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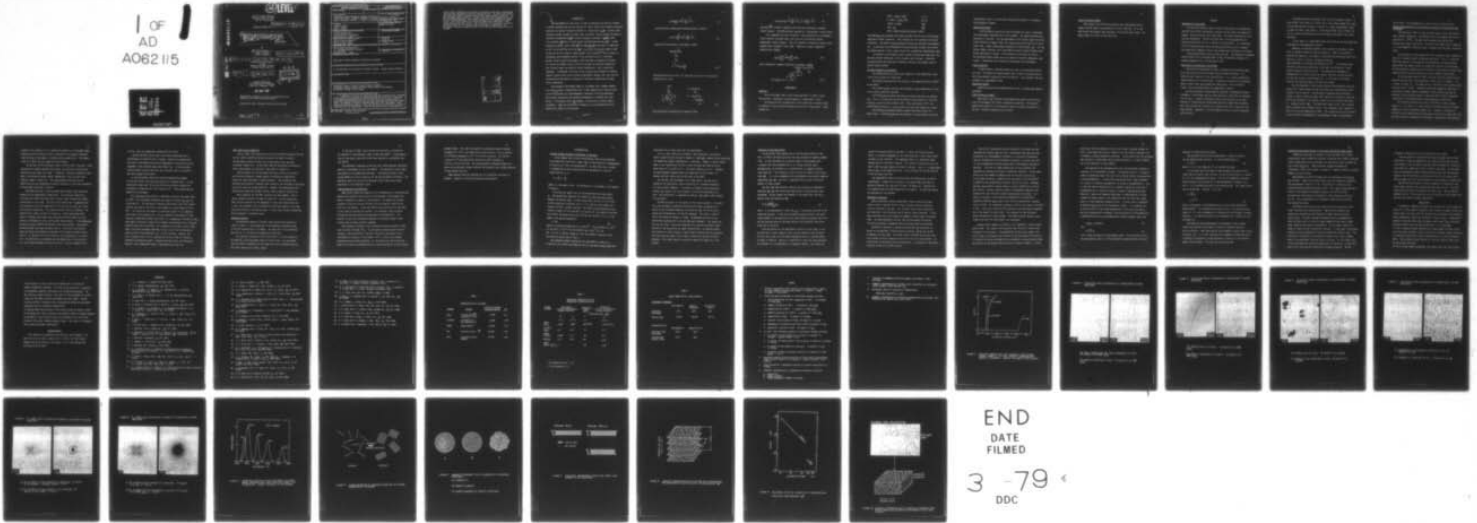
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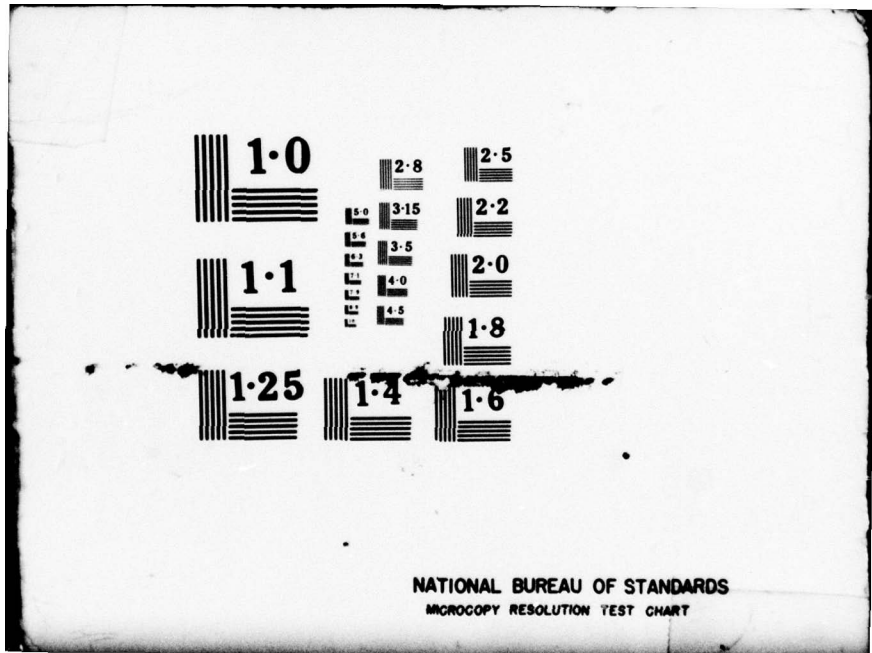
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6 STRUCTURAL INVESTIGATIONS OF POLYMER LIQUID CRYSTALLINE SOLUTIONS, AROMATIC POLYAMIDES, HYDROXY PROPYL CELLULOSE, AND POLY(γ -BENZYL-L-GLUTAMATE).
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A comparative structural investigation of the characteristics of polymer liquid crystalline solutions including Kevlar [®] (PPD-T)/sulfuric acid, poly (Cl-p-phenylene terephthalamide) (Cl-PPD-T)/sulfuric acid, poly(γ-benzyl-L-glutamate) (P _γ BLG)/dioxane and hydroxy propyl cellulose (HPC)/water was undertaken. Experimental procedures included polarized light microscopy, light scattering, absorption spectra, and x-ray diffraction on solutions at various concentrations and temperatures. Both the two phase region at the onset of		

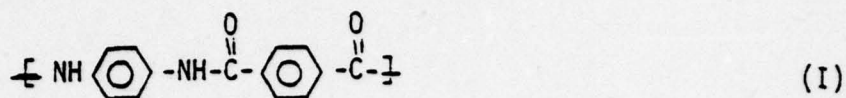
liquid crystal formation and the wholly anisotropic phase were investigated. Each solution exhibited distinctive characteristics. The PPD-T and Cl-PPD-T solutions were nematic and the P γ BLG and HPC solutions were cholesteric. In the two phase region the PPD-T, Cl-PPD-T, and P γ BLG (but apparently not the HPC) exhibited negatively birefringent spherulites and aggregates of spherulites. The HPC solutions only exhibited spherulitic structures in the single phase anisotropic system. The structures and orientations in the anisotropic phase for the various polymer solutions is considered. The helicoidal structural characteristics of the P γ BLG and HPC solutions is contrasted.

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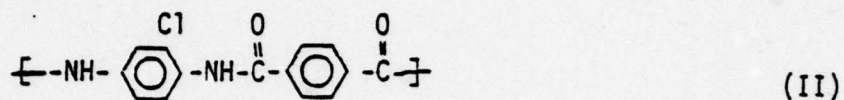
INTRODUCTION

The development of high levels of chain orientation and tensile strength in fibers obtained from the wet spinning of liquid crystalline aromatic polyamide solutions has gained increased attention in recent years (1-8). Various other synthetic polymer systems have been found to exhibit liquid crystalline behavior, including polypeptides (9-22), certain polyester copolymers (23-25), some vinyl polymers (26) and p-linked aromatic polyamide-hydrazides (27). Various biological polymers such as RNA (28) and DNA (13, 29) have been so identified as well as one modified cellulose (30). A critical review has recently been written by two of us (31) on these polymer liquid crystals. While various investigators have presented studies of the characteristics of individual polymer liquid crystalline systems, there have been no comparative studies of a series of polymer liquid crystalline systems nor detailed comparisons with the well known low molecular weight thermotropic liquid crystalline compounds. Furthermore, since the various systems were studied by different research groups often using different experimental methods, both the relative characteristics and peculiar features of individual systems have not been clearly identified.

The purpose of the present paper is to present such a needed comparative study. A major investigative tool is the interaction of various liquid crystalline systems with electromagnetic radiation of varying wavelength. Birefringent, absorption and scattering phenomena are reported and interpreted. Five polymers were investigated, including two p-linked aromatic polyamides. These are Kevlar[®] which appears to be poly(p-phenylene terephthalamide) (PPD-T) with structure



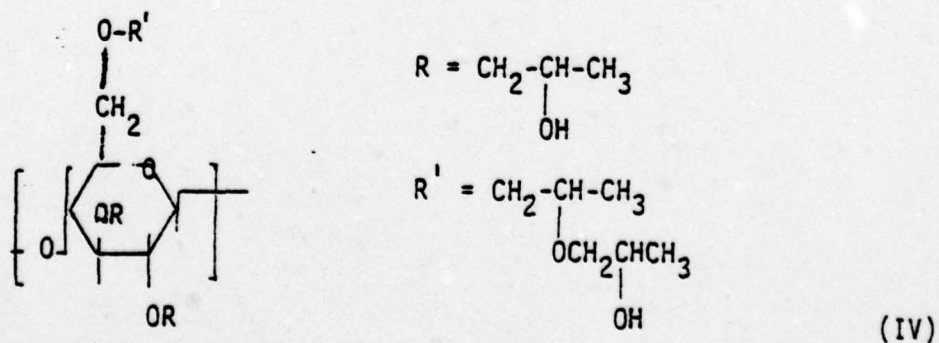
and poly(chloro p-phenylene terephthalamide) (Cl-PPD-T)



