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# A direct correlation function for mesomorphic polymers and its application to the ‘smectic’ phase of isotactic polypropylene

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Dedicated to the Professor Roger S. Porter who made significant contributions in exploiting disorder in polymers to obtain highly ordered materials.

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## Abstract

A general model to calculate the structure of a smectic to nematic-like order in polymer systems is proposed. The model is limited to well-aligned molecules with respect to each other. It is especially suited for systems where the packing between neighboring chains is described by liquid-like disorder with axial registration in the chain-axis direction. In such a case the diffraction pattern from the oriented structure exhibits broad liquid-like reflections on the equatorial but sharper reflections on the layer lines. An Ornstein-Zernike approach is adopted to calculate the inter-chain packing and inter-chain registration, where the direct correlation function of packing and registration are decoupled. The model is applied to quantify the structure of the smectic phase of isotactic polypropylene (i-PP).

## Keywords

Mesomorphic polymers; Smectic phase; Isotactic polypropylene

## 1. Introduction

When isotactic polypropylene (i-PP) is rapidly quenched from its melt to 0°C, a disordered structure is formed. Wide angle X-ray scattering (WAXS) studies indicate that the disordered structure is a well-defined phase with an extent of order intermediate between the crystalline and

amorphous phases [1]. In this phase the chains have undergone a conformational ordering from random coil to 3/1 helix, but the packing of helices are not as well formed as in the (stable) monoclinic crystalline phase (called the  $\alpha$ -form). This results from the fact that the conformational change can occur rapidly, but the (highly) ordered lateral packing requires strict correlation of handedness and direction of the adjacent helices. This may require long range rearrangement that slows down the inter-chain packing process. Annealing studies on the disordered phase indicate that transformation to the  $\alpha$ -form is in two steps: first at annealing below 80°C the helices translate past each other to achieve better registration; then at annealing temperatures in the range 80-150°C, the helices arrange in the lateral direction with further improvement in registration [2].

We note in passing, that the symmetry requirements of the helix handedness and direction further differentiates the ordering hierarchy of the crystal structure into less ordered  $\alpha 1$ -form and more ordered  $\alpha 2$ -form [3]. In the former only the handedness symmetry is achieved while in the latter structure (formed by long time annealing) the chains pack to maintain both the correct handedness and directional symmetries. This transformation of  $\alpha 1$ -form to  $\alpha 2$ -form is slow, corroborating the suggestion of kinetics as the primary reason for the hierarchy of disorder.

Previous studies indicate that the disordered phase is stable below 70°C and transforms to  $\alpha$ -form at higher temperatures [4]. However, more recent careful calorimetry and gas sorption studies on quenched and annealed samples indicate that the disordered phase can be stable up to 155°C [5]. The disordered phase can also be formed when i-PP is deformed in the solid state by uniaxial stretching [6]. The deformation induced disordered phase forms in a two step process: first the helices are “unraveled” or pulled-out from the crystal lamellae (in  $\alpha$ -form); next these helices “quench” at the draw temperature to form the disordered phase [7]. At temperature during deformation below 70°C the disordered phase is stable and is observed ex-situ by WAXS [7]. At temperatures above 70°C the disordered phase forms but “anneals” back to the  $\alpha$ -form, and thus is inferred indirectly by in-situ mechanical measurements [7,8]. This transitory transformation of the  $\alpha$ -form to the disordered phase reverting back to the  $\alpha$ -form is also observed for uniaxial deformation [9]. The deformation induced crystal to disordered phase transformation is also observed for the hexagonal form ( $\beta$ -form) [10].

Natta and Coradini [1], who first observed this disordered phase, termed it the “smectic phase” reflecting the idea that this phase is characterized by parallel helices having disorder in the lateral packing, yet maintaining some degree of positional correlation along the chain axis between adjacent helices.

Previous studies tried to elucidate the structure of the smectic phase in terms of “packing-disorder” in the stable crystalline structure. A qualitative model based on WAXS data from deformed smectic phase was given in terms of paracrystallinity, where systematic (and mutually exclusive) cumulative distortion in the adjacent helix registration with respect to methyl-group position and lateral helix packing was proposed [11]. A quantitative model considering the smectic phase as a mixture of small bundles of the hexagonal ( $\beta$ -) and monoclinic ( $\alpha$ -) forms, was proposed [12]. By optimizing the size and amount of the two crystalline forms, good agreement with experimental data was obtained [12]. However, the reason for a fixed relative fraction of the two crystal forms is not clear.

