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Bilayer Smectic Phases in Polymeric Liquid Crystals with Nonpolar Mesogens

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ABSTRACT: Recent experiments have noted the presence of partial bilayer smectic A (A_d) liquid-crystal phases in several types of side-chain polymeric liquid crystals, which do not contain highly polar groups in the mesogens. We show that the aromatic rigid core overlap between neighboring mesogens seems to be rather fixed among a wide range of materials, possibly determined by dipolar-induced dipolar forces.

Introduction

The appearance of bilayer phases for monomeric liquid crystals is innevitably associated with highly polar chemical groups such as the cyano radical.[1] These mesogens are thought to form dimers as a consequence of polar interactions.[2] To our knowledge, no other type of monomeric liquid crystal forms bilayer phases. The situation is different for polymeric liquid crystals. Although the incorporation of polar mesogens forms bilayer phases, as expected, some nonpolar mesogens are known to dimerize[3] and to form bilayers when they are present in side-chain polymeric liquid crystals.[4] It is generally acknowledged that, in these materials, this effect is initialized by the natural alteration of mesogens in an antiparallel ordering (Figure 1a). This ordering does not necessarily produce a bilayer phase, since a layer spacing, d, equal to a single mesogen length, $d = l$, is also possible in the case that the mesogens lie completely side by side (see Figure 1b). Since nonpolar monomeric liquid crystals almost invariably show monolayer ($d = l$) orderings (for at least the high-temperature phases), we expect that such ordering should be the rule in side-chain polymeric liquid crystals. Exceptions to this rule, which are surprisingly common (as we will show), point out the existence of forces that are manifested when the mesogens are constrained to the antiparallel orderings of Figure 1. Since such phases have many properties in common with *polar* monomeric liquid crystals,[3] we expect that some type of *polar* forces (acting in conjunction with the polymeric backbone) are important in causing these orderings in at least some polymeric liquid crystals.

Results and Discussion

The first thorough study of bilayer-forming polysiloxane polymeric liquid crystals was performed at Bordeaux.[4] Subsequent high-resolution X-ray studies[5] of one member of the polymer family studied at Bordeaux (viz., P4.1) showed that the bilayer phase is a true smectic A phase (commonly known as A_d, i.e., $l < d < 2l$) with phase-transition properties similar to those of monomeric liquid crystals but having surprisingly large bare correlation lengths (which is also found for some polar monomeric liquid crystals[5]). To understand these materials, we developed a molecular drawing computer program that accurately portrays bond lengths and conformations in these chemicals.[6] Comparison of our program results with X-ray crystallography tables on molecules similar to a typical liquid-crystal mesogen showed that our predictions for molecular lengths were accurate to better than 1 Å. In Figure 2b, we depict the molecular organization of P6.1 (whose mesogens are separately drawn in Figure 2a).[7] In Figure 2b, we have assumed that the distance between silicon atoms of neighboring polymers can be identified with the average layer spacing, d, as measured by ref 4 (i.e., ~36.8 Å). The flexible tails are drawn in the all-trans fully extended configuration. (This is consistent with observations that the flexible tail is "melted" at temperatures, $T \gg T_g$,[8] and it will tend to occupy a volume equal to that of a flexible tail in the all-trans fully extended conformation.) The configuration of the core is extrapolated from X-ray crystallography data of a chemically similar species, viz., deoxyanisoin.[9] If we suppose that the core overlap (the core being defined as the atoms including and beyond the oxygen that connects to the $(CH_2)_n$ flexible side chain) is constant for all Pn.1 compounds, then the interlayer spacing, d (at the same reduced temperature), as a function of n can be written as:

$$d\ (\text{Å}) = 36.8\ \text{Å} + (n - 6)2.5\ \text{Å} \qquad (1)$$

Figure 3 plots eq 1 with the experimentally measured layered spacings, d. Excellent agreement is obtained. This highly suggests that the core overlap is constant for all n measured.

It is possible to show that the constant core overlap is not a side effect of a particular polymeric backbone (which is highly unlikely, since the polymeric backbone and me-

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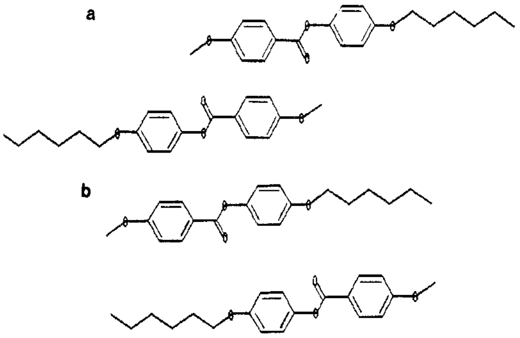

Figure 1. (a) Depiction of antiparallel ordering of mesogens such that the layer spacing is greater than the molecular length. (b) Antiparallel ordering of mesogens such that the layer spacing is equal to the molecular length.

