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Mesomorphic Phases of Flexible Polymers: The Self-Compacting Chain Model†

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ABSTRACT: Correlations are established between structural, thermal, and flexibility data of crystalline, locally flexible polymers giving rise to mesomorphic phases, which can be usefully organized in two classes. While in all mesophases the chain conformation is substantially disordered, in class 1 chain packing is characterized by orientation-dependent attractive interactions, so that the transition enthalpy ΔH_{ML} from the mesophase to the liquid is of the same order of magnitude as the crystal → mesophase transition enthalpy ΔH_{CM}. Conversely, in mesophases belonging to class 2 and in the corresponding melts nonbonded intermolecular interactions and conformational statistics are roughly similar, so that the M → L transition involves very little enthalpy ($\Delta H_{ML} \sim 0$). Consistent with the absence of specific interchain interactions, class 2 mesophases exhibit hexagonal packing and density lower than the corresponding crystalline phase. Polymers giving rise to this type of mesophase are characterized by numerous, regularly spaced side groups, often chemically different from the chain skeleton. The key factor stabilizing class 2 mesophases over the melt appears to be a higher entropy of the side groups, making mesogenic groups unnecessary. Optimization of the intrachain arrangement in class 2 mesophases usually requires a local contraction along the chain axis direction with respect to the extension found in the crystal and the confinement of individual chains within tubes that have a diameter D substantially larger than the average diameter D_C in the crystal. With a simple statistical model based on continuum elasticity (the self-compacting chain), applicable to flexible polymers, we show that, consistent with the available experimental data, the persistence length P is proportional to D^2. As a consequence, the aspect ratio P/D, which is normally assumed to control mesophase stability, is proportional to D. According to our approach, we thus may estimate by simple diffraction measurements of D the persistence length and the class 2 mesophase stability of flexible polymers. In the case of systems which experimentally give rise to class 2 mesophases, relatively large values of P are found despite the relatively low T_g.

Introduction

Mesomorphic phases[1] are characterized by degrees of organization ranging in the wide region between crystalline phases and the liquid state: as such they are sometimes termed intermediate phases. In the case of polymers, mesophases[2−5] tend to develop more easily[6] than in low molecular mass systems, a fact relating to molecular anisotropy and to kinetic factors.

Although it is difficult to draw clear separation lines, the main focus of our discussion will be on thermodynamically stable, thermotropic mesomorphic phases (M). These are characterized by entropy values higher than in the related crystalline phases (C). Near the isotropization temperature the entropy of the mesophase must be lower than the entropy of the isotropic melt (also denoted as "liquid state", or *L*, in the following) while at lower temperatures the reverse may be true.[7−9] The mesophases to be discussed are enantiotropic and stable at temperatures higher than the crystalline state and lower than the melt. The role of pressure is in general dependent upon the relative densities of the various phases (crystalline, mesomorphic, and liquid) and is readily understandable.

Examples of systems that are normally referred to as mesophases in the literature but appear due to kinetic control are the so-called smectic phase of isotactic polypropylene,[10] "mesomorphic" syndiotactic polypropylene,[11] "mesomorphic" PET,[12] and other instances where intermediate degrees of disorder are obtained after quenching polymers from the melt. Such phases are metastable as they usually crystallize upon heating; they will not be further discussed in the present paper.

In low molecular mass systems, mesophases tend to develop easily even with molecules endowed with a substantial flexibility provided that rigid groups are present (rods, ribbons, disks, etc., with high aspect ratios). These groups are called mesogens because anisotropic interactions between such units are generally regarded as a prerequisite for the formation of mesomorphic phases. For the rotator phases of paraffins[13] and perfluoroparaffins[14] the mesogenic unit may be thought to coincide with the molecule itself, which is highly anisotropic although hardly rigid.

Polymer mesophases develop not only in rigid systems (cellulose derivatives, aromatic polyesters and amides, polyaromatics, etc.[2−5]) but also with relatively flexible molecules. For the latter, definitions like conformationally disordered crystals (condis-crystals)[15,16] and columnar phases[17] have been proposed. Whereas rigid and/or mesogen-containing molecules are at this point rather well understood, the origin of mesomorphic behavior in highly flexible systems still needs some clarification and is the focus of the present paper.

Flexibility in polymers is a somewhat elusive concept. High flexibility intuitively implies low values of both T_g and the characteristic ratio C_∞. While this is normally the case, in some instances[18,19] C_∞ values—although hard to measure—turn out to be surprisingly large as

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† This paper is dedicated to our teacher and friend Paolo Corradini.

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compared both to conformational predictions[19] and to T_g. Experience indicates that such systems often give mesophases. It is clear that in such cases main-chain flexibility and side-chain conformational disorder play an important role for developing thermotropic mesophases. Although this problem is hardly dealt with in discussions of condis-crystals,[15,16] stabilization must be achieved either by relatively favorable packing interactions in the mesophase as compared to the melt, or by a higher entropy of the mesophase in appropriate temperature ranges, or by a combination of both effects. A qualitative explanation found in the literature suggests that flexible systems can develop mesophases if they are built with two types of poorly compatible sections whose microphase separation is responsible for the preservation of excess order as compared to the melt.[17,20,21] However, this perspective can hardly explain the established mesomorphic behavior of flexible polymers with no side groups, like polyethylene or PTFE, or with short side chains like polydiethylsiloxane, polydipropylphosphazene, polydimethylsilylene, etc., nor recent work on polysiloxanes with longer side chains.[22] The alternative or complementary concept which will be explored in the present paper is that flexible polymer mesophases are stabilized over the melt by a more effective side-group organization around the chain backbone. Optimization of intra- and interchain arrangement in the mesophase, primarily with respect to entropy, appears to involve a local chain contraction in the axial direction as compared to the crystalline state, which indeed is experimentally observed. This organization requires adequate flexibility of the main chain.

The first purpose of the present paper is to give a general overview of experimental data, i.e., the pertinent thermal and structural properties of flexible crystalline polymers exhibiting also thermodynamically stable mesomorphic phases, and to evidence possible correlations with flexibility features (i.e., the persistence length P and the characteristic ratio C_∞) derived from solution investigations. This attempt is quite problematic in itself because only in relatively few instances such comprehensive data are available. The second goal of the paper is to devise a simple, first-approximation model with a strong reference to experimental data to understand the key features of mesomorphic phases of flexible polymers and allow some predictivity. Inevitably, a number of questions will be left open as they require further refinement of the model and possibly additional experimental data.

The flexible-polymer mesophase model we propose is related to previous theoretical approaches to mesophases of rigid anisotropic molecules,[7,8] where purely athermal transitions have been considered using concentration in an athermal solvent as the driving state variable, under the assumption that the persistence length of the macromolecule is sufficiently large as compared to its diameter.[2,3,8,9] The key assumption shared by these approaches and our model is that, despite the higher apparent order, in the mesomorphic state the polymer may attain a larger entropy than in the liquid state. In the mesophase the entropy loss due to the straight-chain arrangement is overcompensated by the reduction of steric conflicts within the chain and with neighboring molecules, entailing a wider conformational freedom. Accordingly, the liquid → mesophase transition has been described as entropy-driven,[9] and enthalpic contributions are disregarded in this idealized framework. In essence, we will show that chains with a locally flexible backbone may become quite rigid as a consequence of their self-compacting elastic nature.

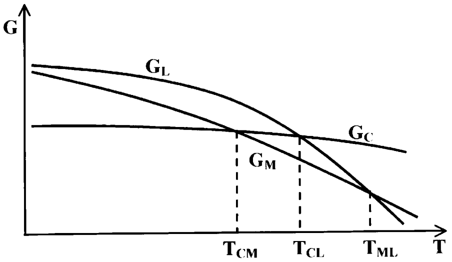

Figure 1. Free energy per chain bond of the liquid (L), of the mesophase (M), and of the crystalline (C) polymer. The equilibrium transition temperatures T_{XY} are shown (XY = CL, CM, ML); T_{CL} is to be regarded as virtual.