The purpose of this study is two fold. (i) We show that a reasonable agreement with experimental data can be obtained with a model having liquid-like lateral packing of parallel helices with a high degree of registry in the helical-axis direction between neighboring chains. Thus we propose a model of a “quenched liquid crystalline” phase rather than a “disordered crystalline phase.” The lateral packing of the helices is dependent only on the density of helices that is determined by the density of the phase. The degree of registration between the helices, is the salient feature of the disordered phase. (ii) In order to obtain a quantitative evaluation of both features: the lateral liquid-like packing and axial registry between neighboring helices, we present a new correlation function which is appropriate for polymeric systems which exhibit this kind of mesoscopic order. Such a structural model has not been addressed before and it may be applicable to other systems such as main-chain thermotropic polymers or lyotropic solutions of polymers with interacting side groups. We aim to show that the disordered phase of i-PP indeed is correctly described as a smectic phase, as first suggested by Natta and Corradini in 1960 [1].

## 2. Experimental

Pellets of i-PP with weight average molecular of  $2.9 \times 10^5$  Da and polydispersity index of 5 was supplied by Philips Co. The smectic phase sample was prepared by molding a 1 mm thick film at 220°C followed by a fast quench in ice/water slurry. Some samples were uniaxially stretched by 300% at a constant rate of 0.1 cm/min. The annealing was performed at 120°C in 0.1 mmHg pressure for 100 min.

The wide-angle X-ray diffraction characterization was performed on the stretched and undeformed sample using a Statton Camera and a Siemen's D-500 diffractometer. In both apparatus, the X-ray radiation was  $\text{CuK}_\alpha$  with a wave length of  $\lambda = 0.1542$  nm.

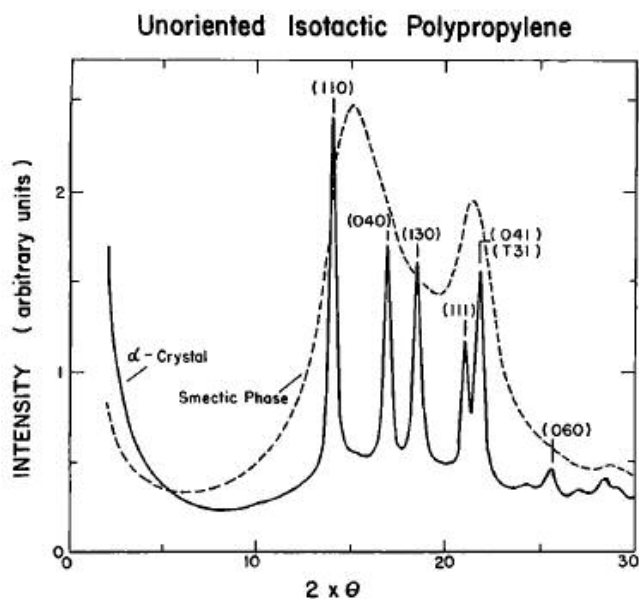


Fig. 1

### 3. Results

Fig. 1 shows the X-ray diffraction curve from an unoriented (*i.e.* undeformed) i-PP sample. The intensity is in arbitrary units and the scattering angle defined as the angle between the source-sample-detector is  $2\theta$ . Curve (a) is the diffraction pattern from the quenched sample and curve (b) is the same sample after annealing. It is apparent from the data that the as-quenched sample is the smectic phase and upon annealing this phase transforms to the stable  $\alpha$ -form.