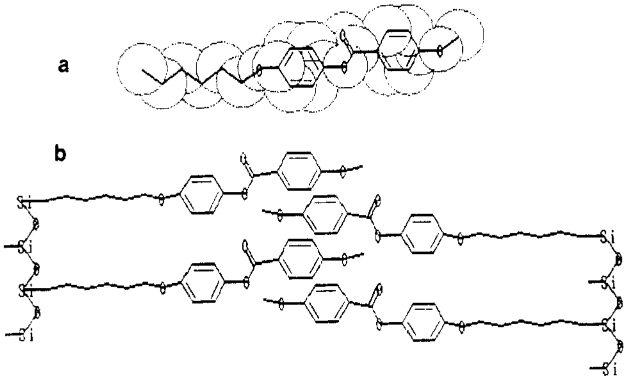

Figure 2. (a) Computer depiction of the 6.1 mesogen. The spheres correspond to the van der Waals radii of the atom. Hydrogens are not shown. The length of the molecule (excluding hydrogens) is calculated to be 20.1 Å. (b) Computer drawing of the molecular ordering in the bilayer smectic A_d phase of P6.1 polysiloxane. The mesogens have been rotated by 20 deg out of the plane in order to depict one possible conformation of the material. The distance between polysiloxane backbones is 36.8 Å.

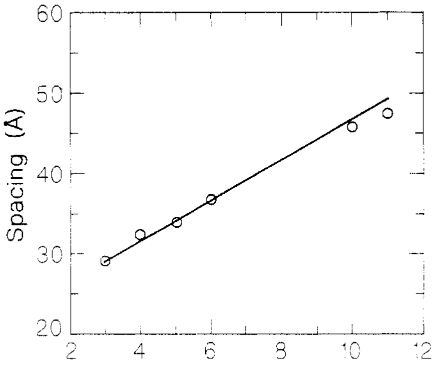

Figure 3. Graph of the measured layer spacings of Pn.1 as a function of n (the number of carbons in the flexible spacer).[4] The solid line corresponds to the layer spacings as determined by eq 1.

sogens are reasonably decoupled for $T > T_g$[5,10]). We had previously measured the X-ray scattering from the smectic A phase of a polyacrylate (PA$\bar{6}$.1) containing the mesogens ($\bar{6}$.1) depicted in Figure 4a. The average layer spacing in the smectic phase was measured to be $d = 24.2$ Å. Using this layer spacing and assuming an antiparallel arrangement of mesogens similar to that present in the Pn.1 compounds gives the result depicted in Figure 4b. The core overlap, d_{ij} [which is defined as the distance along the axis of a mesogen i, from the ketone $(C{=}O)_i$ of that mesogen to the benzene ring attached to the ketone of a neighboring mesogen j; see Figure 4b] is the same ($\simeq$4.5 ± 1.4 Å), within the accuracy of our program, to that found for Pn.1. This is true even though the chemical group between the two benzene rings in Pn.1 is O—C=O (Figure 2a), while it is (C=O)—O for PA$\bar{6}$.1 (Figure 4a). HMO calculations of the charge density for the 6.1 and $\bar{6}$.1 mesogens show that the dipolar moment of these molecules is localized in the ketone (C=O).[10] All together, this suggests that the distance, d_{ij}, between the dipole and the benzene ring (attached to the ketone of the neighboring mesogen) determines the constant core overlap for the Pn.1's and for PA$\bar{6}$.1. Furthermore, high-resolution X-ray measurements of C6 polysiloxane[11] (which contains the $\bar{6}$.1 mesogens) suggest that the core overlap is similar to $\bar{6}$.1-type overlaps as measured for PA$\bar{6}$.1 and quite dissimlar to 6.1(Pn.1)-type overlaps (although a truly reliable comparison can be achieved only by comparing our C6 results to the layer spacings obtained in the smectic C phase of a polymer containing the 6.1 mesogen). The size of d_{ij} can be estimated by a simple model of dipole-induced dipole forces (used to explain the smectic C phase in monomeric liquid crystals[12]). We can assume that the molecules rotate rapidly and unconstrained at our measurement temperatures.[12,13] Free rotations and vibrations of mainly transverse dipole moments, $\vec{p} = \mu\hat{p}$, average out dipole–dipole interactions between mesogens.[12] The next order perturbation to the charge distribution originates when the dipoles induce charges in the polarizable π-electrons associated with the aromatic rings of *neighboring* mesogens.[12] In this approximation, the dipole of molecule, i, induces charges in neighboring mesogens, j, which contain isotropic polarizable centers of polarizability α.[12] In the case of our molecules, the induced charge is concentrated within the nearest aromatic ring of the neighboring mesogen (this is a good assumption since most of the polarizable electrons are associated with the aromatic rings and little electron transfer occurs between the rings). If $\vec{s} = S\hat{s}$ is the distance vector between the dipole and induced dipole, then the induction energy, V_{in}, can be expressed by