In the discussion of experimental data pertaining to flexible polymers, it turns out to be useful to identify two distinct mesophase classes: (i) mesophases from chains with small side groups intermolecularly stabilized by specific packing interactions (class 1) and (ii) mesophases characterized essentially by meltlike interactions among chains (class 2), often resulting with polymers bearing relatively large side groups, chemically different from the backbone. We empirically distinguish class 1 from class 2, observing that for class 2 mesophases the enthalpy ΔH_{ML} of the mesophase–liquid transition (M → L) is much smaller than the enthalpy ΔH_{CM} of the crystalline-mesophase transition (C → M). On the contrary, the two enthalpies are comparable for class 1 mesophases. We anticipate that the predictive power of our statistical treatment is more relevant to class 2 mesophases, although rough estimates of the persistence length of locally highly flexible polymers are obtained in all cases.

Mesophases of Flexible Polymers: General Thermodynamic Considerations and Some Experimental Data

We shall briefly consider the behavior expected for thermotropic mesophases before turning to the analysis of the available experimental data. Denoting with ΔH_{XY} and ΔS_{XY} respectively the crystal to mesophase (C → M) and the mesophase to liquid (M → L) transition enthalpy and entropy per chain bond of a polymer system with three states (X, Y = C, M, L for crystalline, mesomorphic, and liquid, respectively; see Figure 1), we have at constant pressure

$$T_{XY} = \frac{\Delta H_{XY}}{\Delta S_{XY}} \quad (XY = \mathrm{CM, ML}) \tag{1}$$

ΔH_{CM} and ΔH_{ML} are both ≥0 and so must be ΔS_{CM} and ΔS_{ML}. An obvious consequence is that at the transition temperature the higher temperature phase is always affected by a larger structural disorder. In Figure 1 the general form of the free energy plot assumed for the three phases is shown. We point out that, at temperatures sufficiently lower than the isotropization temperature T_{ML}, the plot is consistent with a standard assumption of the athermal theories of liquid crystalline polymers, namely $H_M = H_L$, $S_M > S_L$. In the following sections we will focus on the mesophase–liquid transition, which does not depend on specific packing features. Only some aspects of the crystal–mesophase transition

Table 1. Thermal Data of Selected Semiflexible Polymers Giving Rise to Thermotropic Columnar Mesophases or Main-Chain Disordered Crystalline Phases

	polymer (→ class I mesophases)	T_g (°C)	T_{CM} (°C)	ΔH_{CM} (kJ/mol)[a]	T_{ML} (°C)	ΔH_{ML} (kJ/mol)[a]
1	polyethylene[34−37]	−36	240[b]	3.5[b]	250[b]	0.7
2	poly(*trans*-1,4-butadiene)[34,36]	−83	83	1.9	164	0.9
3	polytetrafluoroethylene[34,38]	−73	19, 30	0.8	332	4.1
4	poly(*cis*-1,4-isoprene)[c,34,36]	−73			28	1.1
5	poly(*cis*-1,4-butadiene)[c,34,36]	−102			12	2.3
	polymer (→ class II mesophases)					
6	polydihexylsilylene[39,40]	−53	41	16.6	>250 (dec)	dec
7	polydimethylsilylene[40]		162	0.6	226	0.2
8	polydiethylsiloxane[16,41]	−138	10	0.9	53	0.2
9	polydipropylsiloxane[21,22,41]	−110	70	1.1	206	0.5
10	polydibutylsiloxane[21,22,41]	−120	−19	0.4	310	<0.1
11	polydipentylsiloxane[21,22,41]	−106	−22	1.0	330	<0.1
12	polydihexylsiloxane[21,22,41]		23	2.6	330	<0.1
13	poly(bis(trifluoroethoxy)phosphazene)[42,43]	−57	70	4.4	240	0.4
14	poly(bis(phenoxy)phosphazene)[42,44]	−4	160	4.1	390	<0.1
15	poly(bis(4-chlorophenoxy)phosphazene)[26,44]	7	180	4.1	360	<0.1
16	poly(bis(3-chlorophenoxy)phosphazene)[26,44]	−24	75	4.0	370	<0.1
17	poly(bis(4-methylphenoxy)phosphazene)[42]	1	160	3.9	420	<0.1
18	poly(bis(4-isopropylphenoxy)phosphazene)[45]	0	141	4.1	>330	<0.1
19	poly(bis(propyl)phosphazene)[28]	−30	248	3.4	310	0.4

[a] Transition enthalpies are given on a per main-chain-bond basis. [b] Data at ~5 kbar. [c] Main-chain-disordered, high-temperature crystalline phases, rather than columnar mesophases; thermal data refer to the melting of the high-temperature crystal phase into the liquid.

will be discussed because it is influenced by the specific packing in the crystal.

In the analysis of the experimental data we will start from the classification given by Ungar,[17] also keeping in mind Wunderlich's[15] condis-crystal definition. The flexible polymers discussed either show characterized hexagonal thermotropic mesophases, following ref 17, or display main-chain conformationally disordered crystalline structures, consistent with Wunderlich's definition, or both. Furthermore, for a polymer to be discussed in the present context, quantitative measurements of its flexibility or of closely related molecules need to be available. From the thermal data reported in Table 1, we can see that the first five entries show comparable, relatively large values of ΔH_{ML} and ΔH_{CM}. The first three polymers also appear in Ungar's table of columnar mesophases.[17] Poly(*cis*-1,4-isoprene)[23] and poly(*cis*-1,4-butadiene),[24] on the contrary, fit the definition of condis-crystals: both polymers present main-chain conformationally disordered crystalline structures while deviating from hexagonal packing. These two examples are meant to highlight the fact that the definition we have given for class 1 polymer mesophases also includes conformationally disordered structures deviating from hexagonal coordination. The first five polymers listed are just a subset of class 1: indeed, most polymer mesophases arising from the rigidity and anisotropy of mesogenic groups are expected to belong to this class since (i) they present more or less extensive conformational and positional disorder, (ii) they have comparable values of ΔH_{ML} and ΔH_{CM}, and (iii) they adopt modes of packing characterized by directional intermolecular interactions.

The members of class 2 in Table 1 present very small enthalpies of the mesophase−liquid transition ($\Delta H_{ML} \le 0.5$ kJ/(mol of chain bonds)), suggesting that their mesophase is hardly stabilized by specific interatomic interactions. By contrast, we point out that in all cases the crystal−mesophase transition has a significant enthalpy value, mostly $\Delta H_{CM} > 1$ kJ/(mol of chain bonds). Consistent with the relatively flexible character of the polymers listed in Table 1, their glass transition temperature is always rather low ($T_g \le 0$ °C).

It is important to notice that class 1 and class 2 mesophases differ rather clearly not only with respect to transition enthalpies but also with respect to degrees of order, as evidenced by diffraction measurements. Class 1 mesophases are normally characterized by a significant intramolecular order, resulting in well-defined meridional reflections in diffraction spectra. Often there is also some intermolecular order involving the relative displacement of neighboring chains in the axial direction, resulting in at least some off-meridional layer-line reflections. Since conformational disorder characterizes both the main and the side chains, for rigorously class 2 mesophases off-meridional layer-line reflections are expected to be absent. On a large-domain scale both class 1 and class 2 present an ordered interchain packing in the axial projection, which is hexagonal for class 2, as in this case the polymer chains are effectively modeled by continuous cylinders. Because of possible directional interactions, the packing of class 1 mesophases may deviate from the hexagonal arrangement, although it is adopted by chains for which such a lattice is efficient. Thus, a hexagonal packing is a necessary but insufficient feature to identify class 2 mesophases.