Fig. 2(a) is a diffraction data from a deformed quenched sample and Fig. 2(b) shows the diffraction pattern from the same sample after annealing. The stretch axis is vertical. The sharp spots indicate that the chains are highly oriented. The broad diffraction spots in Fig. 2(a) compared to the sharper diffraction spots in Fig. 2(b) indicate that the smectic phase is stable during deformation at  $25^\circ\text{C}$ . There are two sets of broad peaks: The two equatorial reflections along the horizontal axis at  $2\theta \sim 14.8^\circ$  correspond to the first broad peak in Fig. 1, curve (a). The four off-meridional peaks at  $2\theta \sim 21.2^\circ$  on the first layer-line correspond to the second broad peak in Fig. 1, curve (a). The third weak peak at  $2\theta \sim 28.8^\circ$  in Fig. 1, curve (a) is not seen in Fig. 2(a) due to quality of the print-production, are also four off-meridional diffraction spots on the second layer-line. The equatorial peak corresponds to inter-chain packing and the off-meridional layer-line peaks are related to the inter-chain registration.

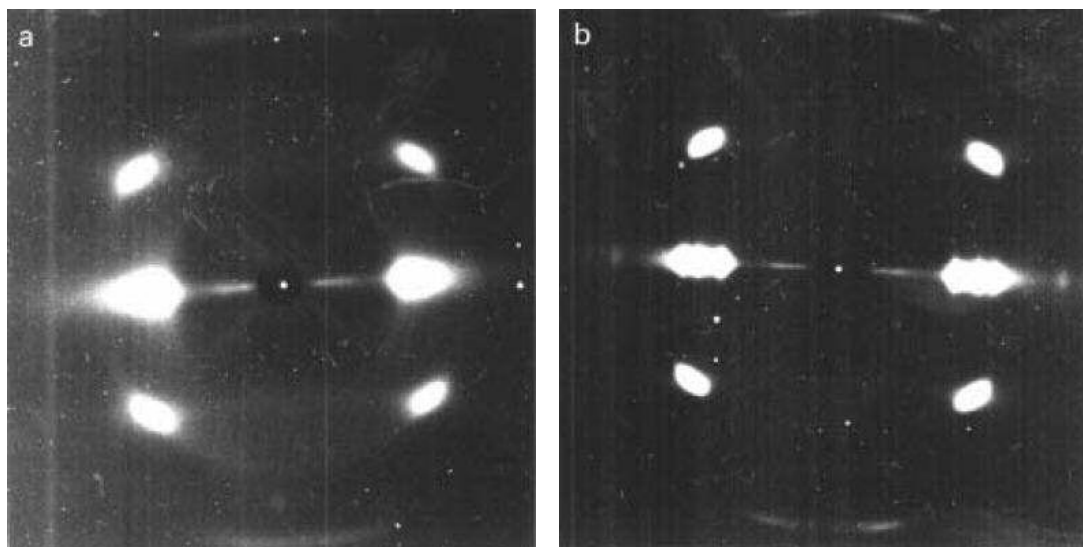


Fig.2

Comparison, of Fig. 2(a) and (b) shows that the extent of inter-chain packing and inter-chain registration is far inferior in the smectic phase when compared with the crystalline state. We note that the high degree of orientation observed in Fig. 2(b), which is achieved by the high draw ratio of 300%, is significantly higher than that which can be obtained by stretching a film of the  $\alpha$ -form crystal to the same draw ratio. The lower activation to flow and better orientability of the smectic phase compared to the  $\alpha$ -form has been demonstrated, quantified and exploited in solid-

state-deformation process [7]. The ease of flow in the smectic phase further supports its name implying that the disordered phase has a liquid-crystalline like order.

#### 4. Model: the smectic phase

We assume the helices in the smectic phase are parallel to each other as in the crystal. Although the cross-section of the helix is triangular [1], we assume that the helices have random rotation about the helical axis, *i.e.* there are no rotational correlations between neighboring helices. This implies that the effective cross-section of the helix is circular. Taking the radius of this effective circular cross-section as the distance between the methyl carbon and the helix axis. We model the lateral correlation between the helices as a two-dimensional liquid of disks.

Assuming that the long-range van der Waals interaction is weak, the pair-potential is assumed to be a “hard-disk” like interaction. Thus the effective model parameters for the lateral packing are the diameter of the disks and their area fraction. The diameter is fixed from the 3/1 helical chain conformation. The area fraction is bound by the total density of the smectic phase that should be between the amorphous and  $\alpha$ -form crystal density. Thus from the inter-disk correlation function for a hard-disk liquid with appropriate area density and disk diameter, the equatorial scattering corresponding to inter-chain packing can be calculated.