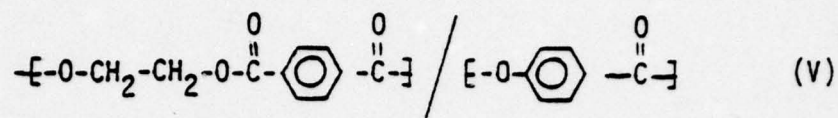
along with poly(γ -benzyl-L-glutamate) (P γ BLG)



hydroxypropylcellulose (HPC) (an idealized structure with a molecular substitution of four)

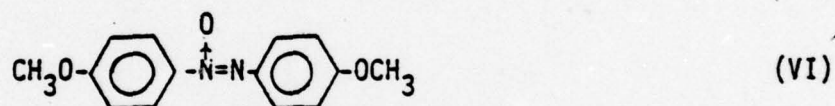


and polyethylene terephthalate co benzoate (PETB)

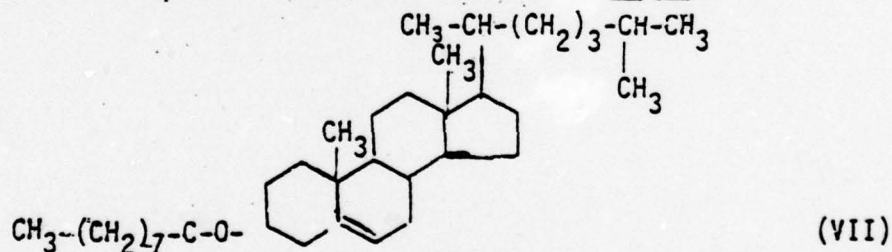


The Kevlar[®], Cl-PPD-T, P_γBLG and HPC have been reported as lyotropic liquid crystals. The PETB has been reported as a thermotropic liquid crystal.

It is important not only to contrast the characteristics of polymeric liquid crystals with each other, but also with low molecular weight thermotropic liquid crystals. Thus two classical low molecular weight liquid crystals were included in this study. These are a nematic compound p-azoxydianisole (32-34)



and a cholesteric compound cholesteryl nonanoate. (35-38)



EXPERIMENTAL

Materials

The five polymers used in this study were PPD-T, Cl-PPD-T, P_γBLG, HPC and PETB. Information on these samples is summarized in Table 1.

The polymer-solvent systems used in this study were in general based on reports of liquid crystalline behavior by earlier investigators. These systems are

PPD-T / H ₂ SO ₄ (100%)	(1, 4)
Cl PPD-T / H ₂ SO ₄ (100%)	(2, 4)
P _γ BLG / dioxane	(10)
HPC / H ₂ O	(30)
PETB / phenol-tetrachloroethane (40/60)	

The 100% H₂SO₄ was prepared from fuming and 96% sulfuric acids of ACS grades supplied by Fisher Scientific. The p-dioxane was also obtained from Fisher Scientific. The phenol-tetrachloroethane mixture was obtained from Reagents, Inc. In the case of the PETB/phenol-tetrachloroethane systems, the solvent was chosen because it was a known solvent for polyethylene terephthalate (39).

In addition to the polymer liquid crystals systems described above, two molecular weight thermotropic liquid crystals were included. These were p-azoxydianisole and cholesteryl nonanoate, obtained from Eastman Kodak in Eastman reagent grades.

Solution Preparation Procedures

The P_γBLG/p-dioxane solutions were prepared at room temperature using a wrist action shaker for three days.

The HPC/H₂O solutions were also mixed at room temperature over a period of two weeks.

The Cl-PPD-T/H₂SO₄ solutions were prepared at room temperature by using a wrist action shaker for two days.

The PPD-T/H₂SO₄ solutions required more severe conditions for preparation. This is in large part due to the material being supplied in the form of highly crystalline and oriented fiber. They were heated to 50°C and intermittently stirred in a mixing bottle with stainless blades for 2 weeks.

The PETB/phenol-tetrachloroethane systems were mixed at 60°C for several days. The PETB polymer was pre-treated in various manners including

being heated to put it in the molten state and extruding it to produce a more amorphous filament.

Optical Microscopy

A Leitz-Ortholux polarizing light microscope was used to investigate the birefringent characteristics of the systems. The sample thickness was controlled in two ways. For the measurement of the thicker sample solutions, Fisher Scientific Litman Slides (for fungus mounts) were used with a glass cover slide. These slides possess depressions of 600 microns (μm). For the thinner sample solutions, cells were made by pressing samples between glass plates separated by a spacer. The thickness of the spacer was 100 μm . The microscope sample holder had a hot stage with accurate temperature regulation. Transmitted light intensity was measured with a photometer.

Light Scattering

A Spectra-Physics 1308 helium-neon gas laser with wavelength 6328 \AA was used. The sample was placed between glass slides as indicated earlier and placed between crossed polarizer and analyzer. The scattered light was recorded on a photographic plate.

Absorption Spectra

Absorption spectra were determined with a Cary 17 double beam spectrophotometer.

X-Ray Diffraction (WAXS)

Wide angle X-ray diffraction measurements were made using a Philips X-ray diffractometer with nickel filtered $\text{CuK}\alpha$ radiation. The solution samples were placed in thin walled glass tubes to minimize the effect of the cell. Exposure times were for 2-4 hours.

X-Ray Diffraction (SAXS)

Small angle X-ray diffraction behavior was investigated using a Rigaku rotating anode X-ray generator with $\text{CuK}\alpha$ radiation. As in the WAXS studies the samples were contained in thin walled glass tubes. Exposure times of 6 hours or more were used.

RESULTS

Appearance of the Systems

The solutions studied showed a range of appearances to the naked eye. The PPD-T and Cl-PPD-T anisotropic solutions are dark brown and essentially opaque. The PETB solutions are light brown. The P γ BLG solutions are colorless and transparent. The HPC solutions have a striking appearance exhibiting colors which vary as a function of concentration. At a concentration of 53 weight percent (wt.%) the HPC/H₂O solutions are an iridescent red orange which changes to blue as the concentration increases to 70 (wt.%).

The p-azoxydianisole liquid crystals are hazy. The cholesteryl nonanoate liquid crystals are a yellowish green at 83°C and gradually change on increasing temperature to a bluish green at 90°C.

Transitions to Anisotropic Fluid Phases

The polarizing microscope was used to determine the conditions under which the solutions and pure systems studied became anisotropic. All solutions were isotropic at low concentrations. In a narrow concentration range characteristic of the polymer, a transition occurred to an anisotropic phase in which light came through the cross polars. This is shown in Figure 1 and the concentrations are summarized in Table 2.

No true anisotropic liquid phase was observed in PETB/phenol-tetrachloroethane. Birefringent particles were observed in solutions of concentration 20 (wt.%). However, shifting one glass slide relative to the other resulted in translating the birefringent particles rather than disrupting the liquid crystalline structure as is observed when this is done with the other systems. Apparently, the birefringent particles are small suspended solid crystals.

The phase transition characteristics vary from system to system. In case of PPD-T and Cl-PPD-T, it occurs over a very narrow composition range. In the P γ BLG and HPC solutions, it occurs in a wider concentration range as shown in Figure 1 and Table 2. In the case of PPD-T and Cl-PPD-T, the $\log I/I_0$ versus concentration curves are steeper than those of the other solutions.

In this paper, all experiments whose conditions are not mentioned were undertaken at room temperature ($\sim 23^\circ\text{C}$).

Generally, anisotropic polymer liquid crystalline solutions, transform to isotropic liquids as they are heated up. When a 9.5 wt% PPD-T solution was heated on a hot stage of the polarizing microscope under cross polars at a rate of 5 min/ $^\circ\text{C}$, the phase transition from anisotropic to isotropic was observed at 57°C . On the other hand, when this solution was cooled down at the same rate (5 min/ $^\circ\text{C}$), liquid crystal formation occurred at 38°C . This supercooling phenomenon is characteristic of liquid crystalline polymer solutions, and was observed for the other polymer systems except HPC. In the case of HPC aqueous solution, HPC molecules begin to precipitate at 38°C .

The two thermotropic liquid crystals exhibit transformations from the crystal to a liquid crystalline melt and show clear transformations to an isotropic melt on heating. The cholesteryl nonanoate melts exhibited a crystal to smectic transition about 73°C , smectic to cholesteric transition at 81°C and cholesteric to isotropic liquid at 91°C on heating (See Table 3). (Compare Ennulat (40)). The cholesteric phase of this liquid crystal shows a greenish blue iridescent color. This iridescent color changes to blue on raising the temperature to 90°C . The p-azoxydianisole melts exhibit a liquid crystalline mesophase in the temperature range of approximately

120 to 140°C. This mesophase has a yellow color and high fluidity.

Detailed Observations of Liquid Crystalline Phases from Polarized Light Microscopy

The solutions of PPD-T in the two phase region (9~9.5 wt%) display small globular structures. The average size of the globular particles is about $5\mu\text{m}$ ($5 \times 10^4 \text{ \AA}$). The particles are spherulites exhibiting a Maltese cross under cross polars. The sign of the spherulites is negative, i.e., the tangential refractive index is greater than the radial refractive index.