Table 2 shows geometrical and flexibility data pertaining to the same polymers analyzed in Table 1. Although both the persistence length P and the characteristic ratio C_∞ basically characterize the same feature, i.e., the overall chain flexibility, both quantities are reported. A connection between the two parameters may be established as for wormlike chains: indicating respectively as l_0 and l the chemical bond length and its average projection on the chain axis of the mesomorphic chain and assuming this projection to be retained in the melt, we have (ref 25, Appendix G)

$$\langle r^2 \rangle_0 = N C_\infty {l_0}^2 = 2LP \quad (L = Nl) \tag{2}$$

$$P = \frac{C_\infty {l_0}^2}{2l} \tag{3}$$

N being the number of chain bonds. We may also

Table 2. Geometric Data of Selected Polymers Giving Rise to Thermotropic Mesophases to Thermotropic Columnar or Main-Chain Disordered Crystalline Phases[a]

	polymer (→ class I mesophases)	l_{crys} (Å)	l_{meso} (Å)	D (Å)	C_∞[46]	P (Å)
1	polyethylene[47]	1.27	1.20[b]	4.9[b]	6.5[48]	6.5
2	poly(*trans*-1,4-butadiene)[49]	1.21	1.16	5.0	5.6[50]	5.6
3	poly(tetrafluoroethylene)[51]	1.31	1.30	5.7	7[52]	6
4	poly(*cis*-1,4-isoprene)[c,23,24]	1.01		4.45	5.1[53]	5.4
5	poly(*cis*-1,4-butadiene)[c,24]	1.08		4.34	5.0[54,55]	5.0
	polymer (→ class II mesophases)					
6	polydihexylsilylene[39,40]	2.0	~1.8[d,e]	15.5	20[19]	31 (29[19])
7	polydimethylsilylene[40]	1.9	1.9	7.8	10[i]	15[i]
8	polydiethylsiloxane[16,56]	1.19	1.22	9.6	7.7[57]	8.1
9	polydipropylsiloxane[21,22,56]	~1.2[f]	~1.1[d,e]	11.2	13[58]	15
10	polydibutysiloxane[21,22,56]	~1.2[f]	~1.1[d,e]	12.3	(21)	(24)
11	polydipentylsiloxane[21,22,56]	~1.2[f]	~1.1[d,e]	13.4	(25)	(29)
12	polydihexlysiloxane[21,22,56]	~1.2[f]	~1.1[d,e]	14.6	(29)	(34)
13	poly(bis(trifluoroethoxy)phosphazene)s[43,59]	1.22	1.05[g]	11.9	(20)	(23)
14	poly(bis(phenoxy)phosphazene)[42]	1.21	1.05[d,g]	13.2	20[18]	24
15	poly(bis(4-chlorophenoxy)phosphazene)[26,44]	1.20	1.05[g]	14.2	33[18]	40
16	poly(bis(3-chlorophenoxy)phosphazene)[26,44]	1.21	1.05[g]	14.2	32[i,18]	39[i]
17	poly(bis(4-methylphenoxy)phosphazene)[42,60]	1.24	1.05[d,g]	13.5	33[i]	40[i]
18	poly(bis(4-isopropylphenoxy)phosphazene)[60]	1.22	1.0 [g,h]	16.7	33[i]	40[i]
19	poly(bis(propyl)phosphazene)[28]	1.22	1.0[d,g]	11.3	(18)	(20)

[a] Values of l_{crys} and l_{meso} are average projections per main-chain bond on the axis direction respectively in the crystal and in the mesophase. l_{meso} coincides with l in our model and is typically 10−20% smaller than l_{crys}[27,42] for class 2 polymers. D are average chain interaxial distances. These parameters were derived from diffraction data, in the case of l_{meso} combined with dilatometric data. Values of the persistence length P are generally calculated using the expression $P = C_\infty l_0^2/2l$ from C_∞ data, while for l_0 the following bond lengths were adopted: C−C (single) 1.54 Å, C−C (double) 1.34 Å, Si−O 1.60 Å, Si−C 1.89 Å, Si−Si 2.35 Å, P−N (phosphazenic) 1.59 Å. P values in parentheses were calculated from the expression $P = \gamma D^2$ using the best fit value 0.16 Å^{-1} for γ; while the corresponding values of C_∞ (also in parentheses) are obtained from eq 3. [b] Data at ~5 kbar. [c] Main-chain-disordered, high-temperature crystalline phases, rather than mesomorphic. [d] Since dilatometric data are unavailable, at T_{CM} a 10% molar volume increase has been assumed. [e] A typical chain cross section expansion of 20−30%, with the assumed specific volume expansion leads to the discussed reduction of per bond axial advance. [f] Values assumed in analogy to polydiethylsiloxane and polydiphenylsiloxane. [g] Oriented polyphosphazene mesophases show anisotropic amorphous maxima which on the meridian imply a periodicity of 4.2−4.4 Å roughly consistent with the reported value of l_{meso}. [h] Unpublished dilatometric data (S. V. Meille). [i] Values adopted from experimental data for polymers which are structurally closely related (e.g., for 17 and 18 the C_∞value of poly(bis(4-ethylphenoxy)phosphazene) is used).

establish a correlation of C_∞ with the length of the statistical segment Λ. According to the definition proposed by Flory,[25] (i) each segment is spatially uncorrelated with any other and (ii) their overall length is equal to the fully extended chain length. Labeling with n the total number of statistical segments in the chain, we have from Flory's definition

$$\langle r^2\rangle_0 = n\Lambda^2; \quad L = n\Lambda; \quad \Lambda = \frac{\langle r^2\rangle_0}{L} = \frac{C_\infty l_0^{\,2}}{l} = 2P \qquad (3')$$

For the first five polymers (class 1), the average chain-to-chain interaxial distance D is smaller than 6 Å, unlike all the following polymers (i.e., no. 6−19 in Tables, class 2); of course, this is a consequence of the relatively bulky substituents carried by class 2 polymer chains. Unfortunately, for some of the polymers in Tables 1 and 2, the C_∞ and P literature values are widely scattered or unavailable. Since one result of the present work will be to evaluate P from experimentally determined geometrical parameters, in such cases C_∞ and P values predicted from our model by suitable interpolation are reported in Table 2 within parentheses.

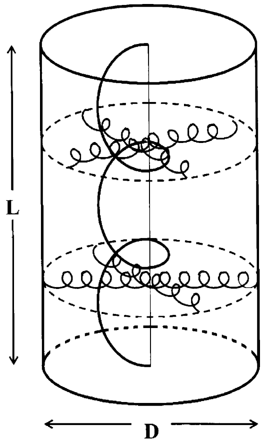

Figure 2. Idealized elastic model of the chain in the mesophase. The chain cylinder with diameter D is regarded as a uniform-density elastic body; the main chain and the side chains are ideal springs contributing to the overall elastic energy (see text).

From the data in Table 2 we will now identify the essential features of polymers giving rise to class 2 mesophases. We see that (1) the chain backbone is at least as flexible as sp^3 carbon-chain polymers and (2) it carries two identical side groups on every second chain atom, except in the case of the polysilylenes where longer skeletal bonds allow each main-chain atom to be doubly substituted; as a result, we have a considerable and regular side-group crowding around the chain skeleton; (3) in the mesophase the chain backbone is generally less extended than in the crystalline state, typically with a 10% contraction along the chain axis direction (cf. l_{crys} and l_{meso}), whereas the chain diameter is expanded with respect to the crystalline state;[26−28] (4) increasing the size of the side groups for a given main chain structure yields both an increasing chain diameter D and a larger persistence length P. These characteristics may be interpreted by a model in which the main chain of polymers giving rise to class 2 mesophases acts as a sort of entropic spring that pulls together the side groups giving rise to a compact cylindrical organization of the macromolecule and the side chains around the chain axis (see Figure 2). Indeed, the distance D between neighboring chain axes is large enough as to ensure that interdigitation between their side groups

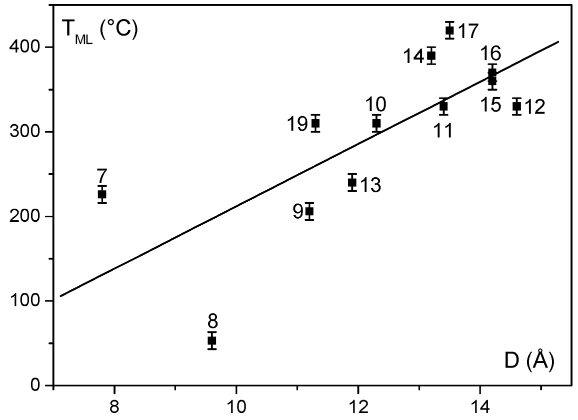

Figure 3. Plot of T_{ML} vs the chain diameter D for class 2 polymers as reported in Tables 1 and 2 (see Figure 2). The best-fitting straight line is evaluated giving the same weight to all the experimental points. The ratio between the rms error of its slope and the slope itself is 0.29.