The inter-chain registration, *i.e.*  $c$ -axis correlation of the helices is modeled as a paracrystalline disordered state. In the crystalline state neighboring helices are in perfect registry due to interactions between the pendant methyl groups. In our model, the helices are allowed to rotate freely around their axis with respect to their neighbor, the helices are effectively cylinders with three equally spaced “stripes” per pitch length that correspond to the locus of the methyl groups. To account for registration disorder, the registry between neighboring helices is assumed to have a Gaussian distribution about the perfectly aligned state. The breadth of the Gaussian distribution can vary: from zero to infinity, corresponding to the range of helical registration ranging between perfect to random alignment. The width of this Gaussian distribution is the only fitting parameter in the proposed model.

The total scattered intensity from the structure is obtained using the relationship provided for a dense packing of identical objects [13]. We consider these objects to be a cylindrically averaged polypropylene helix, which is averaged by rotating around the helical axis. This follows our model for the disordered phase in which the helices assume random uncorrelated rotation angles about this axis. Thus the scattering pattern is given by a product of the averaged form factor of the helix and an inter-helix interference factor:

$$I(\mathbf{k}) \propto \langle FF^* \rangle \psi(\mathbf{k}) [1 + \rho H(\mathbf{k})] \quad (1)$$

where  $(FF^*)\psi$  is molecular transform of the helix averaged over all angles of rotation about the helix axis,  $\mathbf{k}$  is the scattering vector of magnitude  $(2\lambda)\sin \theta$  and  $\rho$  is the number-density of helices.  $H(\mathbf{k})$  is the Fourier transform of the total correlation function  $h(r) = g(r) - 1$ , where  $g(r)$  is the pair-correlation function which accounts for both the liquid-like lateral packing of the helices as well as their axial registry .

Since the conformation is a 3/1 helix, the Cochran-Crickdash;Vand formula [14] is applied and integrated over  $\psi$  to calculate the averaged molecular transform,  $F$ . Multiplying with its complex conjugate  $F^*$  and integrating over  $\psi$ ,  $(FF^*)_\psi$  is given by

$$\begin{aligned} & \langle FF^*(R, \frac{l}{c}) \rangle_\psi \\ &= \sum_n \left\{ \sum_j f_j(\mathbf{k}) J_n(2\pi R r_j) \cos\left(-n\psi_j + \frac{2\pi l z_j}{c}\right) \right\}^2 \\ &+ \left\{ \sum_j f_j(\mathbf{k}) J_n(2\pi R r_j) \sin\left(-n\psi_j + \frac{2\pi l z_j}{c}\right) \right\}^2 \end{aligned} \quad (2)$$

where,  $(r_j, z_j, \psi_j)$  are cylindrical coordinates of the atoms and  $f_j(\mathbf{k})$  is the atomic scattering factor of the  $j$ th atom;  $c$  is pitch of the helix, and  $l$  is the order of the layer line ( $l = 0$  being the equatorial layer).  $J_n$  is the Bessel function of order  $n$ .  $R$  is the distance in the reciprocal space from the meridian (*i.e.* helix axis). Since the atomic coordinates of 3/1 helix and atomic structure factors are known [15], the molecular structure factor  $(FF^*)_\psi$  can be computed. In this study, we calculate only the 0th, 1st and 2nd layer lines.

We express the total correlation function,  $h(\mathbf{r})$  in terms of the direct correlation function,  $c(\mathbf{r})$ , defined by Ornstein and Zernike as: [16]

$$c(\mathbf{r}) = h(\mathbf{r}) - \rho \int_0^r h(\mathbf{r}') c(\mathbf{r} + \mathbf{r}') d\mathbf{r}' \quad (3)$$

which by Fourier Transformation yields

$$1 + \rho H(\mathbf{k}) = \frac{1}{1 - \rho C(\mathbf{k})} \quad (4)$$

A major objective of this paper is to provide a precise and useful formulation for the correlation function of oriented polymers having liquid-like lateral packing and a significant degree of axial registry. We chose to approach this using the direct correlation function, which provides for the correlation between two independent units without the effect of all other units in the system. We postulate that in k-space the direct correlation function for such a system can be given as a product of a two-dimensional correlation function for the lateral packing of chains and



