mesophase. From *Figure 1*, it is evident that the experimental scatter in n' was of the order of 0.002, about 35 times smaller than $n'_0 - n'_e$ values typical of liquid crystalline phases, e.g. $|n'_0 - n'_e| \simeq 0.07$ reported for cellulose[4]. Any orientation for $\vec{n}$ close to the refracting surface therefore does not explain the change of $\frac{dn'}{dc}$ at c_1^{**} in *Figure 1*.

Another possibility is that the glass prism induced a cholesteric–nematic phase transition near its surface and that $\vec{n}$ was orientated normally to the surface, i.e. a homeotropic state. This kind of transition, without the aid of an externally applied field, has never been reported and we regard it as unlikely that weak surface forces could induce such a phase change.

The explanation which we favour is as follows. The solutions became turbid above c_1^{**}. This is usually ascribed to spontaneous fluctuation of the alignment $\vec{n}$, the alignment having a mean coherence length ρ[5]. The theory of refraction in scattering media shows that the effect of scattering by discrete objects can decrease the refractive index of the medium, depending on the size of the scattering object[6]. E.g., it can be shown[6] that $\frac{dn'}{dc}$ of a dispersion of spheres decreases rapidly with increasing sphere diameter, for diameters exceeding about 1 μm. Thus, the fluctuations of $\vec{n}$ in regions of mean size ρ probably accounts for the difference in $\frac{dn'}{dc}$ below and above c_1^{**}.

It is of interest to consider the Flory[7] and Pincus–De Gennes[8] theories of lyotropic liquid crystal formation in the light of our results and conclusions. The Flory theory predicts the ordering of semiflexible or rigid macromolecules as their concentration increases. The ordering begins at a concentration c_1^{**} and continues until the fully ordered phase is reached at c_2^{**}. The interval $c_1^{**} < c < c_2^{**}$ is biphasic, i.e. a coexistence of isotropic and liquid crystalline phases is predicted. The Pincus–De Gennes theory predicts an isotropic liquid crystalline transition at c_1^{**} with no biphasic interval. On the basis of refraction theory as discussed above for scattering media, $\frac{dn'}{dc}$ would not be constant in the biphasic region as the regions of the liquid crystalline phase increased in size. The constant value of $\frac{dn'}{dc}$ observed above 0.34 g ml^{-1} could be explained on the Flory theory by assuming that c_1^*–c_2^* was too small to detect. A more likely explanation is that the formation of liquid crystals in the CTA/TFA system is described by the Pincus De Gennes theory. This theory explains qualitatively our results with no further assumption than the fluctuations of alignment $\vec{n}$ over regions similar to, or larger in size than the optical wavelength. Considerable independent experimental evidence exists for these fluctuations in the liquid crystal phase of CTA/TFA[9].

Note added in proof

We have noted the paper of Tseng *et al.* (Macromolecules, 1980, **14**, 715). Using acetoxypropyl cellulose, these workers have measured the refractive index below and above the critical concentration. Although their data also shows a change in the refractive index increment at the critical concentration, it is smaller than we found and not discussed by the authors. Above the critical concentration Tseng *et al.* found a spontaneous birefringence which we did not observe.

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Microheterogeneous structure of liquid crystalline polymers

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Liquid crystalline polymers with phenyl benzoate side groups with various lengths of flexible chain-end were synthesized. Small-angle X-ray scattering studies were carried out. Layer structures in the liquid crystalline polymers were characterized and the microheterogeneous structure was investigated. It was concluded that the microstructure is dependent on the length of the flexible mesogenic chain-end.

Keywords Structure; polymers; liquid crystalline; microstructure; chain-end; mesogenic; small-angle X-ray scattering

Liquid crystalline (LC) polymers exhibit both the properties of liquid crystals and the traditional advantages of polymeric materials, while behaving as a new class of macromolecular systems, being models of 'ordered' amorphous polymers or 'disordered' crystalline polymers.

Studies of short-range order in LC polymers resulted in certain relationships governing structure formation[1]. Data on the microphase structure of the polymers are few, even though it is this structure which determines the LC properties.