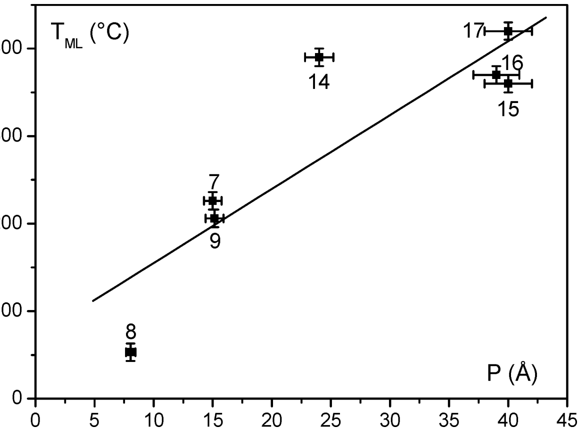

Figure 4. Plot of T_{ML} vs the chain persistence length P for class 2 polymers (see Tables 1 and 2). Symbols are as in Figure 3. The ratio between the slope rms error of the best-fitting straight line and the slope itself is 0.40.

is extremely unlikely and intermolecular interactions occur only at the lateral surface of such cylinders. Considering for example the five polydialkylsiloxanes, the unperturbed root-mean-square distances between the substituted silicon atom and the last carbon atom of the side group, evaluated from Flory's results for polyalkanes[25] after correction for the Si−C bond length, turn out to be smaller than $D/2$ by more than 1 Å. Consequently, no interdigitation between the side groups of neighboring chains occurs consistent with the analysis of the structural projections along the chain axis of several crystalline polymers. It is reasonable to expect that, in view of the regular and symmetrical chemical arrangement of the side groups along the chain, the statistically cylindrical structure tends to be maintained even in the melt. In fact, for molecules giving rise to class 2 mesophases sharp bending of the chain axis is contrasted by nonbonded repulsive interactions between the side groups, filling up the volume around the chain axis according to cylindrical symmetry. As a result, a relatively large value of the persistence length P is expected despite the extensive chain conformational disorder.

We will now deal with the issue of the thermodynamic stability of class 2 mesophases, which we expect to correlate with the isotropization—or melting—temperature T_{ML}. Figures 3 and 4 show the plots of T_{ML} respectively as a function of the diameter D and of the persistence length P. The latter plot has fewer experimental points because few data are available, reflecting the higher experimental difficulty involved in measuring the chain dimensions in unperturbed solution rather than in determining the chain diameter by X-ray diffraction (see also Table 2). The mesophase melting temperature increases with either D or P, the average slope parameter being respectively 3.5 and 2.5 times its standard deviation. Qualitatively, it appears reasonable that an increase of either the chain diameter or the persistence length should be reflected into an increased mesophase stability (i.e., an increased T_{ML}) to the extent that, with the macromolecules we are considering, either increase should entail an increase in repulsive nonbonded interactions between side groups, for a given degree of bending of the chain axis. We address the reader to the next section for a quantitative interpretation.

Liquid-crystalline order has been investigated hitherto especially when involving rigid molecules with large aspect ratios L/D, L being the molecular length. Classical theories consider the isotropic−nematic transition as a function of either concentration (in athermal systems) or of both concentration and temperature.[1−3,7,9] In all cases a large value of the aspect ratio shifts the isotropic−nematic transition either to higher temperatures or to lower concentrations or both. Khokhlov and Semenov[8] extended the theory to polymer solutions ($L \to \infty$), considering both freely jointed (FJ) and wormlike (WL) chains (we use the symbol P to denote either the half-length $\Lambda/2$ of the freely jointed segment in the FJ model or the persistence chain length in the WL model; see eqs 2−3′). Rather intuitively, in the polymer case the role of the aspect ratio is replaced by P/D. The critical polymer concentration for an athermal solution to develop a nematic phase turns out to be inversely proportional to that ratio, indicating a higher thermodynamic stability of the mesophase with increasing values of P/D. Accordingly, in the pure-polymer case, for comparable values of the interchain interaction energies we expect higher values of T_{ML} for larger P/D ratios. The T_{ML} vs P/D plot is not reported here because, although showing a positive correlation between the two variables, its statistical significance is very limited due to superposition of uncertainties of both P and T_{ML} as well as to the few experimental points. In the following section we shall discuss a statistical model of chains giving rise to class 2 mesophases, based on simple criteria derived from rubber elasticity. The model will clarify the physical significance of the data correlation suggested by Figures 3 and 4 and enable to establish a quantitative correlation between P and D.

The Self-Compacting Chain and Its Persistence Length

We shall model the mesomorphic chain as a compact, cylindrical structure undergoing dynamic conformational disorder. According to the classical theory of polymer elasticity, all the system configurations are regarded as isoenergetic, and its structural disorder, i.e., entropy, is naturally associated with elastic behavior. The chain in the mesophase is reduced to an elastic cylinder, and both the backbone and the side groups are

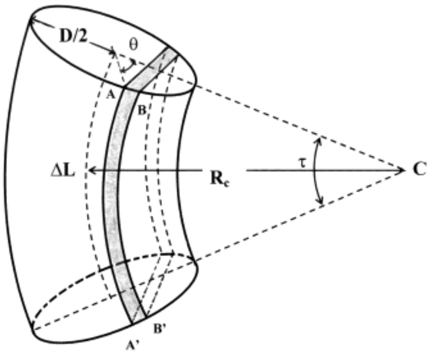

Figure 5. Side view of a uniformly bent chain portion. The meaning of the symbols is given in the text. The shaded volume slice is obtained by cutting the chain with two coaxial cylinders; their axis goes through the center of curvature C and is orthogonal to the plane defined by the chain axis and the radius of curvature R_C.

represented by ideal springs (see Figure 2). To enforce the constant-density requirement, the cylinder volume is kept constant by volume forces so that a single elastic parameter is required to describe its elastic response under uniaxial deformation. The mesomorphic state will arise by close-packing of these straight cylindrical chains on a two-dimensional hexagonal lattice. Considering instead the chain to be either in the molten state or in an athermal dilute solution, we will derive a quantitative estimate of its persistence length, adopting the wormlike chain representation. In both cases we disregard side-group swelling relative to the mesophase, in the assumption that the chain entropy is close to its largest value when its side groups are tightly packed around the main chain. As a result, the overall chain conformation in the liquid state may be described by a distorted cylinder whose axis keeps the same length and whose transverse circular section is the same as in the mesophase (see Figure 5).