a one-dimensional correlation function for the axial registry between the chains in the direction of the chain or helical axis. We thus propose that:

$$C(\mathbf{k}) = C_R(R)C_Z(Z) \quad (5)$$

where  $R$  and  $Z$  are cylindrical coordinates in the reciprocal space, such that  $\|\mathbf{k}\| = \mathbf{k} = (R^2 + Z^2)^{0.5}$ . The assumption implies that there is cylindrical symmetry and the inter-chain correlation and inter-chain registration are uncorrelated. Both the assumptions are consistent with the model discussed above.

For the correlation function of the lateral packing of helices  $C(R)$  we use the direct correlation function of a hard disk fluid,  $C_{HD}(R)$ , which we calculate from expressions for the pair correlation function of a hard-disk fluid derived by Chae *et al.*[17], using the Percus Yevick approximation by a procedure which is described elsewhere, [18].  $C_{HD}$  is calculated from the results of Chae *et al.*[17] as a function of the dimensionless area density  $nD_H^2$ , and radial distance  $R/D_H$ , where  $n$  is the number of density of disks per unit area and  $D_H$  is the effective diameter of the 3/1 helix, which according to the model discussed above is twice the distance between the methyl carbon and the helix axis. The pair correlation functions derived by Chae *et al.* [17] were shown to fit well the results of Monte Carlo simulations, as we have also verified independently. The inter-chain registration is calculated by assuming that the correlation has a Gaussian probability distribution about a mean position, which is taken to be perfect alignment

$$C_z(Z) = \exp(-2\pi^2\Delta_C^2Z^2) \quad (6)$$

where,  $\Delta_C$  is the width of the Gaussian distribution such that  $\Delta_C = 0$  implies that  $C_Z(Z) = 1$  : full correlation or perfect registration (as in a crystal).  $\Delta_C = \infty$  : implies that  $C_Z(Z) = 0$  : no correlation or random registration (as in a nematic liquid crystal).

Thus, the direct correlation function is given by

$$C(\mathbf{k}) = C_R(R)C_Z(Z) = C_{HD}(R; D_H)\exp[-2\pi^2\Delta_C^2Z^2] \quad (7)$$

Combining Eqs. (I), (2), (6) and (7), and substituting for  $Z = l/c$  where  $l$  is the order of the layer line (*i.e.*  $l = 0, 1, 2, \dots$ ) and  $c$  is the lattice parameter along the  $c$ -axis (*i.e.* the pitch of the 3/1 helix)

$$I = \langle FF^*(R, \frac{l}{c}) \rangle \frac{1}{1 - qC_{HD}(R; D_H)\exp[-2\pi^2\Delta_C^2(l/c)^2]} \quad (8)$$

In this study we calculate the intensity distribution for equatorial ( $l = 0$ ) and the first and second layer lines ( $l = 1$  and  $2$ , respectively). The parameters of the model are  $D_H$ ,  $n$  and  $\Delta_C$ . The first two parameters have rather strict values, but the latter parameter – the degree of axial registry – can be varied from zero to infinity.  $D_H$  is taken from the  $\alpha$ -helix structure of i-PP to be  $D_H = 0.52$

nm, twice the radial distance between the pendant methyl carbon and the helix axis. The volume fraction of helices ( $v_f = 0.545$ ) is evaluated from the mass density of the smectic phase, estimated by small angle X-ray scattering to be  $0.91 \text{ gr/cm}^3$  [19].\* Using the dimensions and structure of the 3/1 helix, the volume fraction of helices can be converted to an area density as:  $n = 4v_f/(\pi D_H^2)$ . The only parameter which is allowed to vary (from zero to infinity) is  $\Delta_C$ , which defines the extent of axial registry between parallel chains.