The structure of single phase PPD-T and of polymer liquid crystalline solutions in general cannot be characterized easily. This is in part because the features of the solutions are affected by the shearing force applied when the sample solution is poured into the cell for microscopy. As the orientation relaxation time of polymer liquid crystals is quite long, characterization requires several days for the sample to equilibrate.

In the two phase region of PPD-T solutions the small spherulites are observed and some form large aggregates of about $50 \mu\text{m}$ in diameter. This is shown in Figure 2-a. Individual units of the PPD-T liquid crystals seem to be very small ($<10\mu\text{m}$). Threadlike structures resembling those seen in low molecular weight nematic thermotropic liquid crystals (41, 42) are observed if the anisotropic phase is melted at 90°C to form an isotropic liquid which is then cooled down to room temperature (Figure 2-b).

The Cl-PPD-T solutions are similar to the PPD-T in the two phase region (11 ~ 11.5 wt%), i.e., small globular structures having an average diameter of $10 \mu\text{m}$ are observed (Figure 2-c). However, in the case of Cl-PPD-T not only spherulites but many globular particles of same order size but having uniaxial orientation are detected. (Spherulites having Maltese

crosses do not change at all by rotating the sample in a microscope stage. Globular particles having a uniaxial orientation axis become alternately light and dark as the sample is rotated under crossed polars. The spherulites of Cl-PPD-T are also negatively birefringent.

We now turn to the anisotropic region of the Cl-PPD-T solutions. After preparation of samples between glass plates, the globular structures were observed to grow larger and larger. Threadlike structures resembling those seen in low molecular weight nematic thermotropic liquid crystals were formed as shown in Figure 2-d. The large globular particles are not spherulites here but aggregates of smaller particles in which the orientation of the polymer molecules is uniaxial.

The PyBLG solutions in the two phase region exhibit both individual spherulites and aggregates of spherulites. The individual spherulitic structures are larger than those seen in other liquid crystalline systems investigated in this study. The size of the spherulites is dependent upon the concentration and the temperature of the solution and upon the history of the sample preparation. They range from 20 to 300 μm in diameter. The spherulites of PyBLG are shown in Figure 2-e. These large spherulites exhibit a Maltese cross under cross polarizers and were found to be negatively birefringent by using a first order red wave plate. In the aggregated anisotropic phase, parallel equidistant lines were observed. The periodic distance between the layers was about 100 μm . The periodic distance between the layers were observed to decrease with increasing polymer concentration. In the case of a 20 wt.% solution, the distance was 9 μm (Figure 2-f). The periodicity also depends upon the temperature of the solution, i.e., the distance between the layers of 20 wt.% solution changed from 9

to 27 μm when the temperature changed from 25 to 61°C.

The HPC solutions do not show a distinctive morphology until a concentration of order 40 wt.% is reached. Above this concentration very small birefringent particles and aggregates of these particles are suspended in the isotropic phase (See Figure 2-g). In the two phase region the HPC solutions show very fine structure that is not found in the other systems studied here.

In the anisotropic region with the HPC concentration between 53 wt.% and 70 wt.%, the solutions exhibit an iridescent color. At concentrations higher than 70 wt.% the HPC solutions exhibit spherulitic structures of dimensions 20 ~ 80 μm (Figure 2-h). These spherulites are negatively birefringent.

The p-azoxydianisole exhibits a threadlike structure from about 120°C to 140°C. This presumably represents the nematic structure (41, 42) discussed earlier. The cholesteryl nonanoate shows broken focal conic smectic textures (41, 42) of size 20 μm in the temperature range between 73°C and 83°C. The transition from smectic to cholesteric phase is not completely clear under the microscope, but it can be detected by the amount of light intensity transmitted through cross polars. At a temperature from 83°C to 90°C, some domain structures of about 30 μm diameter are observed and an iridescent greenish blue color can be seen. At a temperature from 90°C to 91°C, these domain structures disappear completely and the view of the microscope becomes as dark as that observed in an isotropic solution. However, the blue iridescent color is still observed and the color does not change by changing the observation angle. Judging from these facts, the cholesteric texture in this temperature range is considered to be very fine.

Small Angle Light Scattering

The H_V (laser light scattering with cross polarizers) patterns for the various liquid crystalline polymer solutions are shown in Figure 3.

The two phase solutions of the 10 wt.% PyBLG show a four leaf SALS H_V pattern (Figure 3-a). On the other hand the anisotropic solutions exhibit a SALS pattern of concentric rings shown in Figure 3-b.

The H_V patterns for the two phase solutions of HPC do not exhibit any distinct scattering, though globular structures are observed by polarizing light microscopy in these solutions. The anisotropic HPC solutions which exhibit iridescent color caused by the cholesteric structures also do not show any strong scattering. However, the concentrated solutions having spherulites exhibit the four leaf H_V pattern (Figure 3-c).

The H_V patterns for the PPD-T solutions are more complex. One of the H_V scattering pattern is shown in Figure 3-d. As this anisotropic PPD-T solution consists of the aggregates of many small spherulitic particles, the scattered light is affected by the birefringence of the other particles existing in the optical path. In this case, multiple scatterings may be supposed to inevitably occur.

Absorption Spectra

The absorption spectra of the HPC liquid crystalline structure is shown in Figure 4. The maximum peak of the absorption spectrum shifts as the HPC concentration is increased. The peak shift is also observed when the cell is inclined to the measuring light beam.

In anisotropic solutions of PPD-T and Cl-PPD-T, no such absorption was observed in the wavelength range of visible light. At wavelengths less than 4200 \AA , absorption of this type could not be detected owing to the strong absorption of phenyl groups.

In the case of PyBLG liquid crystalline solutions, no absorption was observed in the wavelength range of more than 3200 \AA . Strong absorptions by the benzyl group and solvent were observed at wavelengths less than 3200 \AA .

The cholesteryl nonanoate anisotropic melt showed apparent absorption spectra at wavelengths of less than 3800 \AA . The absorption shifts longer wavelengths as the temperature decreases. The absorption peak of this system seemed not to be as sharp as for the HPC cholesteric structure. The absorption peak also could not be detected clearly due to the strong absorption of the cholesteryl group.

X-Ray Scattering and Diffraction

When liquid crystalline materials are investigated by x-ray diffraction method, much attention must be paid to the selection of the sample cell which is necessary to contain a liquid sample. The sample cell absorbs scattered x-rays and also may diffract the x-ray beam by itself and exhibit an x-ray pattern. A very thin walled glass capillary cell was used in this study to minimize this effect. For lyotropic liquid crystals, diffraction from the solvent molecules must be considered too. The analysis of the x-ray diffraction patterns of lyotropic polymer liquid crystals thus has many difficult problems.

WAXS patterns of polymer liquid crystalline solutions exhibit strong inner and outer diffused rings. As the polymer systems studied here are lyotropic liquid crystalline, the outer ring which corresponds to the intermolecular distance of the systems, 4.6 \AA , is found to be largely determined by the solvent molecules. On the other hand, the diffraction angle of the inner ring becomes smaller as the concentration of the solution

becomes higher. The inner ring generally represented repeat distances averaging $10 \sim 15 \text{ \AA}$. For P γ BLG solution the value for a 9 wt.% solution is 12 \AA which increases to 14 \AA for a 20 wt.% solution. For the HPC a value of 11 \AA was obtained for the 40 wt.% which increases to 16 \AA for a 70 wt.% solution. No distinguishable difference between isotropic and anisotropic polymer solutions was observed from the WAXS patterns of each polymer solution.

SAXS patterns were also obtained for all anisotropic solutions of polymers. However, no distinct diffraction was observed.

INTERPRETATION

Critical Volume Fraction at Transition in Solution

We may compare the critical concentrations that we have measured with predictions from Flory's theory (43) of the statistical thermodynamics of solutions of rigid rod macromolecules. He shows that such a system is incompatible at high concentrations and separates at a critical volume fraction ϕ_c of

$$\phi_c = \frac{8}{x} \left(1 - \frac{2}{x}\right) \quad (1)$$

where x is the aspect ratio. This mechanism is illustrated in the diagram of Figure 5.

If we know the aspect ratio of the macromolecules we may predict ϕ_c . The appropriate dimensions for PyBLG have been described by Doty, Bradbury and Holtzer (44). In the α -helix form, the rod is 15.4 Å wide and the length per structural unit is 1.5 Å. They are also readily calculable for PPD-T, Cl-PPD-T and HPC. The former two macromolecules have "width" of about 5.9 Å and the HPC is of order 8 Å. The length of the PPD-T and Cl-PPD-T structural units are 5.6 Å and for the HPC it is 5.1 Å, the aspect ratio may be expressed as

$$x = KM \quad (2)$$

where M is molecular weight and K is 0.44×10^{-3} for the PyBLG, 8.1×10^{-3} for the PPD-T, 7.0×10^{-3} for the Cl-PPD-T and 1.6×10^{-3} for the HPC. We list in Table 2 values of x for the systems in question using the molecular weight data of Table 1.