In the straight-chain portion shown in Figure 2, the average length and radius of the undistorted cylinder are L and $D/2$, respectively. We confine detailed analysis to class 2 polymers with a number n of bonds in the main chain equal to the number of the side groups, but the results obtained apply with minor changes also to other structures. The main chain has a mean-square length $\langle r^2{}_L\rangle_0 = nC_{\infty B}\, l_0{}^2$ in the bare unperturbed state, defined as the ideal solution of the bare backbone polymer wherein the side chains are replaced by hydrogen atoms. The unperturbed mean-square distance from the chain axis to the end of each side chain is $\langle r^2{}_{D/2}\rangle_0$. The free energy of the chain portion comprised within the cylinder is equal to the elastic energy provided by the main-chain and the side-group springs, i.e.

$$G(L,D) = \frac{3}{2}k_{\mathrm{B}}T\left\{\frac{L^2}{\langle r_L{}^2\rangle_0} + n\,\frac{(D/2)^2}{\langle r_{D/2}{}^2\rangle_0}\right\} \tag{4}$$

We notice that, considering a different chain portion with $n' = cn$ skeletal bonds, the average length changes from L to cL, while $\langle r_L{}^2\rangle_0$ also increases by a factor c; consequently, $G(L,D)$ changes to $cG(L,D)$, as expected. As an equivalent statement, any chain portion with n skeletal bonds may be regarded as a series of n spring elements each having an average skeletal length L/n. Considering a uniaxial deformation that changes L to λL at constant volume, the diameter D must change in turn to $D/\sqrt{\lambda}$. Imposing the stationarity condition for $\lambda = 1$, the free energy is given by

$$G(\lambda) = G(\lambda L, D/\sqrt{\lambda}) = \frac{3}{2}k_{\mathrm{B}}T\,\frac{L^2}{\langle r_L{}^2\rangle_0}\left(\lambda^2 + \frac{2}{\lambda}\right);\quad \left(n\frac{(D/2)^2}{\langle r_{D/2}{}^2\rangle_0} = 2\,\frac{L^2}{\langle r_L{}^2\rangle_0}\right)_{\lambda=1} \tag{5}$$

Notice that the last equality is roughly verified by class 2 polymers from 8 to 19 (see Table 2) if we take $n = 1$, $L^2 = \langle r_L{}^2\rangle_0$ as the smallest spring element. Let us now see the implications of this result on the random bending of the chain as produced by Brownian forces in a melt or in an athermal solution where its axis may bend freely. We subdivide the chain into chain elements comprising ν skeletal bonds (see Figure 5). The average axial length $\Delta L = \nu l$ of each chain element will be determined by requiring that its average thermal energy of bending is $k_{\mathrm{B}}T$. The physical implication of this requirement is that bending may be regarded as uniform within each chain element, in analogy with the behavior of a single molecular degree of freedom. Defining the bending plane as containing the center of curvature C and the bent axis of the chain element, as shown in Figure 5, the bending planes of contiguous elements along the chain may be regarded as uncorrelated. On these premises, denoting with τ the root-mean-square angle between the axial chain directions at the two ends of the chain element, the chain persistence length P will be given by

$$P = \frac{2\Delta L}{\tau^2} \tag{6}$$

according to a recognized mathematical property of the wormlike chain.[29]

From what precedes we may assume any section orthogonal to the chain axis to remain planar under bending. We also take the chain element radius of curvature $R_{\mathrm{c}} \gg D/2$. Let us consider the family of cylinders with a common axis that goes through the center of curvature C and is orthogonal to the bending plane. We consider two points A and B on the upper circular edge of the chain element. From Figure 5 we have $\overline{\mathrm{AB}} = (D/2)\,\mathrm{d}\theta$, $\mathrm{d}\theta$ being a small increment to the angle θ. The thin portion of the chain element (henceforth slice), comprised between the two cylinder surfaces passing through the points A and B, has a uniform strain ratio $\lambda(\theta)$ given by

$$\lambda(\theta) = \frac{R_{\mathrm{c}} - (D/2)\cos\theta}{R_{\mathrm{c}}} \tag{7}$$

Notice that $\lambda = 1$ is the average value of the strain parameter. The volume fraction of the slice is equated to the surface fraction on the chain section:

$$\mathrm{d}v(\theta) = \frac{2(D/2)^2\sin^2\theta\,\mathrm{d}\theta}{\pi D^2/4} = \frac{2}{\pi}\sin^2\theta\,\mathrm{d}\theta \tag{8}$$

and from eq 5 the corresponding free energy is

$$\mathrm{d}G(\theta,R_{\mathrm{c}}) = \frac{3}{2}k_{\mathrm{B}}T\,\frac{\Delta L^2}{\langle r_{\Delta L}{}^2\rangle_0}\left(\lambda(\theta) + \frac{2}{\lambda(\theta)}\right)\mathrm{d}v(\theta)$$

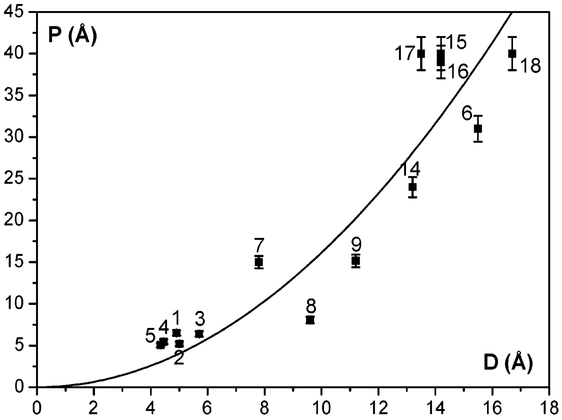

Figure 6. Persistence length P is plotted vs the chain diameter D for both class 1 and class 2 polymers (see Table 2). The best fitting function $P = \gamma D^2$ is shown with $\gamma = 0.16 \pm 0.01$ Å^{-1}.

After subtracting the undeformed free energy contribution, the bending energy of the chain element is

$$\Delta G(R_c) = \int_{\theta=0}^{\theta=\pi} \mathrm{d}G(\theta,R_c) - G(R_c \rightarrow \infty) \qquad (9)$$

Since $D/2 \ll R_c$, we may write $1/\lambda(\theta,R_c) \cong 1 + [(D/2)/R_c] \cos\theta + [(D/2)/R_c)^2] \cos^2\theta$, and eq 9 reduces to

$$\Delta G(R_c) \cong \frac{9}{4} k_B T \frac{\Delta L^2}{\langle r_{\Delta L}{}^2\rangle_0} \left(\frac{D}{2R_c}\right)^2 \qquad (10)$$

Putting $\Delta G(R_c) = k_B T$, we have

$$\tau = \frac{\Delta L}{R_c} = \frac{4\sqrt{\langle r_{\Delta L}{}^2\rangle_0}}{3\ D} \qquad (11)$$

We may obtain now the persistence length P from eq 6 and eq 11, remembering $\Delta L = nl$ and $\langle r_{\Delta L}{}^2\rangle_0 = C_{\infty B}\nu\, l_0{}^2$, l and l_0 respectively being the projected and the chemical bond length. The final result is

$$P \cong \frac{9}{8} \frac{lD^2}{C_{\infty B} l_0{}^2} = \gamma D^2; \quad \gamma = \frac{9l}{8C_{\infty B} l_0{}^2} \qquad (12)$$

We notice that neither the length ΔL nor the angle τ is uniquely determined, unlike the ratio $2\Delta L/\tau^2$ that yields a single value for the persistence length P (see Figure 5 and eq 6). Taking indicative values for $C_{\infty B} \approx 4$, for $l \approx 1.2$ Å and for $l_0 \approx 1.6$ Å, from eq 12 we can estimate $\gamma = 0.13$ Å^{-1}. A small value of $C_{\infty B}$ is chosen on account of the large flexibility of the bare backbones of the polymers we are considering. Figure 6 shows the plot of P vs D for the class 2 polymers reported in Table 2. The best-fitting $P = \gamma D^2$ curve appears encouraging and yields $\gamma \approx 0.16 \pm 0.01$ Å^{-1}, in semiquantitative agreement with the value estimated from eq 12.[30] We notice that the best-fitting value of γ is influenced by the quality of experimental C_∞*'s* for class 2 polymers which, as discussed in ref 18, may present aggregation in solution, poor solubility in noncoordinating solvents, and high polydispersity.