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\* The scattering invariant obtained for small angle X-ray scattering from a quenched i-PP (with smectic and amorphous phase) was measured to be  $7.5 \text{ g}^2/\text{cm}^6$ . Using a two phase model with amorphous density of  $0.85 \text{ g/cm}^3$  the density of the smectic phase was estimated to be  $0.91 \text{ g/cm}^3$ . The percent crystallinity was estimated from the shape of the one dimensional correlation function and the over all density of the sample.

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## 5. Results and discussion

Fig. 3 shows a simulated scattering curve from an unoriented smectic phase by adding (*i.e.* superimposing) the intensity distribution for layer lines,  $I_0$ ,  $I_1$ ,  $I_2$  corresponding to  $l = 0$ , 1, and 2, respectively. Based on experimental observations, the scattering from higher order layer lines is significantly weak and therefore ignored in the calculation. Thus

$$I = I_0 + 2 I_1 + 2 I_2 \quad (9)$$

The factor of 2 for  $I_1$  and  $I_2$  occurs because the scattering pattern is symmetric about the  $Z = 0$  plane, where the  $Z$ -axis is parallel to the helix axis. The calculated curve qualitatively compares with the experimental scattering curve for the smectic plane. The comparison is qualitative, since the scattering from the unoriented phase (which would invoke more fitting parameters such as percent crystallinity) is not included. An observation to note from the qualitative comparison is that the  $\Delta_C/c$  is certainly below 0.3. A small  $\Delta_C/c$ , specifically below  $c/3$  indicates that there is good registration between the adjacent helices thus the phase is indeed “smectic-like.”

A more quantitative comparison is possible by comparing the calculations with observed layer lines. Here we use the experimental data corrected for amorphous scattering obtained by Corradini *et al.* [12]. Fig. 4 shows the comparison with  $l = 0$  and 1 layer lines. The equatorial and first layer line compares well with the experimental data for  $\Delta_C/c < 0.1$ . The higher order peaks in  $l = 0$  and 1 are stronger for the calculated curve than experimentally measured. This may be due to the thermal fluctuation (*i.e.* the Debye factor) not included in the calculation, that would broaden the peaks and diminish the higher order reflections.