The agreement between theoretical and experimental values of ϕ_c is good for the Cl-PPD-T and PyBLG but not for the other systems where the

predicted value is much lower than the experimental.

As it is very difficult to dissolve PPD-T obtained in the form of highly crystalline and oriented filaments in 100% H_2SO_4 , severe mixing conditions are needed and chemical degradation is inevitable. Indeed in various experiments in our laboratories the $[\eta]$ of such solutions was found to be reduced from 6.2 to as much as 1.4. This would reduce ϕ_c to 0.11. Probably the good agreement between theory and experiment for the Cl-PPD-T indicates that this should also be the case for the PPD-T.

For the HPC, the discrepancy is so large that it can only be accounted for by association, chain flexibility or a different mechanism of liquid crystal formation. If we were to consider binary association side by side chains, this could reduce x to 18 and the predicted ϕ_c to 0.40. Such association is suggested by Samuels' (45) model of HPC crystalline structure.

The PETB solutions did not appear to form liquid crystals. The value of ϕ_c was estimated by computing the molecular weight corresponding to the $[\eta]$ using the Moore-Sanderson $[\eta]$ -M equation (39) for PET and evaluating the corresponding x for the PET backbone. This gives a value of 0.06 if the molecular weight is 10,000. We prepared solutions at concentrations exceeding this value and they were isotropic. The reasons for this are not clear. First our calculator of ϕ_c must be considered rough. Flexibility and association are again possibilities. As benzoate dimers and trimers are liquid crystals, liquid crystal formation may be associated with low molecular weight liquid crystal interactions between different backbones. This might require a solubility beyond the capability of our solvent.

Structure of Two Phase Region

The polarized light observations of the two phase regions of the PPD-T, Cl-PPD-T and P γ BLG solutions show the existence of negative spherulites. As the polarizability along the length of the aramide chain is greater than that perpendicular to it, we may conclude these macromolecules are oriented in a circumferential or tangential manner (see Figure 6A). The situation is not so clear with P γ BLG in the α -helix form (46). It is to be remembered that polyethylene also exhibits negative spherulites (47, 48). But this is apparently due to chain folding not present in these systems.

The four leaf SALS patterns indicate the occurrence of spherulitic structure (49, 50) and confirm the observations of the polarized light microscope. We may compute the diameter of the spherulites from the H_V pattern using the expression (50)

$$R = \frac{4.09 \lambda}{2\pi \sin(\alpha_{\max}/2)} \quad (3)$$

where λ is the wavelength of light and α_{\max} is the angular position of the scattering maximum. In the case of P γ BLG two phase solutions, the calculated diameter of the spherulites from light scattering patterns was 22 μm , and the observed values of the same solution from polarized light microscopy were 20 to 50 μm .

From the analysis of the experimental results of this study, it can be found that in early stage of liquid crystal formation from isotropic solution three types of birefringent aggregates exist in isotropic phase as shown in Figure 6. Type A is a spherulite in which the rigid molecules are oriented in a circumferential or tangential manner. This can be ob-

served in two phase region of the PPD-T, Cl-PPD-T and P γ BLG solutions. Type B is a globular aggregate of the rigid molecules in which they orient uniformly to one direction. This aggregate forms in a spheroidal shape perhaps owing to interfacial tension. This globular structure can also be seen in the two phase region of Cl-PPD-T solutions. Type C is a random aggregate of small birefringent particles. This structure can only be observed in HPC two phase solutions.

Our experimental results are consistent with observations of earlier investigators. Spherulitic structures in two phase P γ BLG have been reported by Robinson (11, 13) and in Cl-PPD-T by Morgan (2). Robinson has also reported that the P γ BLG spherulites are negative. No detailed studies are reported for the aramides.

Cholesteric Character

Many low molecular weight thermotropic liquid crystals have been found to have an internal twist in their structure and are classified as being cholesteric (41, 42). This internal twist leads to selective and directional light scattering and to optical rotary character. It has been associated with the existence of asymmetric carbon atoms in the molecules. The name cholesteric derives from the cholesteryl derivatives (including cholesteryl nonanoate) which strikingly show this character.

Cholesteric character in polymer solutions has been previously reported for polypeptides including P γ BLG by Robinson (10-13) and for HPC by Werbowyj and Grey (30). The latter authors reported that the HPC solutions showed striking iridescent colors which vary with concentration. As noted earlier we have made similar observations. No evidence for cholesteric structure in PPD-T or Cl-PPD-T exists.

The pitch of low molecular weight cholesteric structures has been determined by Ferguson (36) and later investigators (37, 38) analyzing diffraction of electromagnetic radiation as a function of wavelength. When the orientation of the cholesteric structure is uniform, the pitch 'p' can be determined from the maximum peak of the apparent absorption spectrum. The pitch is indeed proportional to the wavelength corresponding to maximum diffraction or absorption intensity. We have been able to use this method to compute pitch for the HPC solutions but not the other solutions. Generally this was found to vary from 5200 Å to 2600 Å as the concentration increases from 53 to 70 wt.%. Werbowjy and Grey using optical rotation report a value of 3600 Å for a 66 wt.% HPC solution. Optical rotation studies for polypeptide generally show pitches which vary with both polymer concentration and solvent. For P γ BLG in p-dioxane, values ranging from 800,000 Å to 48,000 Å were reported by Robinson *et al* (12) as the solution concentration increases from 10 to 40%. For cholesteryl nonanoate, the pitch was found to be 3400 Å at 76°C. The pitch of both the HPC solutions and the cholesteryl nonanoate are in the range of visible light. This accounts for the strikingly optical properties of these systems. The P γ BLG solutions possess a much larger pitch and, not surprisingly, are transparent.

We have found a sample size effect in our 'absorption' spectra experiments on HPC. This leads to the conclusion that the walls influence the orientation of the layers. From experimental studies using sample cells with a range of thicknesses the structure of the anisotropic HPC solutions in narrow cells can be concluded to be a cholesteric structure where planes are parallel to the plane of the cell walls as shown in Figure 7. On the

other hand, from the studies with cells with larger distances between the walls it was found that the wall planes of the cell play an important role in forming a uniform cholesteric structure. In the thicker cell the structure near the walls (within about 120 μm from the surface) is highly ordered, but in the inner part is less ordered.

The ordering of the macromolecules within the helicoidal cholesteric structure is of considerable interest. The observed pitch 'p' is several orders of magnitude larger than that of any internal helical structure within the macromolecule. It would thus seem obvious that it may correspond to a twist in a direction perpendicular to planes of macromolecules. This is the view taken by Robinson and his coworkers (10-13) for solutions of polypeptides and it should also apply to planes of macromolecules. (See Figure 8). Bernal and Fankuchen (50) argue in investigations of liquid crystalline tobacco mosaic virus suspensions that the rigid rod viruses exist in a two dimensional hexagonal array. A similar view is expressed by Robinson *et al* (12) for the polypeptide systems. If we presume such an array to exist in the planes perpendicular to the pitch and take d_1 and d_2 as characteristic distances in the plane parallel and perpendicular to macromolecules and d_3 the perpendicular distance between layers then

$$\phi d_1 d_2 d_3 = \text{constant} \quad (4)$$

and

$$p = \frac{2\pi}{\theta} d_3 \quad (5)$$

with θ being the angle of twist between layers. The distances d_2 and d_3 may correspond to the $10 \sim 15 \text{ \AA}$ concentration dependent WAXS reflection

observed in P_γBLG and HPC solutions.

The variation of pitch with concentration is shown in Figure 9 for the P_γBLG and HPC solutions. It varies approximately as

$$p = K\phi^{-a} \quad (6)$$

where 'a' is '2' for P_γBLG and '3' for the HPC solutions.

If the inter-layer twist angle θ were constant and p were to vary simply due to dilution, then from Eqs. (4) and (5) the value of 'a' should be '1/3' for 3-dimensional dilution, '1/2' for a 2-dimensional dilution which excludes variation parallel to the macromolecule (constant 'd₁') and '1' if it excludes the plane of the macromolecules. This seems clearly not to be the case. From Eqs. (4) to (6)

$$\theta = \frac{2\pi}{p} d_3 \sim \phi^{a-1/n} \quad (7)$$

where n corresponds to the dimensionality of the dilution between the macromolecules. This probably may be taken as two. For P_γBLG solutions where a is '2', this corresponds to θ varying with the 3/2 power of volume fraction ϕ . For the HPC solutions this corresponds to θ varying with the 5/2 power of ϕ .

The P_γBLG and HPC macromolecules are cholesteric liquid crystals differ from the PPD-T and Cl-PPD-T in having an internal twisted or helical structure. Both P_γBLG and HPC have asymmetric carbon atoms in each structural unit. It is this character of an asymmetric carbon atom which is generally attributed to induce cholesteric character in low molecular weight liquid crystals. This may also be the case here.