Electron-microscope studies on cholesterol-containing

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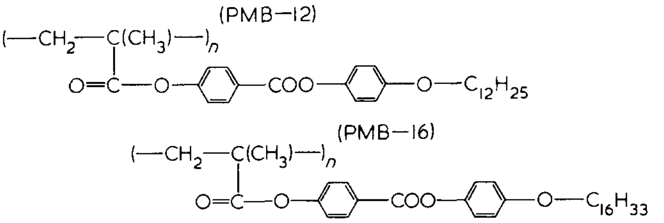
polymers detected a mosaic-type microstructure with sperical domains several μm in diameter[1,2]. Small-angle X-ray studies led to the discovery of lower limits for the radii of gyration of the heterogeneous regions[3] equal to 5–7 nm. Analysis of diffraction maxima broadening for polymers with phenylbenzoate side groups showed LC regions of about 200 nm[4]. The sizes of LC ordered regions in polymers with various lengths of spacer groups are 10–20 nm[5].

We have studied the microphase structure of some LC polymers using correlation functions obtained by Fourier-transformation of the small-angle X-ray scattering and transmission electron microscopy (*TEM*) spectra.

Results and Discussion

LC polymers with phenyl benzoate side groups, with various lengths of flexible chain-end were chosen. The monomer unit structure was:



These polymers were synthesized as described earlier[6].

Polymer films 0.5 mm thick were obtained on 10 μm lavsan films from solutions in benzene. After solvent evaporation films were physically aged at temperatures 5°–10°C below the glass transition (413K and 433K for PMB-12 and PMB-16, respectively) under vacuum for 5–7 h. Polymer samples for the electron microscope were obtained as thin films on water. These were annealed, electrodeless-gas-discharge-plasma-etched, and a thin carbon layer tangentially evaporated onto them.

Small-angle studies were carried out in a Kratky diffractometer, using a conventional procedure[7]. A standard Lupolen sample was used to reduce scattering data to the absolute intensity units. The instrument background and lavsan film scattering were subtracted from the results. Full treatment of small-angle data and correlation function calculation were carried out using Vonk's procedure[8,9]. The electron microscope was a JEM-100C with an accelerating voltage of 80 kV.

Figure 1 shows small-angle X-ray scattering curves reduced to the absolute units for both polymers.

The curves exhibit strong zero-angle scatter and well-defined maxima in the range of $2\theta = 2°$. Such diffraction effects occurring at essentially different angles may be considered independently.

A small-angle maximum in the scattering curve reflects the existence of layer packing of mesogenic groups characteristic of smectic liquid crystals[2,4]. The powerful increase in scattering intensity when approaching the primary beam, can be attributed to non-homogeneous regions randomly distributed in the bulk polymer[11]. Diffraction effects that result from micro-region distribution and layer packing can be differentiated in the scattering curves using these considerations (portions I and II in *Figure 1*).

Layer structures in LC polymers are characterized by one-dimensional order normal to the layers[4,10]. To analyse order of this type, the one-dimensional