Discussion and Concluding Remarks

Considering mesomorphic polymers free of classical mesogenic groups, we propose a classification scheme based upon the thermodynamics of the mesomorphic ↔ liquid transition. Flexible polymers may give rise to mesophases characterized either by specific, orientation-dependent interactions (class 1) or by aspecific interchain interactions, much like in the melt except that the chain axes are straight and parallel (class 2).

The specific object of the present paper is represented by class 2 mesophases. Polymers giving rise to mesophases of this class are characterized by a flexible backbone and identical side groups, often chemically different from the main chain, regularly branching from it (see Tables 1 and 2). The experimental side-group density along the chain axis is in the range 0.8−1.2 groups/Å, corresponding to one group per chain atom with the exception of polysilylenes where two side groups per chain atom are present, but main chain bonds are distinctly longer. The possibility of other side-chain topologies is not ruled out, but at present we are not aware of pertinent cases. Class 2 mesophases are apparently stabilized by optimal interactions of the side groups around the backbone, with essentially no intertwining between adjacent chains. X-ray diffraction does not yield any evidence of order beyond the parallel, hexagonal arrangement of the chain axes, along which density measurements indicate that the macromolecules contract by about 10% of their extension in the crystalline state. The conformational disorder of both the chain backbone and the side groups is confirmed by the very small values of the melting enthalpies (see ΔH_{ML} in Table 1).

We propose that the tendency to produce a mesomorphic state, despite the flexible main chain, originates from the optimization of the organization of the side groups and the chain backbone, leading to an overall straight arrangement of the macromolecule. As a result, even in the absence of enthalpic factors, the mesophase achieves entropy stabilization as the side groups of each chain have a larger conformational freedom than in the melt, thus overcompensating for the entropy loss due to suppression of chain bending. To account for the large degree of conformational disorder, we propose an idealized elastic model whereby the external shape of the cylinder comprising the chain is produced by a system of axially symmetrical springs (see Figure 2). Regarding the cylinder as an elastic continuum with constant volume and extending some results of classical elasticity, we derive the persistence length P from the length of a suitable cylinder portion whose thermal energy of bending is equated to $k_B T$. The result is given in eq 12 as $P = \gamma D^2$; the theoretical value of γ ($\sim$0.13 Å^{-1}) appears to be in rough agreement with the experimental data reported in Figure 6, yielding $\gamma \sim 0.16$ Å^{-1}. These values of γ correspond to polymers with flexible, nonpolar side groups and a single backbone within the chain cylinder and are likely to increase with more rigid polymers. As an example, the double helix of DNA has a diameter $D = 22$ Å, yielding a value $P \sim 60$ Å if we take $\gamma \sim 0.13$ Å^{-1} (or $P \sim 75$ Å with the best fit $\gamma \sim 0.16$ Å^{-1}), whereas the currently accepted value of P is about 300 Å. We suggest that $\gamma \sim 0.13-16$ Å^{-1} may be taken as lower limits, applicable to highly flexible polymers.

Although the simplified elastic model giving rise to the $P = \gamma D^2$ correlation curve was derived for polymers giving class 2 mesophases, Figure 6 shows that other flexible polymers, such as those belonging to class 1, also fit quite well. We believe this functional dependence should be applicable to all flexible polymers whose rigidity (persistence length) depends essentially on the entropic balance between backbone conformational flexibility and steric crowding of the side groups, hydrogens included. In this respect statistical studies on comblike polymers in good solvents, where chain density considerations do not play a direct role, also suggest a roughly similar dependence, namely $P = \gamma D^m$, where m is comprised between $^5/_2$ and $^8/_3$.[31]

In a different perspective we recall that, consistent with their low T_g values, all polymers we are discussing are basically flexible. However, their T_g's and also their T_{CM} and T_{ML} values experimentally tend to increase with the size of the side groups (see Tables 1 and 2). In the case of polyphosphazenes a linear correlation between side group bulkiness, T_g, and T_{CM} has been found.[42] Although no clear implication with respect to the mesomorphic behavior was proposed, such observations also involve a correlation between side group bulk and chain rigidity.

In the case of highly flexible main-chain polymers, as the side chains get longer beyond a critical value, the constraint imposed by the main chain on the side-chain organization will become less stringent and the polymer organization may be determined predominantly by the side chains.[22] Our model does not tell us anything with respect to this critical side-chain length although it is reasonable to assume that it is of the order of the persistence length of the side chains. The issue is made more intricate because both the stability of the melt and of the crystalline phase play a role.

Physical intuition and the leading theories predict the thermodynamic stability of mesophases[2,7−9] to increase with the aspect ratio P/D. Since we have found $P \propto D^2$, the aspect ratio should be proportional to D and the thermodynamic stability should also increase with both P and D. Taking the melting temperature T_{ML} as a measure of such stability, the experimental plots reported in Figures 3 and 4 appear to confirm the prediction. The thermodynamically stable class 2 mesophases we are discussing result from self-assembly on a two-dimensional hexagonal lattice of polymer chains which adopt a cylindrical shape to maximize main-chain and side-group conformational entropy. In the melting transition the cylinders undergo some bending, although both their statistical structure and their external surface area remain basically unaltered, so that the entropy gain is modest. The model we propose implies that both the density and the enthalpy of the mesophase and the liquid are likely to be very close at sufficiently low temperatures ($T \ll T_{ML}$, see Figure 1) as they are controlled by van der Waals interactions between conformationally disordered side groups at the same average distances. Under these assumptions, from $H_M = H_L$ and $G_M < G_L$ we have $S_M > S_L$. We thus recover one important feature of athermal liquid−nematic transitions, namely that the entropy of the seemingly more ordered (nematic) phase is larger than the liquid's.[2,7−9] As the temperature rises toward T_{ML}, thermal activation increases chain bending, leading to a decrease of the persistence length P in the melt, and consequently we have an increase of both the entropy and the enthalpy of the liquid (see Figure 1). It also is pertinent to recall in this context that some experimental scattering data,[32,33] obtained from melts of polymers giving rise to class 2 mesophases, present surprisingly sharp low-angle maxima very closely corresponding to the interchain distance D in the mesophase. This fact supports the idea that, at a scale close to the distance D, the structure of the melt must be close to that of the corresponding class 2 mesophases.

The correlation between P and D presented in Figure 6 suggests a semiquantitative estimate of the persistence length P from the interchain distance D in the mesophase using the best-fitting value of γ in the equation $P = \gamma D^2$. Figure 6 and the preceding discussion indicate that such a procedure should also be applicable to flexible class 1 polymers. Furthermore, because of the analogy between the local structure of melts and class 2 mesophases, it may turn out to be possible to evaluate the persistence length of flexible polymers simply from amorphous interchain distance data. We are presently investigating these issues.

The data in Table 2 and Figure 6 require some additional comment: it is apparent that polymers giving rise to class 1 mesophases are clustered at small D and P values while class 2 mesophase polymers are characterized by larger values of the two parameters. More precisely, defining the aspect ratio $x = P/D = \gamma D$, polymers giving rise to class 1 mesophases are characterized by $1 < x < 2$, whereas polymers producing class 2 mesophases tend to $x > 2$. This observation qualitatively reconciles our views about flexible polymer mesophases with the theoretical approaches of Flory,[2] Kokhlov,[8] etc., to polymer liquid crystals, even though the critical value of the aspect ratio is somewhat lower in our case. While this smaller value may relate to the fact that we are considering mesomorphic behavior in bulk and not in solution, it should be noted that values of x are given by other authors in terms of the statistical segment which is twice the persistence length (see eq 3′). The requirement $x > 2$ along with the functional relationship $P = \gamma D^2$ and the experimentally determined value of γ of 0.16 implies the possibility to predict which polymers are likely to give class 2 mesophases merely from the value of their diameter D, with the critical value appearing to be about 10 Å. In fact, some polymers with D around that value represent borderline cases: while polydiethylsiloxane ($D = 9.6$ Å) presents a mesophase with a very limited temperature stability range, the closely related polydiethylphosphazene polymer apparently does not afford a thermotropic mesophase, at least for the relatively low molecular weights of this polymer available to date. On the contrary, both the polyphosphazene and the polysiloxane dipropyl derivatives ($D = 11.2$ Å) give rise to class 2 mesophases, whereas both dimethyl polymers do not. While the equivalent criteria $x > 2$ and $D > 11$ Å are to be taken as semiquantitative indications for a class 2 mesophase to form, other requirements need to be met, which basically relate to the propensity of the chain to adopt a cylindrical envelope. Among them, substitution regularity, side-chain size, main- and side-chain flexibility, molecular weight, and microphase separation effects, etc., may all play significant roles which at present we can only hint to.