Orientation and Superstructure in the Single Anisotropic Phase System

Threadlike structures are observed in both the PPD-T and Cl-PPD-T single phase liquid crystalline solutions indicating their nematic character. Similar observations for such polymers are reported by Panar and Beste (5) and by Arpin et al (6). These structures suggest macromolecular orientation in the fluid as shown in Figure 10. Generally these two systems appear to be very similar.

WAXS patterns for PPD-T solutions are also reported by Arpin et al (6) for PPD-T. They find a similar inner ring with dimensions increasing with concentration from 9 to 11.3%. The spacing d is related to the distance between neighboring polymer chains. Arpin et al accept Robinson's view of a two dimensional hexagonal peaking to be valid for PPD-T solutions and the distance to correspond to the distances d_2 and d_3 of Eq. (4). This interpretation for cholesteric PyBLG and HPC solutions has already been noted.

The PyBLG and HPC solutions have both distinctive cholesteric helical structures and superstructures. Robinson and coworkers have extensively characterized the structure of PyBLG single anisotropic phase (11-13). The model proposed by Robinson can be diagrammatically drawn as Figure 8 and is similar in many respects to the liquid crystal phase formed by derivatives of cholesterol. In this model, there are a number of layers of near to molecular thickness. In each layer, the polymer molecules orient preferentially having two-dimensional nematic order. The direction of orientation of the molecules rotates with a small constant angle in the same manner from one layer to the next. In this figure, only a few of the molecular layers have been shown for simplicity, in which the short solid lines show the orientation of polymer molecules. The HPC

cholesteric structure may also be explained by this model.

From the results of the polarizing light microscopy and the light diffraction, it may be suggested for the P γ BLG solutions that the molecular planes of the helicoidal structure orient preferentially normal to the surface of a sample cell which is used in this study. On the other hand, our absorption spectra scattering studies show that the molecular planes of the HPC helicoidal structure which exist within about 120 μm from the sample cell wall orient parallel to the surface of a sample cell.

The HPC solutions exhibit a striking spherulitic structure in the single phase region at the concentrations more than 70 wt.%. The light scattering gives typical H_v patterns for spherulites. The size may be computed from Eq. (3) and works out to be of order 30 μm which agrees with the polarized light microscopy observations.

CONCLUSIONS

A fundamental comparative study of the structure of liquid crystalline phases of p-linked aromatic polyamides, poly- γ -benzyl glutamate (P γ BLG) and hydroxy propyl cellulose (HPC) are reported and contrasted to low molecular weight thermotropic nematic and cholesteric liquid crystals. Experimental methods include polarized light microscopy, small angle light scattering, absorption spectra and wide angle diffraction. It is concluded.

(1) With increasing polymer concentration, these polymer solutions transform from normal isotropic liquid structures to two phase systems containing an anisotropic phase and at higher concentrations to a single anisotropic phase. The two phase systems (except HPC) exhibits negative spherulites and anisotropic particles.

(2) The p-linked aromatic polyamides form nematic while the P γ BLG and HPC

form cholesteric liquid crystals and resemble their low molecular weight thermotropic analogues. The pitch of the solutions is concentration dependent, generally decreasing with increasing wavelength. The HPC solutions possess pitches in the region of the wavelength of visible light, but the PyBLG solutions wavelengths are much longer. The HPC solution exhibits iridescent colors corresponding decreasing wavelength (red \rightarrow blue) with increasing concentration.

(3) One may model the structure of the liquid crystalline phase in terms of two dimensional layer structures which perhaps contain a hexgonal packing. In cholesteric liquid crystals these are arranged to form a helicoidal structure with angle θ between adjacent layers. The value of θ increases with increasing polymer concentration.

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TABLE 1

CHARACTERISTICS OF POLYMERS

<u>Polymer</u>	<u>Source</u>	<u>Viscosity Average Molecular Weight</u>	<u>[η]</u>
PPD-T	Du Pont Kevlar [®] , (synthetic fiber)	41,000	6.2
Cl-PPD-T	synthesized in our laboratories	10,000	1.59
PyBLG	Sigma Chemical	142,000	1.67
HPC	Hercules Klucel - L [®]	140,000	1.35
PETB	Tennessee Eastman Company	~10,000	0.58

TABLE 2

TRANSITION CHARACTERISTICS OF
ANISOTROPIC POLYMER SOLUTIONS

Polymer Systems	Experimental critical concentration (weight fraction)		Theoretical Aspect Ratio	Theoretical critical concentration (volume fraction)
	C_A	C_B	X	ϕ_c
PPD-T/ H_2SO_4	0.090	0.095	420 *(70)+	0.02 *(0.11)+
C1 PPD-T/ H_2SO_4	0.11	0.12	73	0.11
PyBLG/ Dioxane	0.085	0.11	63	0.12
HPC/ H_2O	0.42	0.50	220	0.04
PETB/ phenol $C_2H_2Cl_4$	--	--	130	0.06

* For sample with $[\eta] = 6.2$ + If $[\eta]$ reduced to 1.4

TABLE 3

PHASE TRANSITION OF LIQUID CRYSTALS

Cholesteryl Nonanoate

	Solid→Smectic	Smectic→ holesteric	cholesteric→ liquid
Polarized Microscopy	73°C	83°C	91°C
Ennulat (41)	76.3°C	80.6°C	92.1°C

p-Azoxydianisole

	Solid→Nematic	Nematic→Liquid
Polarized Light Microscopy	120°C	140°C
International Critical Table	116°C	136°C

FIGURES

1. Relative transmitted light intensity thru crossed polars, where I_0 is light intensity observed when sample is isotropic. Sample thickness is 100 microns.
2. Polarizing photo micrographs of birefringent polymer solutions.
 - a. Small spherulites and their aggregates of PPD-T. 9.2 weight% in 100% H_2SO_4 .
 - b. Nematic structure of PPD-T. 11 weight% in 100% H_2SO_4 .
 - c. Spherulites of Cl-PPD-T. 11 weight % in 100% H_2SO_4 .
 - d. Nematic structure of Cl-PPD-T. 15 weight % in 100% H_2SO_4 .
 - e. Spherulites of P γ BLG. 10 weight % in dioxane.
 - f. Parallel line structure of P γ BLG, 20 weight % in dioxane.
 - g. Aggregates of anisotropic particles of HPC, 42 weight % in H_2O .
 - h. Spherulitic structure of HPC. 70 weight % in H_2O .
3. H_V laser light scattering patterns of anisotropic polymer solutions.
 - a. H_V pattern of P γ BLG spherulitic structure, 10 weight % in dioxane, l (camera length) = 50 m.
 - b. H_V pattern of P γ BLG parallel line structure, 20 weight % in dioxane $l = 10$ cm.
 - c. H_V pattern of HPC spherulitic structure. 70 weight % in H_2O , $l = 30$ cm.
 - d. H_V pattern of PPD-T anisotropic solution, 9.5 weight % in 100% H_2SO_4 , $l = 10$ cm.
4. Absorption spectra of HPC anisotropic solutions whose concentrations range from 56.7 weight % to 70 weight %. Sample thickness is 700 microns.
5. Simple mechanism of mesophase formation as polymer concentration increases.
6. Schematic representation of aggregates of mesophase structures.
 - a. spherulitic
 - b. nematic globular
 - c. random aggregate of nematic structures

7. Structural arrangements explaining sample size effects in HPC solutions.
8. Schematic representation of polymer chain orientation for cholesteric liquid crystals, after Robinson (11).
9. Helicoidal pitch as a function of concentrations
PyBLG data from Robinson (13)
10. Schematic representation of threadlike superstructure and polymer chain orientation for nematic PPD-T and C1-PPD-T.