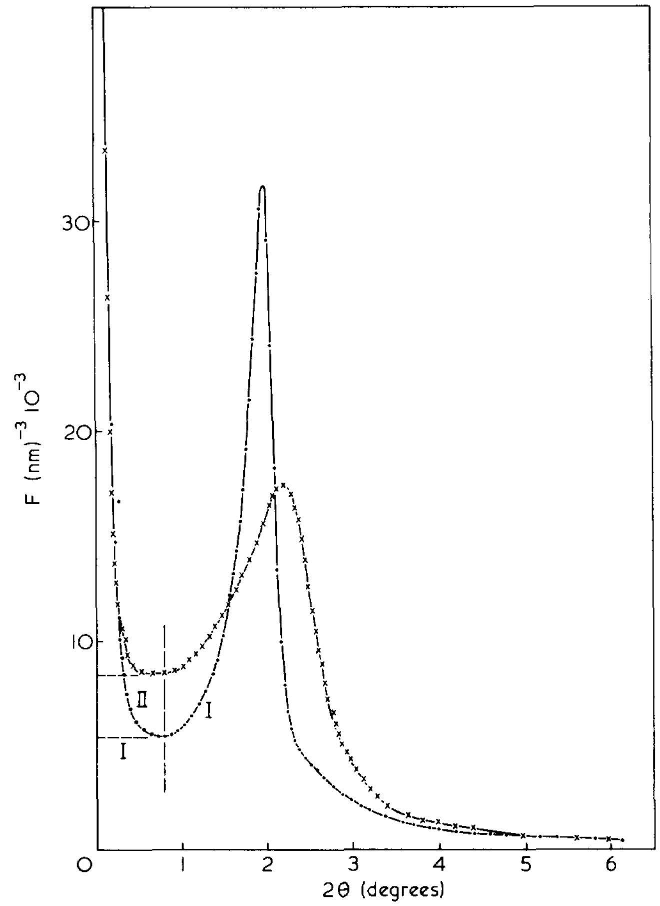


Figure 1 Small-angle X-ray scattering curves: — — —, PMB-12; · · · ·, PMB-16

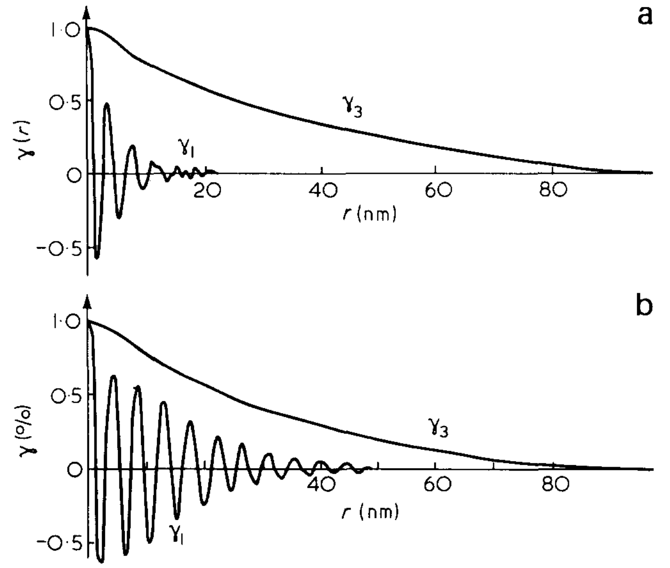


Figure 2 Correlation functions of the polymers: (a) one-dimensional correlation function $\gamma_1(r)$ and three-dimensional correlation function $\gamma_3(r)$ for PMB-12; (b) one-dimensional correlation function $\gamma_1(r)$ and three-dimensional correlation function $\gamma_3(r)$ for PMB-16

correlation function $\gamma_1(r)$ (= the Fourier transform of portion I) can be used (*Figure 1*). For this case, portion II reflects the distribution of micro-regions with uniform density. Since these micro-regions are randomly distributed in the bulk, the spherically-symmetric correlation function $\gamma_3(r)$ can be used to analyse the polymer microstructure on this level[11] (*Figure 2*).

The curve $\gamma_3(r)$ for both polymers has the form characteristic of correlation curves for dilute heterogeneous systems and indicates an absence of ordering in the arrangement of non-homogeneous regions. Therefore, curve $\gamma_3(r)$ characterizes a separate, statistically-averaged micro-region.

According to Guinier[11], the size of this region is determined by r_{max} value at which $\gamma_3(r) \rightarrow 0$ and is equal to 90–95 nm for both polymers.

It is interesting to compare this value with average 'mosaic' microstructure dimensions observed in electron microscopy (*Figure 3a*). Calculations of microregion average diameter based on size distribution result in a value of 85–90 nm (*Figure 3b*).

Thus microregion size estimates from correlation functions coincide with the values from electron microscopy. It is also noteworthy that 'mosaic' morphology is observed in polymer films only after prolonged annealing, whereas unannealed films are 'structureless'.

The $\gamma_1(r)$ for both polymers are gradually-damped oscillating functions (*Figure 2*). The value of r_{max}, at which $\gamma_1(r)$ is damped to zero, determines the distance at which correlation still exists in the packing of layers. r_{max} for PMB-12 is about 18 nm, and for PMB-16 it is about 45 nm (*Figure 2*). Since layer thicknesses for PMB-12 and PMB-16 are 3.5 and 4.4 nm, respectively, correlation in the packing exists among 5–6 and 9–10 adjacent layers of the polymers. Such closely packed layers form a separate 'layered pack'. Since 'pack' size is sometimes smaller than the size of an LC microregion, it is natural to suppose that the microregions themselves are arrays of 4–5 (PMB-12) and 2 (PMB-16) 'packs'. This model of the LC microphase agrees with the model proposed earlier for another series of polymers[5] and is similar to the De Gennes–Sarma model for low molecular weight ordered smectics[12].