How does our attempt compare with classifications proposed by other authors for mesophases of flexible polymers?[15,17] We notice that both class 1 and class 2 fit into the conformationally disordered crystals scheme proposed by Wunderlich et al.,[15] as all the systems we consider show some degree of dynamic conformational disorder. The polymer mesophase concepts considered by us are also strongly related to the columnar phase classification based on positional and orientational longrange order discussed by Ungar.[17] Specifically all of group A in ref 17 (aperiodic and periodic linear macromolecules) polymers fit well into our class 1, while group B polymers of the classification (comblike macromolecules with a flexible backbone) correspond in essence with our class 2. In our opinion mesophases grouped in class 2 also fit quite well the hexatic phase definition,[1] while class 1 mesophases could probably be better described as highly disordered crystalline phases rather than liquid-crystalline phases.

We conclude pointing out that the self-compacting chain model, although a first approximation, represents so far the only viable alternative to the microphase separation concept[17,20,21] to account for the stability with respect to the melt of mesophases of flexible polymers. Examination of the available experimental data hardly supports the microphase separation approach because, due to the high side-group density in macromolecules yielding class 2 mesophases, their intermolecular interactions are bound to always occur essentially between chemically similar side chains. Furthermore, if class 2 mesophases arose due to microphase separation, their formation should not be inhibited by irregular side chain substitution,[32,33] by low molecular weights,[33] or by excessive bulkiness or anisotropy of the side groups.[22]

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References and Notes

(1) De Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Oxford University Press: Oxford, England, 1993. Kumar, S. *Liquid Crystals*; Cambridge University Press: Cambridge, England, 2001.

(2) Flory, P. J. *Adv. Polym. Sci.* **1984**, *59*, 1.

(3) *Liquid Crystallinity in Polymers*; Ciferri, A., Ed.; Cambridge University Press: New York, 1991.

(4) Noël, C.; Navard, P. *Prog. Polym. Sci.* **1991**, *16*, 55.

(5) Samulski, E. T. The Mesomorphic State. In *Physical Properties of Polymers*, 2nd ed.; American Chemical Society: Washington, DC, 1993.

(6) Percec, V.; Keller, A. *Macromolecules* **1990**, *23*, 4347.

(7) Onsager, L. *Proc. N.Y. Acad. Sci.* **1949**, *51*, 27.

(8) Khokhlov, A. R.; Semenov, A. N. *Macromolecules* **1986**, *19*, 373. Grosberg, A. Y.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; AIP Press: New York, 1994.

(9) Frenkel, D. *Physica A* **1999**, *263*, 26. Holyst, R.; Oswald, P. *Macromol. Theory Simul.* **2001**, *10*, 1.

(10) Natta, G.; Peraldo, M.; Corradini, P. *Rend. Accad. Naz. Lincei* **1959**, *26*, 14. Corradini, P.; Petraccone, V.; De Rosa, C.; Guerra, G. *Macromolecules* **1986**, *19*, 2699.

(11) Vittoria, V.; Guadagno, L.; Comotti, A.; Simonutti, R.; Auriemma, F.; De Rosa, C. *Macromolecules* **2000**, *33*, 6200.

(12) Imai, M.; Kaji, K.; Kanaya, T. *Macromolecules* **1994**, *27*, 7103.

(13) Müller, A. *Proc. R. Soc. London* **1932**, *A138*, 514. Ungar, G. *J. Phys. Chem.* **1983**, *87*, 689. Sirota, E. B.; Herhold, A. B. *Polymer* **2000**, *41*, 8781.

(14) Campos-Valette, M.; Ray-Lafou, M.; Lagnier, R. *Chem. Phys. Lett.* **1982**, *89*, 189.

(15) Wunderlich, B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60/61*, 1. Wunderlich, B.; Möller, M.; Grebowicz, J.; Baur, H. *Adv. Polym. Sci.* **1988**, *87*, 1.

(16) Godovky, Yu. K.; Papkov, V. S. *Adv. Polym. Sci.* **1989**, *88*, 129. Molenberg, A.; Möller, M.; Sautter, E. *Prog. Polym. Sci.* **1997**, *22*, 1133.

(17) Ungar, G. *Polymer* **1993**, *34*, 2050.

(18) Bravo, J.; Tarazona, M. P.; Saiz, E. *Macromolecules* **1991**, *24*, 4089. Tarazona, M. P. *Polymer* **1994**, *35*, 819. Burdàlo, J.; Tarazona, M. P.; Carriedo, G.; García Alonso, F. J.; Gonzalez, P. *Polymer* **1999**, *40*, 4251.

(19) Cotts, P. M.; Miller, R. D.; Trefonas, P. T. III; West, R.; Fickes, G. N. *Macromolecules* **1987**, *20*, 1046. Neuburger, N.; Bahar, I.; Mattice, W. L. *Macromolecules* **1992**, *24*, 2447.

(20) Weber, P.; Guillon, D.; Skoulios, A.; Miller, R. D. *J. Phys. (Paris)* **1989**, *50*, 793.

(21) Kögler, G.; Loufakis, K,: Möller, M. *Polymer* **1990**, *31*, 1538. Möller, M.; Siffrin, S.; Kögler, G.; Ölfin, D. *Macromol. Chem., Macromol. Symp.* **1990**, *34*, 171.

(22) Out, G. J. J.; Turetskii, A. A.; Möller, M.; Ölfin, D. *Macromolecules* **1994**, *27*, 3310. Out, G. J. J.; Turetskii, A. A.; Möller, M. *Makromol. Chem., Rapid Commun.* **1995**, *16*, 107.

(23) Bunn, C. W. *Proc. R. Soc. London* **1942**, *A180*, 40. Nyburg, S. C. *Acta Crystallogr.* **1954**, *7*, 385.

(24) Natta, G.; Corradini, P. *Angew. Chem.* **1956**, *68*, 393. Natta, G.; Corradini, P. *Nuovo Cimento Suppl.* **1960**, *15*, 112.

(25) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.

(26) Desper, C. R.; Schneider, N. S. *Macromolecules* **1976**, *9*, 424.

(27) Chatani, Y.; Yatsuyanagi, K.; Komori, A.; Haruna. H.; Namichi, Y.; Suzuki, A.; Takahashi, A. *32 IUPAC Symposium on Macromolecules*, Kyoto, 1988.

(28) Corradi, E.; Farina, A.; Gallazzi, M. C.; Brückner, S.; Meille, S, V. *Polymer* **1999**, *40*, 4473. Corradi, E.; Porzio, W.; Gallazzi, M. C.; Allegra, G.; Meille, S. V. *Makromol. Chem., Rapid Commun.*, submitted for publication.

(29) Allegra, G. *J. Chem. Phys.* **1983**, *79*, 6382.

(30) The quadratic dependence $P \propto D^2$ may also be justified through a relatively direct argument. Let us consider a very thin, elementary wormlike chain with a persistence length Π. It will be conveniently regarded as a sequence of "bonds" with a length Λ. Assuming bond correlation to be limited to first neighbors, and the statistical distribution of the bending angle T between first-neighboring bonds to be Gaussian, i.e. $W(T) \propto \exp(-T^2/2\bar{\tau}^2)$ (elastic bending), the persistence length Π will be given by $2\Lambda/\bar{\tau}^2$. Let us now suppose that N elementary chains are bound together sidewise to produce a thicker wormlike chain. Obviously enough, the Boltzmann statistical weight will be the Nth power of $W(T)$ and we shall have $W_N(T) \propto \exp(-NT^2/2\bar{\tau}^2)$; since the new value of $\bar{\tau}^2$is $\bar{\tau}^2/N$, the persistence length P changes to $N\Pi = 2N\Lambda/\bar{\tau}^{2\cdot}$ In a real class 2 polymer chain the number N of elementary chains constrained to the same space conformation is proportional to the transverse sectional area, i.e., to D^2; as a consequence, we have $P \propto D^2$.