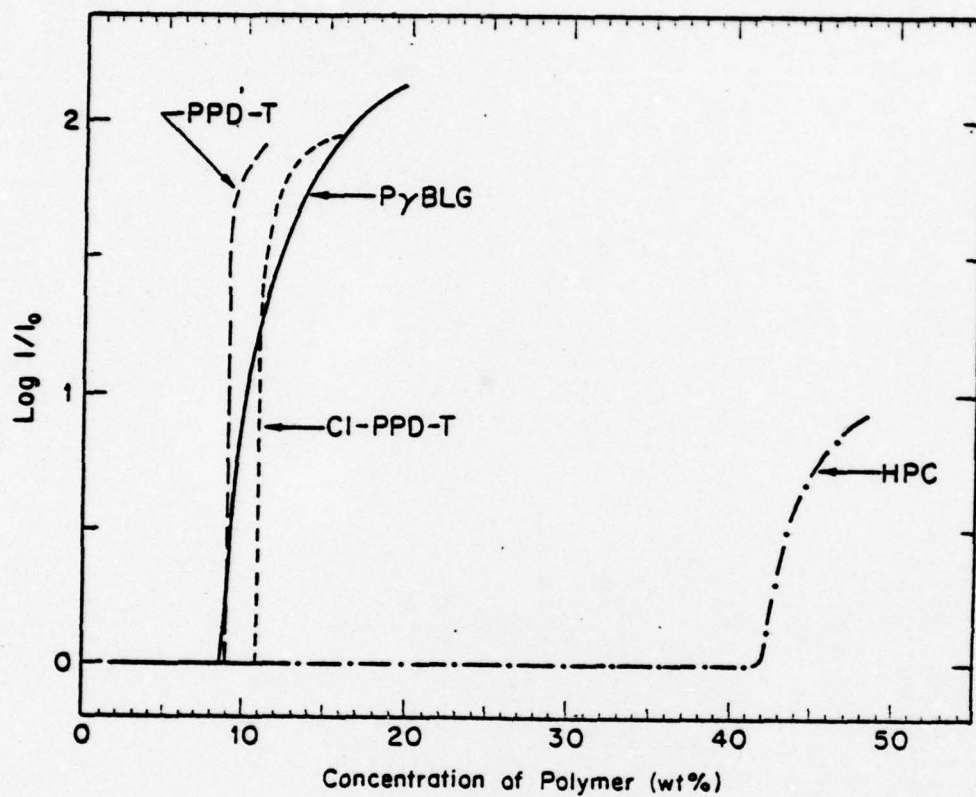
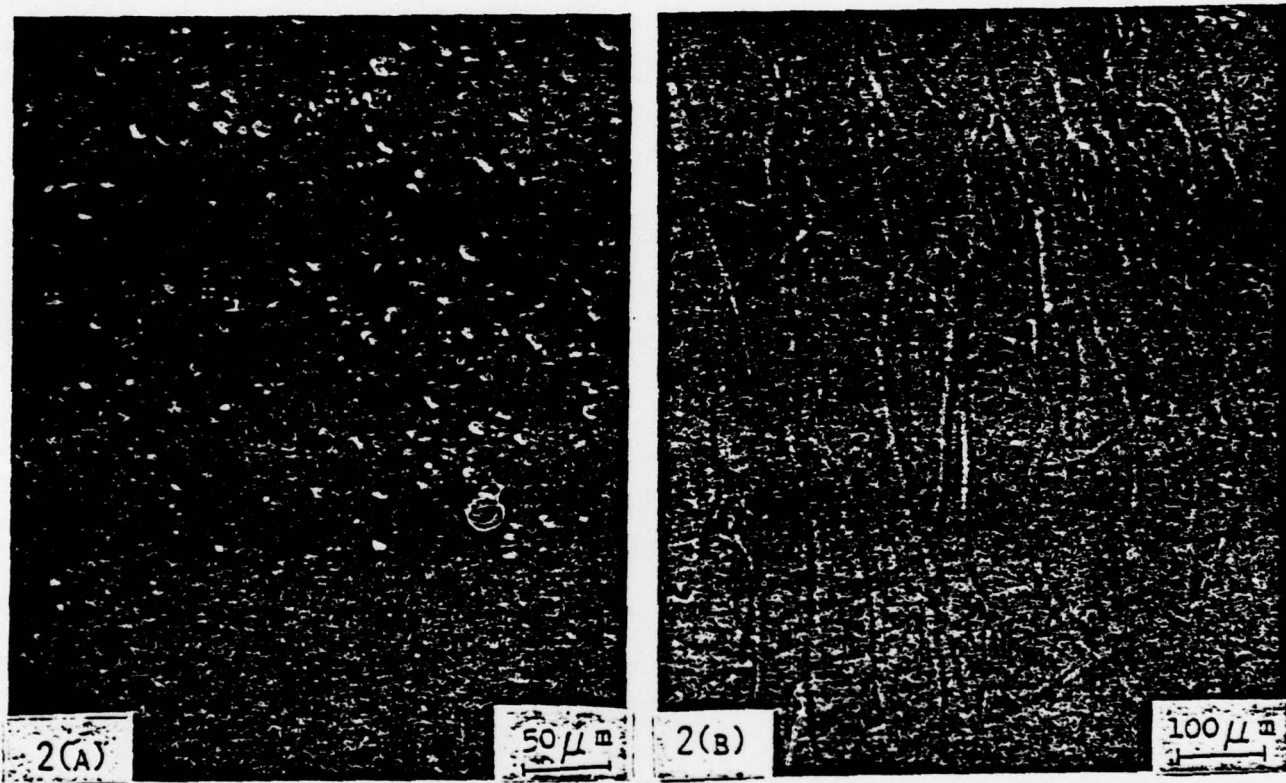


FIGURE 1. RELATIVE TRANSMITTED LIGHT INTENSITY THRU CROSSED POLARS, WHERE I_0 IS LIGHT INTENSITY OBSERVED WHEN SAMPLE IS ISOTROPIC. SAMPLE THICKNESS IS 100 MICRONS.

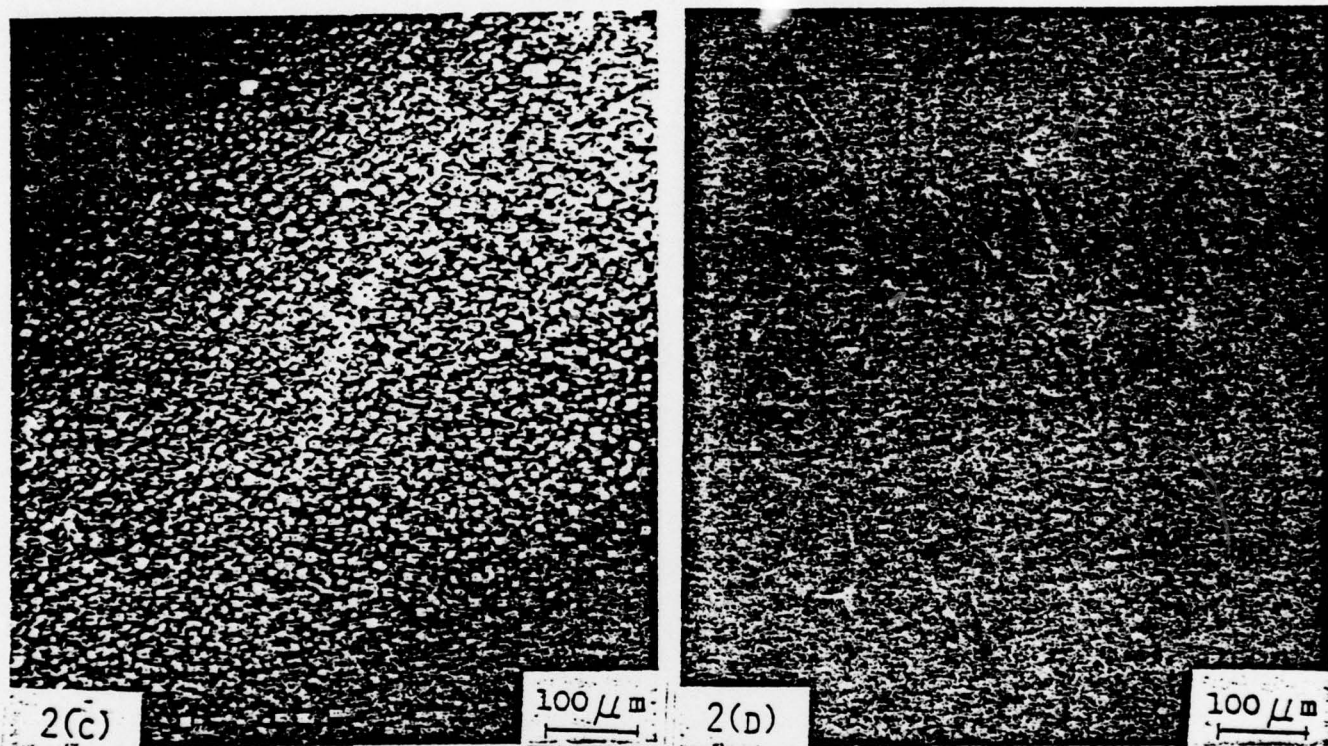
FIGURE 2. POLARIZING PHOTO MICROGRAPHS OF BIREFRINGENT POLYMER SOLUTIONS.