$$V_{in} = -\alpha\mu^2/S^6\{1 - 3\langle(\hat{p}\cdot\hat{s})^2\rangle\} \qquad (2)$$

where $\langle\ \rangle$ means a time averaging over the rotation (and $-\alpha\mu^2/S^6 \sim kT$ for these mesogens at room te mperature). When it is assumed that, on the average, the dipoles are oriented 60 deg to the rotation axis of the molecule and a unitless parameter is defined, $x = d_{ij}/B$, where B is the average distance between mesogens; then

$$V_{in} = -\alpha\mu^2/8B^6[(2x^2 - 1)/(1 + x^2)^4] \qquad (3)$$

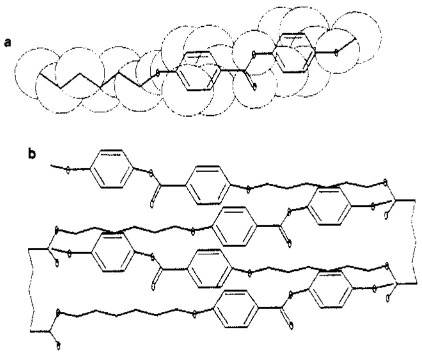

Figure 4. (a) Computer depiction of the $\bar{6}$.1 mesogen. The spheres correspond to the van der Waals radii of the atom. Hydrogens are not shown. The length of the molecule (excluding hydrogens) is calculated to be 20.0 Å. (b) Computer drawing of the molecular ordering in the smectic A phase of PA$\bar{6}$.1 polyacrylate. The mesogens have been rotated by 20 deg out of the plane in order to depict one possible conformation of the material. The distance between polysiloxane backbones is 24.2 Å.

$|V_{\mathrm{in}}|$ is a maximum for $x \approx 1$; i.e., $d_{ij} = B$. Measurements of the in-plane distances of C6 polysiloxane[14] showed that $B \sim 4.5$ Å (B will not vary much between mesogens of similar cross-section), giving a d_{ij} that is indeed very close to the predicted value (4.5 ± 1.4 Å) determined from Figures 2b and 4b (note that the molecules depicted in Figures 2b and 4b do not all lie in the plane of the paper and the distance B has a component vertical to the plane of the drawings).

Summary and Conclusions

We summarize our results as follows. X-ray measurements of the layer spacing, *d*, of P*n*.1 polysiloxanes and PA$\bar{6}$.1 show that the mesogens of these polymeric liquid crystals maintain a constant core overlap independent of the type of polymeric backbone or of the oxygen–ketone order within the mesogen. A simple estimate of dipolar-induced dipolar forces suggests that the constant core overlap is due to the action of these forces between mesogens. We stress again that, experimentally, dipolar-induced dipolar forces, also present in "nonpolar" monomeric liquid crystals, are not found to induce bilayer phases between monomeric liquid crystals. Rather, one experimentally finds these phases only if the nonpolar mesogens are ordered into an antiparallel arrangement within side-chain polymeric liquid crystals. *The role of the polymeric backbone in the production of bilayer phases in these materials is to bring about an antiparallel arrangement of the mesogens which facilitates orderings dependent on dipole-induced dipole forces between the molecules.* We note that adding long alkyl tails to the 6.1 or $\bar{6}$.1 mesogens might hamper free rotation of the dipoles and benzene groups, thereby changing the core overlap (as seems to be the case[4]).

We conclude with a suggestion for further experimentation. Namely, the efficacy of dipolar-induced dipolar forces in producing preferred orientation in side-chain liquid crystals could be tested by replacing the ketones in the P6.1 and P$\bar{6}$.1 mesogens with a chemical group of approximately the same length that (1) gives the mesogens a zero net dipole moment (2) without totally destabilizing the smectic A mesophase.

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