(31) Subbotin, A.; Saariaho, M.; Ikkala, O.; ten Brinke, G. *Macromolecules* **2000**, *33*, 3447.

(32) Tur, D. R.; Provotorova, N. P.; Vinogradova, S. V.; Bakhmutov, V. I.; Galakhov, M. V.; Zhukov, V. P.; Dubovik, I. I.; Tsvankin, D. Ja.; Papkov, V. S. *Makromol. Chem. Phys.* **1991**, *192*, 1905.

(33) Nakamura, T.; Masuko, T.; Kojima, M.; Magill, J. H. *Makromol. Chem. Phys.* **1999**, *200*, 2519.

(34) White, M. L.; Montague, R. A.; Matyjaszewski, K.; Pakula, T. *Polymer* **1995**, *36*, 3493.

(35) Wunderlich, B. *Thermal Analysis*; Academic Press: New York, 1990.

(36) Gaur, U.; Wunderlich, B. *J. Phys. Chem. Ref. Data* **1981**, *10*, 119. Grebowicz, J.; Aycock, W.; Wunderlich, B. *Polymer* **1986**, *27*, 575. Fintner, J.; Wegner, G. *Macromol. Chem.* **1981**, *182*, 1859.

(37) Yasuniwa, M.; Enoshita, R.; Takemura, T. *Jpn. J. Appl. Phys.* **1976**, *15*, 1421. Bassett, D. C. In *Developments in Crystalline Polymers*; Bassett, D. C., Ed.; Applied Science: London, 1982. Wunderlich, B.; Czornyj, G. *Macromolecules* **1977**, *10*, 906. Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 445.

(38) Lau, S. F.; Wesson, J. P.; Wunderlich, B. *Macromolecules* **1984**, *17*, 1102. Lau, S. F.; Suzyki, H.; Wunderlich, B. . *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 379.

(39) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2657. Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611. Schilling, F. C.; Bovey, F. A.; Lovinger, A. J.; Zeigler, J. M. In *Silicon-Based Polymer Science—a Comprehensive Resource*; Zeigler, J. M., Fearon Gordon, F. W., Eds.; *Adv. Chem. Ser.* **1990**, *224*. Patnaik, S. S.; Farmer, B. L. *Polymer* **1992**, *33*, 4443.

(40) Lovinger, A. J.; Davis, D. D.; Schilling, F. C.; Padden, F. J.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1991**, *24*, 132.

(41) Papkov, V. S.; Godovky, Yu. K.; Svistunov, V. S.; Litvinov, V. M.; Zhdanov, A. A. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3617. Beatty, C. L.; Karasz, F. E. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 971.

(42) Schneider, N. S.; Desper, C. R.; Singler, R. E. *J. Appl. Polym. Sci.* **1976**, *20*, 3087. Sun, D. C.; Magill, J. H. *Polymer* **1987**, *28*, 1243. Kojima, M.; Magill, J. H. *Polymer* **1989**, *30*, 579.

(43) Choy, I. C.; Magill, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2495. Masuko, T.; Simeone, R. L.; Magill, J. H.; Plazek, D. J. *Macromolecules* **1984**, *17*, 2857.

(44) Kojima, M.; Young, S. G.; Magill, J. H. *Polymer* **1992**, *33*, 4538. Young, S. G.; Kojima, M.; Magill, J. H.; Lin, F. T. *Polymer* **1992**, *33*, 3215.

(45) Meille, S. V.; Porzio, W.; Bolognesi, A.; Gleria, M. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 43.

(46) Kurata, M.; Tsunashima, Y. Viscosity-Molecular Weight Relationship and Unperturbed Dimensions of Linear Chains Molecules. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; J. Wiley & Sons: New York, 1989.

(47) Bunn, C. W. *Trans. Faraday Soc.* **1939**, *35*, 482. Swan, P. R. *J. Polym. Sci.* **1962**, *56*, 409. Kavesh, S.; Schultz, J. M. *J. Polym. Sci., Part A-2* **1970**, *8*, 243. Basset, D. C.; Block, S.; Piermarini, G. J. *J. Appl. Phys.* **1974**, *45*, 4146. Yamamoto, T.; Miyaji, H.; Asai, K. *Jpn. J. Appl. Phys.* **1977**, *16*, 1891.

(48) Chiang, R. *J. Phys. Chem.* **1965**, *69*, 1645. Chiang, R. *J. Phys. Chem.* **1966**, *70*, 2348. Kotera, A.; Matsuda, H.; Wada, A. *Rep. Prog. Polym. Phys. Jpn.* **1965**, *8*, 5. Nakajima, A.; Hamada, F.; Hayashi, S. *J. Polym. Sci., Part C* **1966**, *15*, 285.

(49) Natta, G.; Corradini, P. *Nuovo Cimento Suppl.* **1960**, *1*, 9. Iwayanagi, S.; Sakurai, I.; Sakurai, T.; Seto, T. *J. Macromol. Sci., Phys.* **1968**, *B2*, 163. Sueshiro, K.; Takayanagi, M. *J. Macromol. Sci., Phys.* **1970**, *B4*, 39. Rastogi, S.; Ungar, G. *Macromolecules* **1992**, *25*, 1445.

(50) Mark, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 6829.

(51) Sperati, C. A.; Starkweather, Jr., H. W. *Adv. Polym. Sci.* **1961**, *2*, 465. Bunn, C. W.; Howells, E. R. *Nature (London)* **1954**, *174*, 549. Clark, E. S.; Muus, L. T. *Z. Kristallogr.* **1962**, *117*, 119. Corradini, P.; Guerra, G. *Macromolecules* **1977**, *10*, 531. Yamamoto, T.; Hara, T. *Polymer* **1982**, *23*, 521.

(52) Chu, B.; Wu, C.; Zuo, J.*Macromolecules* **1987**, 20, *700.* Stockmayer, W. H. In *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*; Nagasawa, M., Ed.; Elsevier: Amsterdam, 1988.

(53) Wagner, H. L.; Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 195.

(54) Mark, J. E. *J. Am. Chem. Soc.* **1966**, *88*, 4354.

(55) Poddubbnyi, Ya, I.; Erenberg, Ye. G.; Yeremina, M. A. *Vysokomol. Soedin., Ser. A* **1968**, *10*, 1381.

(56) Tsvanin, D. Ya.; Papkov, V. S.; Zhukov, V. P.; Godovky, Yu. K.; Svistunov, V. S.; Zhdanov, A. A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1043. Grigoras, S.; Qian, C.; Crowder, C.; Harkness, B.; Mita, I. *Macromolecules* **1995**, *28*, 7370.

(57) Mark, J. E.; Ciu, D. S.; Su, T. K. *Polymer* **1978**, *19*, 407.

(58) Lee, C. L.; Emerson, F. A. *J. Polym. Sci., Part A-2* **1967**, *5*, 829.

(59) Kojima, M.; Magill, J. H. *Polymer* **1985**, *26*, 1971. Kojima, M.; Kluge, W.; Magill, J. H. *Macromolecules* **1984**, *17*, 1421.

(60) Meille, S. V.; Porzio, W.; Allegra, G.; Audisio, G.; Gleria, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 217. Magill, J. H.; Riekel, C. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 287. Hozumi, H.; Kohama, C.; Yonetake, K.; Masuko, T. *J. Mater. Sci. Lett.* **1991**, *10*, 1187.

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