(A) SMALL SPHERULITES AND THEIR AGGREGATES OF PPD-T.
9.2 WEIGHT % IN 100% H_2SO_4

(B) NEMATIC STRUCTURE OF PPD-T. 11 WEIGHT % IN 100%
 H_2SO_4

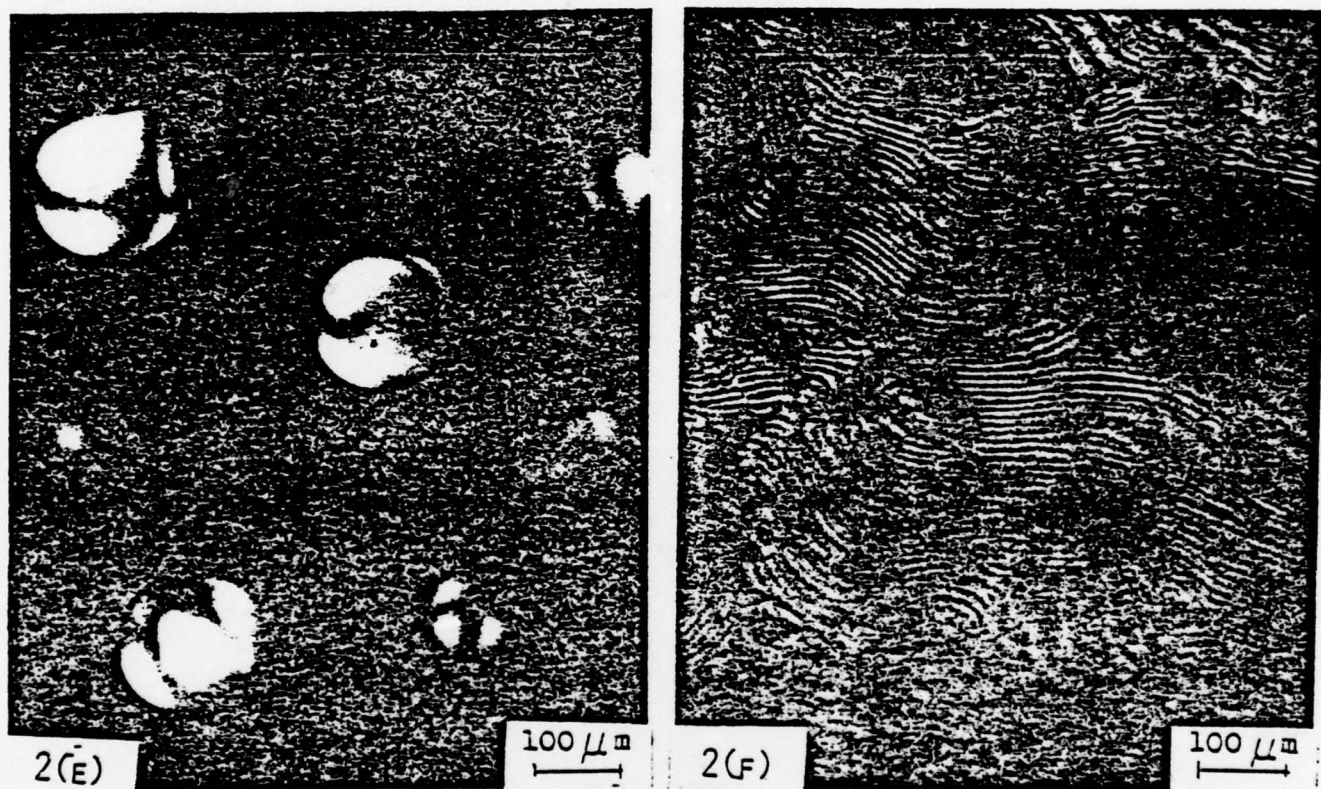
FIGURE 2. POLARIZING PHOTO MICROGRAPHS OF BIREFRINGENT POLYMER SOLUTIONS.



(c) SPHERULITES OF CL-PPD-T. 11 WEIGHT % IN 100%
 H_2SO_4

(d) NEMATIC STRUCTURE OF CL-PPD-T. 15 WEIGHT % IN
100% H_2SO_4

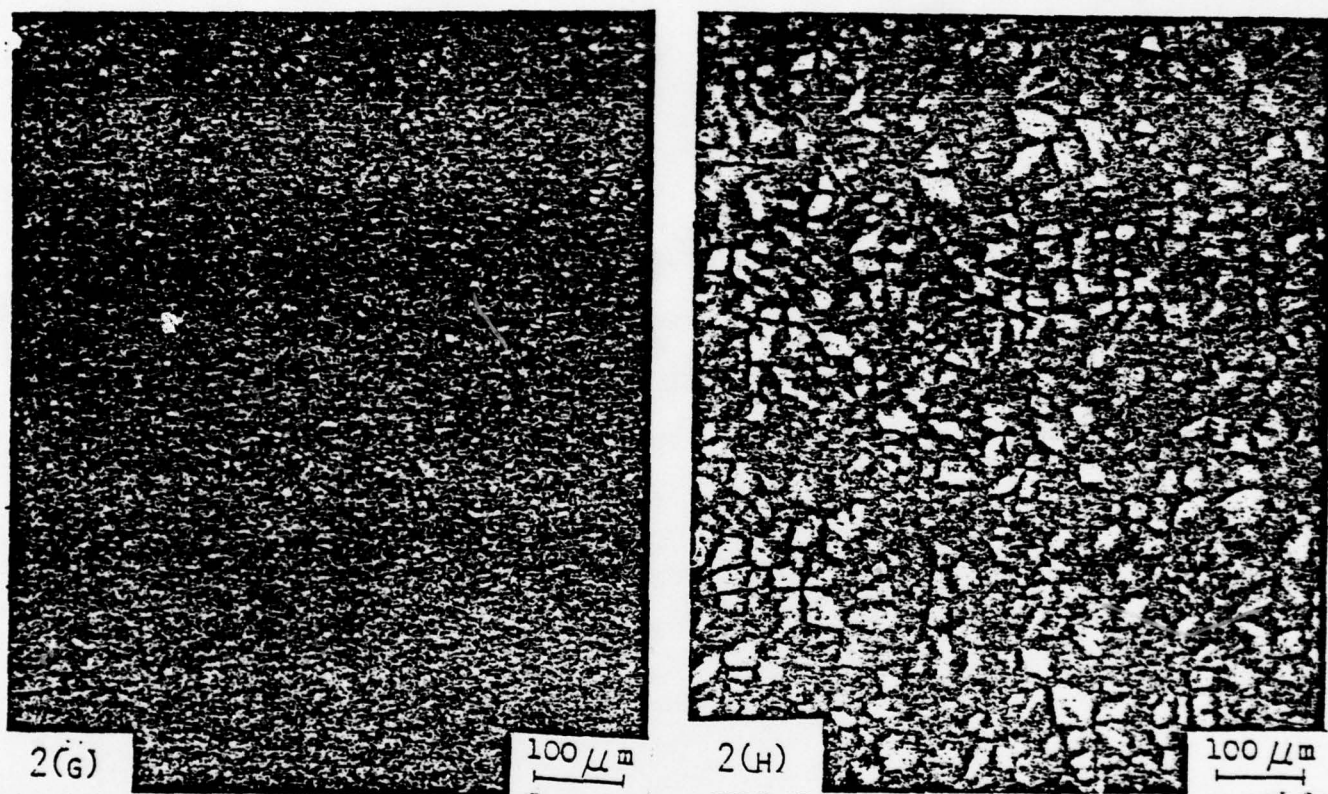
FIGURE 2. POLARIZING PHOTO MICROGRAPHS OF BIREFRINGENT POLYMER SOLUTIONS.



(E) SPHERULITES OF PYBLG, 10 WEIGHT % IN DIOXANE.

(F) PARALLEL LINE STRUCTURE OF PYBLG, 20 WEIGHT % IN DIOXANE

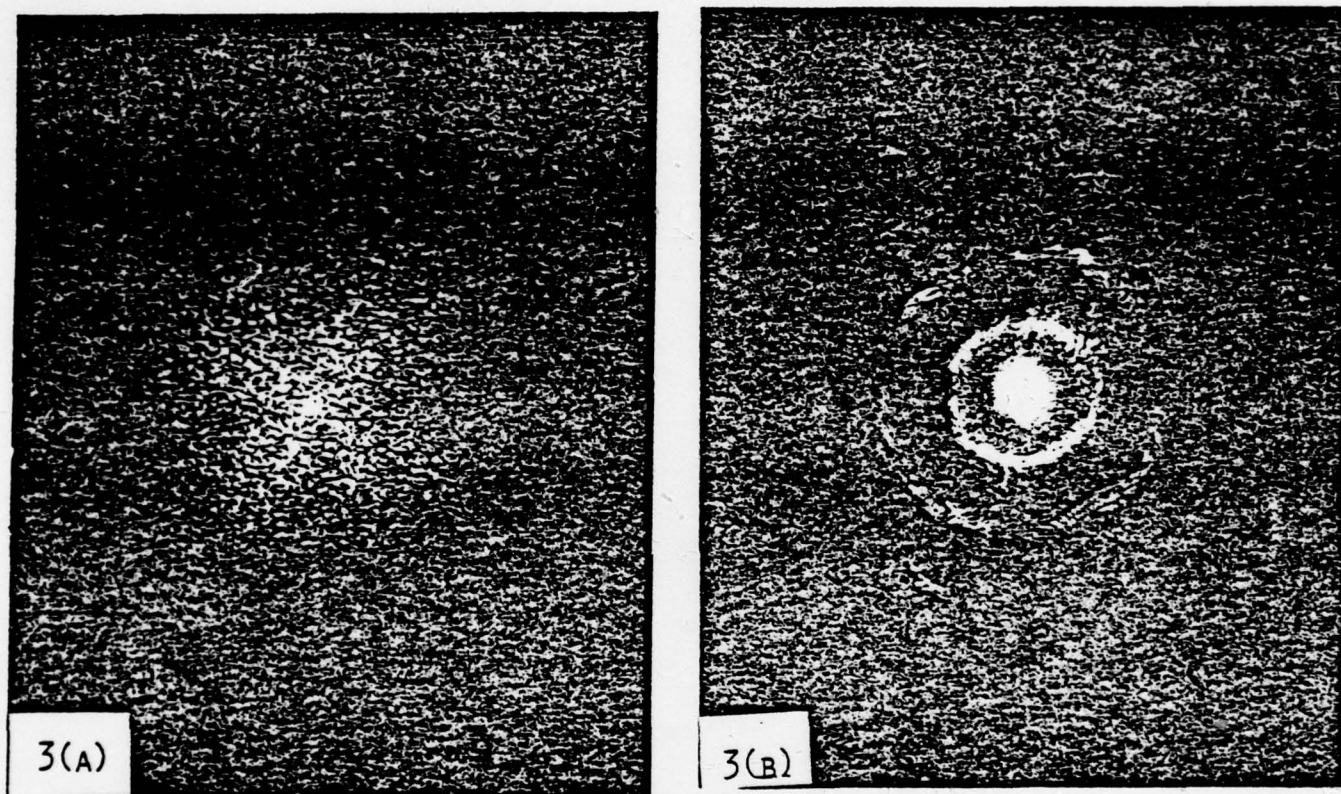
FIGURE 2. POLARIZING PHOTO MICROGRAPHS OF BIREFRINGENT POLYMER SOLUTIONS.



