with other side chains in the same plate. (See Fig. 1.) Each ln Ω_k and E_{Ik} has been multiplied by $x_k = m_k/(\Sigma_i m_i)$, where m_k is the total number of segments in a repeat unit ($k = 1$) or a side chain ($k = 2$ or 3). For backbone LCPs, $\Omega_1 \neq 0$, $E_{I1} \neq 0$, and $\Omega_2 = \Omega_3 = E_{I2} = E_{I3} = 0$. In the calculations with this theory for side-chain LCPs and combined LCPs (including SS LCPs), it has been found that the N and I phases for these LCPs involve the packing of plate like sections of backbones and side chains (i.e., $\Omega_1 \neq 0$, $\Omega_2 \neq 0$, $\Omega_3 = 0$, $E_{I1} \neq 0$, $E_{I2} \neq 0$, and $E_{I3} = 0$), and the SA phase for these LCPs is a local SA phase which involves the packing of side chains within a plate-like section (i.e., $\Omega_1 = \Omega_2 = 0$, $\Omega_3 \neq 0$, $E_{I1} = E_{I2} = 0$, and $E_{I3} \neq 0$).

Here, $\omega_{yzk} = \Sigma_{j=1}^{4} \omega_{yzjk}$, where $j = 1$ refers to LJ interactions, $j = 2$ refers to dipole/induced dipole interactions, $j = 3$ refers to dipole/dipole interactions, and $j = 4$ refers to hydrogen-bonding interactions. Here, $\mu_{D\perp k}{}^2 = \Sigma_{i,j}\, \mu_{D\perp ki}\mu_{D\perp kj} / \Sigma_{i,j}$, where one can have the following three cases depending on the positional order of the molecule parts involved in the $\underline{k}$-type packing and on the symmetry of the transverse dipoles in the molecule part: sum over (1) all ii pairs and ij pairs (where $i \neq j$), (2) all ii pairs only, or (3) all ij pairs only. Also, $\omega_{yz4k} = 4\epsilon_{yzhk}[(a_{\sigma hk}/a_k)^{12} - (a_{\sigma hk}/a_k)^{6}]$, where $y = z = c$, ϵ_{cch1} is the absolute value of the minimum of energy for hydrogen bonding between two "core" segments in the backbones, and 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 $k = 2$ packing and $k = 3$ packing, respectively. $\omega_{cc4\parallel k} = \omega_{cc4\perp k}$. For backbone LCPs, $v_{o1}{}^{1/3} = 1.96$ A. (This value led to a good calculated value of the $\underline{N}$ to $\underline{I}$ transition temperature for the LC PAA.) For side-chain LCPs and combined LCPs, $v_{o3}{}^{1/3} = 1.96$ A.

In addition, the backbones of side-chain LCPs and combined LCPs use the equations for backbone LCPs in Ref. 3, with the following exceptions: $v_{o1}{}^{1/3} = v_{o2}{}^{1/3} = [2v_{o3}{}^{1/3} + (m_1X_2) + (m_2X_1)]/(m_1 + m_2)$, where $X_k = ZL_k/4$, $L_k = a_w m_k$, and a_w is length of a segment in the backbone. These equations reflect the fact that the presence of the side chains will increase the effective hard-repulsive volume v_{o1} of a backbone segment in 1 of 4 possible orientations for packing and that the presence of backbones will increase the effective hard-repulsive volume v_{o2} of a side-chain segment in 1 of 4 possible orientations for the packing of plates of side chains. For Case 1 (i.e., the side chains of a molecule pack on alternating sides of the backbone), $Z = 2$. For Case 2 [(i.e., either (1) all the side chains of a molecule pack on one (i.e., the same) side of the backbone or (2) the side chains of a molecule interdigitate on alternating sides of the backbone with the side chains of neighboring molecules], $Z = 1$. For Case 3 [i.e., the side chains of a molecule interdigitate on one (i.e., the same) side of the backbone with the side chains of a neighboring molecule], $Z = 1/2$. These different values of Z reflect the fact that the effective hard-repulsive volume $v_{o1} = v_{o2}$ depends on the mode of packing of the side chains.

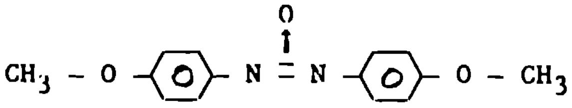
For k = 2 packing, the side chains use the equations for side chains in Ref. 3, with the following exception: ${v_{o2}}^{1/3}$ as given above.

For k = 3 packing, the side chains use the equations for side chains in Ref. 3, with the following exception: The length along the backbone between side chains is given by $a' = a_w(r_1 + f_1[(1 + 2P_{2i1})/3])$. $a_3 = 2a'$ for Case 1, $a_3 = a'$ for Case 2, and $a_3 = a'/2$ for Case 3.

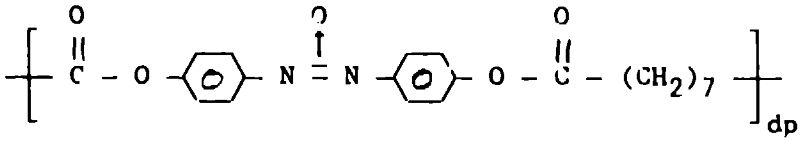
APPENDIX B: MORE TEST OF THEORY WITH EXPERIMENT

Here, we show a comparison of this theory with experiment for some existing backbone LCPs with the following molecule chemical structures:

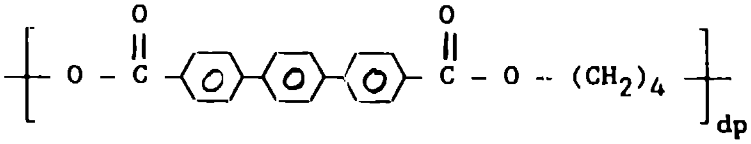
PAA:



B1:



N1:



DDA-9:

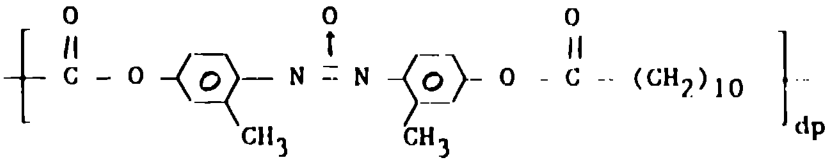


Table IV compares theoretical results of this paper with experimental results[18-20] for T_{NI}. Table V compares theoretical results of this paper with experimental results[21-22] for P_2 for the rigid sections in the N LC phase. The relative deviations between theory and experiment in Table IV and Table V are less than 3% and approximately 3%, respectively.

TABLE IV. Theoretical and experimental T_{NI} in K for some existing backbone LCPs and for PAA at P = 1 atm. * indicates that the experimental dp was large enough that the properties had reached their asymptotic values; in this case, the theoretical dp is 1000.

molecule	dp	theor. T_{NI}	exper. T_{NI}	exper. ref.
PAA	1	413	409	18
B1	15	554	544	19
N1	*	698	680	20

TABLE V. Theoretical and experimental P_2 for an existing backbone LCP and for PAA at P = 1 atm. T is given as a fraction of T_{NI} for each material.

molecule	dp	T	theor. P_2	exper. P_2	exper. ref.
PAA	1	$0.88T_{NI}$	0.793	~0.77	21
DDA-9	9	$0.92T_{NI}$	0.855	0.83	22

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