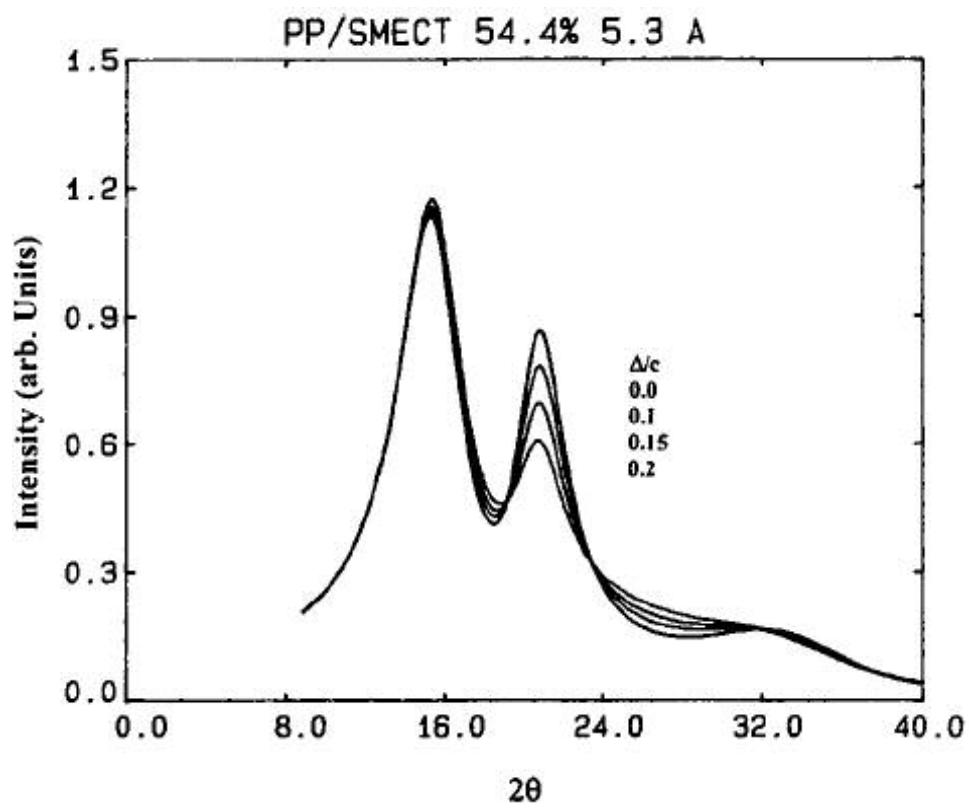


Fig. 3

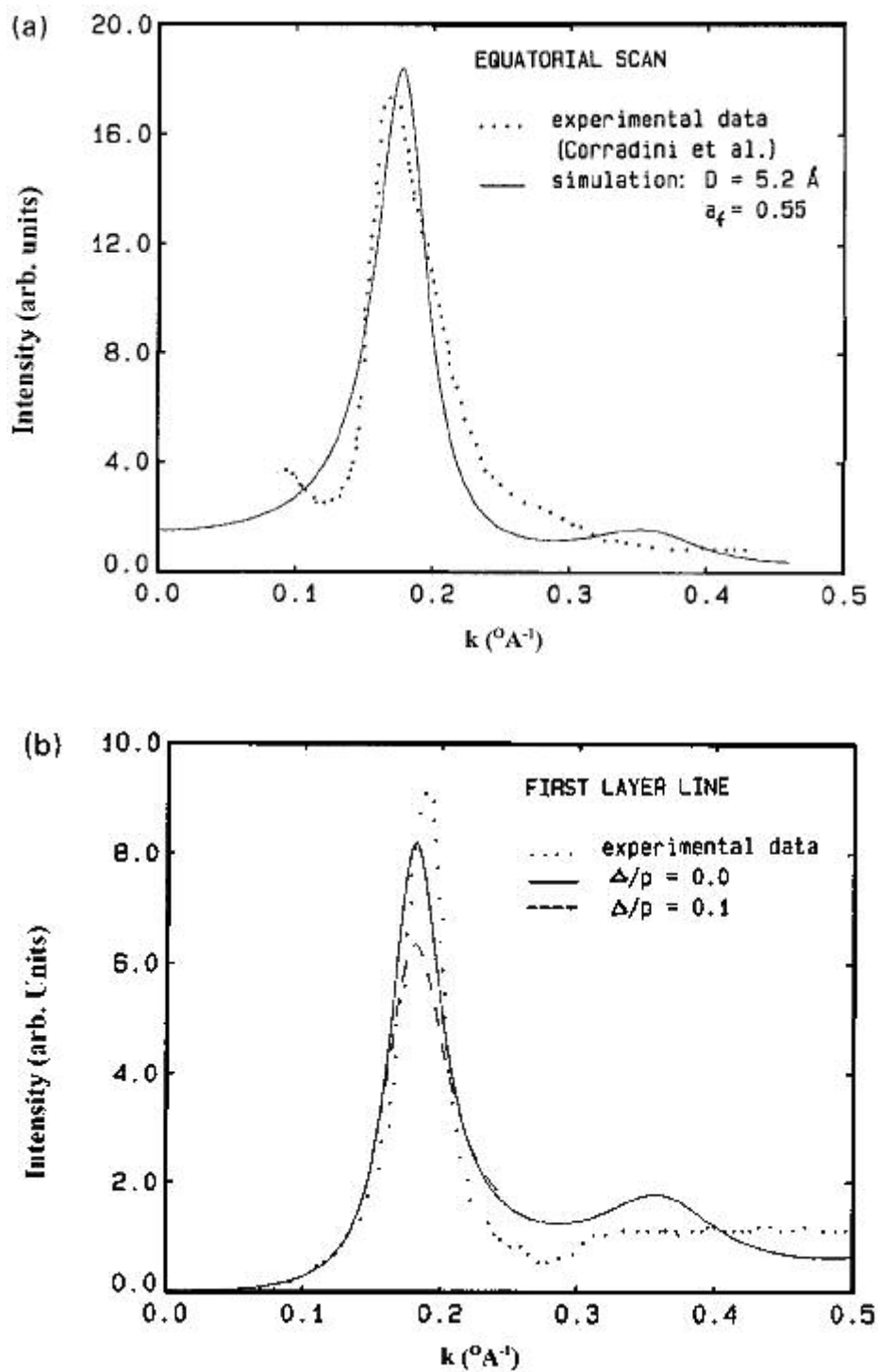


Fig. 4

The model can be further improved in several ways. (i) The inter-chain packing can be modeled by considering the actual cross-section of the polymer chain. For i-PP it will be triangular. (ii) The hard-disk potential can be replaced by a pseudo-potential that considers longer range of interaction. (iii) The inter-chain registration can be coupled to the lateral order by say making  $\Delta_C$  dependent on the nearest neighbor distance, *i.e.* the first maxima of the inter-chain correlation function. These refinements will invoke more fitting parameters and make the calculation more complex leading to a better agreement with experimental observation, yet preserve the basic intuitive model of calculating the structure of the mesomorphic phase. Other than i-PP, this model may be used to understand structures of disordered phases in other polymer such as, polyallene, poly[3,3-bis(chloromethyl)-oxycyclobutane] and poly( $\beta$ -methyl- $\beta$ -propiolactone) [20].

## 6. Conclusions

A physically intuitive model to describe the smectic phase in terms of “liquid crystalline model” agrees reasonably well with the experimental observation. The fit of the proposed model with experimental observations is certainly not as good as the structure proposed by Coradini *et al.* [12], which requires more than two fitting parameters. However, we present a simple model for a specific kind of disordered phase in long chain molecules, in which the chains are packed parallel to each other such that the correlation between neighboring chains is liquid-like in the lateral direction yet shows a significant degree of axial registration in the chain-axis direction. Such a structure may indeed be described as a “smectic” phase.