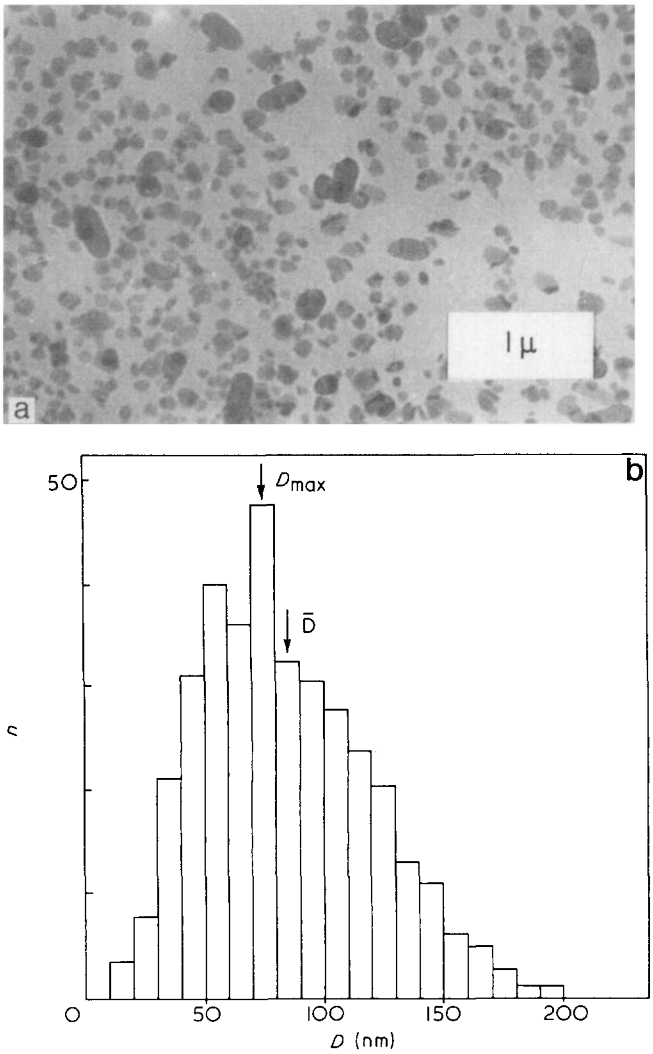


Figure 3 Electron microscopic data for PMB-16. (a) Electron micrographs of thin films; (b) size distribution of microregions (average diameter $\bar{D} = \Sigma_i n_i D_i / \Sigma_i n_i$ and the most probable diameter D_{max} are marked with arrows)

From the analysis for PMB-12 and PMB-16 we can make a conclusion that the microstructure depends on the length of the flexible mesogenic chain-end. Differences in the microstructure of the polymers manifest themselves in different packing of adjacent layers within one 'layered pack'. Aggregation of the 'packs' themselves differs considerably within a separate LC ordered micro-region. Indeed, in PMB-16 with the longer flexible chain-end, the number of closely packed layers in a 'pack' is sometimes higher than in PMB-12. And the number of 'layered packs' making an LC ordered microregion is considerably smaller.

These differences are apparently connected with a growing degree of perfection in mesogenic group packing due to increasing potential barriers for longitudinal sliding with elongation of a flexible chain-end[12]. They are also determined by variations in layer packing connected with the extent of interpretation of flexible chain-end of adjacent mesogenic groups in these polymers[5].

Thus, the Fourier analysis of small-angle curves together with electron microscopic data make it possible to obtain reliable quantitative information on the ordering of adjacent macromolecules and on microheterogeneity of the phase structure in LC polymers. Besides these data, the procedures allow a series of structural characteristics[8–10] to be elucidated. Detailed analysis of these characteristics will be given in a separate article.

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