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## References

- [1] Natta G, Corradini P. *Nuovo Cimento. Suppl* 1960;15:40–51.
- [2] Ferrero A, Ferracini E, Mazzavillani A, Malta V. *J Macromol Sci Phys* 2000;B39:109–29.
- [3] Guerra G, Petraccone V, Corradini P, De Rosa C, Napolitano R, Pirozzi B. *J Polym Sci, Polym Phys* 1984;22:1029.
- [4] Zannetti R, Celotti G, Fichera A, Francesconi R. *Makromol Chem* 1969;128:137.
- [5] Natael R, Russo R, Vittoria V. *Material J. Science* 1993;27:4350.
- [6] Sobue H, Tabata Y. *J Polym Sci* 1959;39:427.
- [7] Saraf RF, Porter RS. *J Polym Engng Sci* 1988;28:842–51.
- [8] Saraf RF, Porter RS. *J Rheol* 1987;31:59–94.
- [9] Seguela R, Staniek E, Escaig E, Fillon E. *J Appl Polym Sci* 1999;71:1873 –85.

- [10] Chu F, Yamaoka T, Kimura Y. *Polymer* 1995;36:2523–30.
- [11] Saraf RF, Porter RS. *Mol Cryst Liq Cryst Lett* 1985;2:85–93.
- [12] Corradini P, Petraccone V, De Rosa C, Guerra G. *Macromolecules* 1986;19:2699.
- [13] Guinier A, Fournet G. *Small angle X-ray scattering*. New York: Wiley, 1955.
- [14] Original derivation was by Cochran W, Crick FHC, Vand V. *Acta Crystallogr* 1952;5:581, but the derivation followed is in Tadokoro H. *Structure of crystalline polymers*. New York.: Wiley, 1979, p. 431, Appendix D.
- [15] Menick Z. *J Macromol Sci, Phys* 1972;B6:101–15.
- [16] Ornstein LS, Zemike F. *Proc. Akad. Sci. Amsterdam*, 1914;17:793. See also: McQuarrie DA. *Statistical Mechanics*. New York: Harper and Row, 1976, chap. 13.
- [17] Chae DG, Ree RH, Ree T. *J Chem Phys* 1961;50:1581.
- [18] Cohen Y, Thomas EL. *J Polym Sci, Part B: Polym Phys* 1987;25:1607.
- [19] Private communication with Dr. C. Vonk, 1985.
- [20] Saraf RF, Porter RS. *J Polym Sci, Part B: Polym Phys* 1988;26:1049–57.