(G) AGGREGATES OF ANISOTROPIC PARTICLES OF HPC, 42
WEIGHT % IN H₂O

(H) SPHERULITIC STRUCTURE OF HPC, 70 WEIGHT % IN H₂O

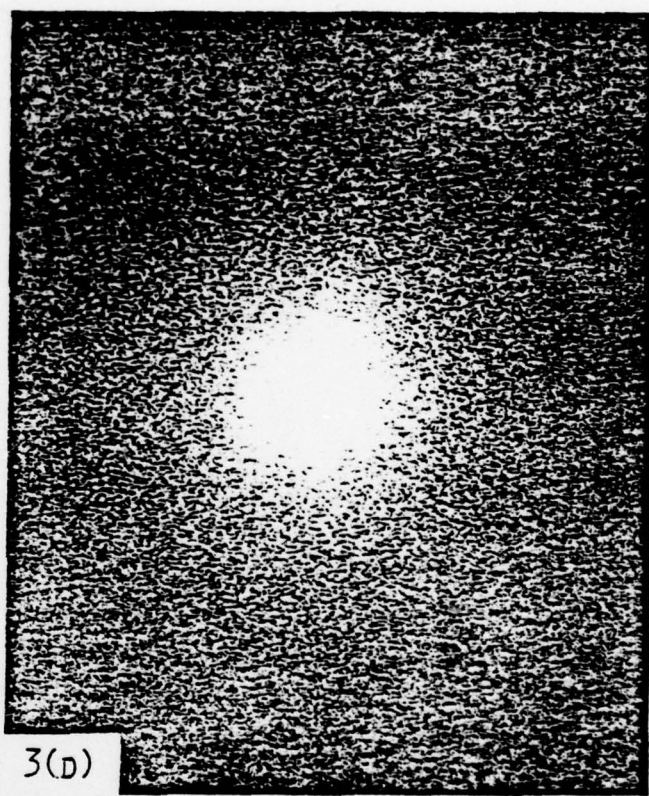
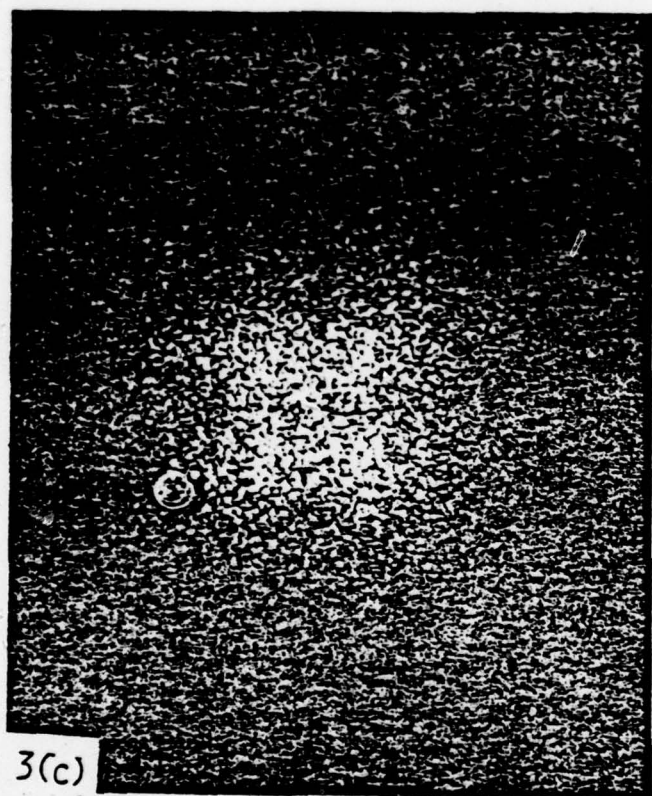
FIGURE 3. H_V LASER LIGHT SCATTERING PATTERNS OF ANISOTROPIC POLYMER SOLUTIONS.



(A) H_V PATTERN OF PYBLG SPHERULITIC STRUCTURE, 10 WEIGHT % IN DIOXANE, l (CAMERA LENGTH) = 50 M

(B) H_V PATTERN OF PYBLG PARALLEL LINE STRUCTURE, 20 WEIGHT % IN DIOXANE $l = 10$ CM

FIGURE 3. H_V LASER LIGHT SCATTERING PATTERNS OF ANISOTROPIC POLYMER SOLUTIONS.



(c) H_V PATTERN OF HPC SPHERULITIC STRUCTURE, 70 WEIGHT
% IN H_2O , $l = 30$ CM

(d) H_V PATTERN OF PPD-T ANISOTROPIC SOLUTION, 9.5 WEIGHT
% IN 100% H_2SO_4 , $l = 10$ CM

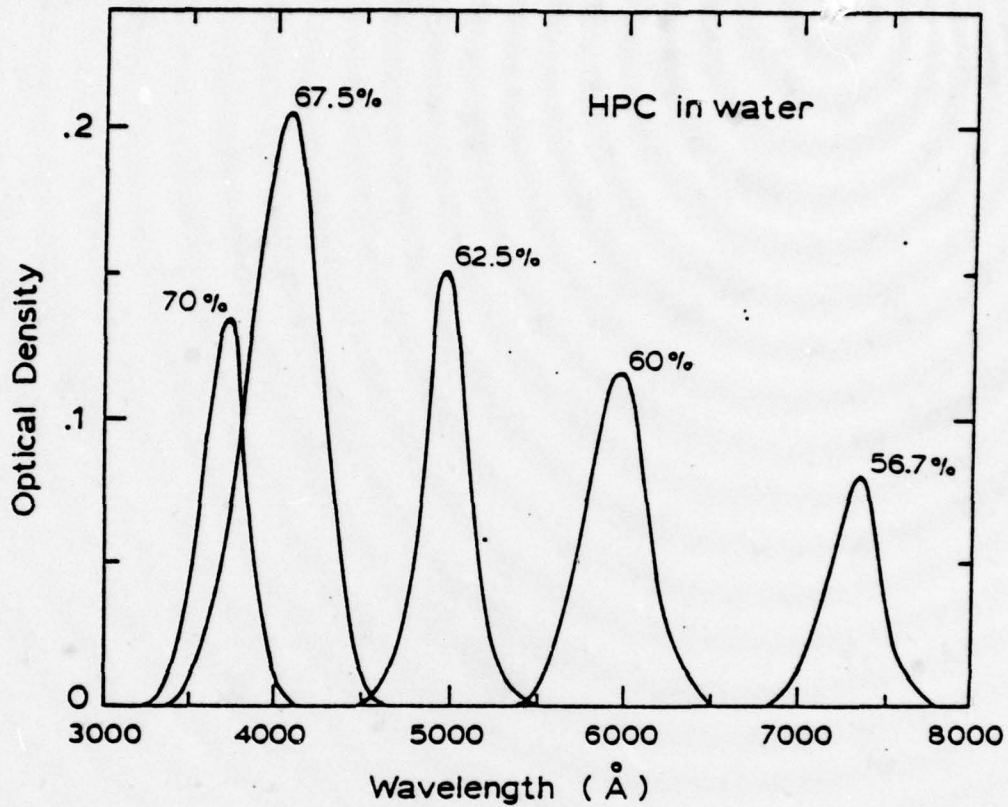


FIGURE 4. ABSORPTION SPECTRA OF HPC ANISOTROPIC SOLUTIONS WHOSE CONCENTRATIONS RANGE FROM 56.7 WEIGHT % TO 70 WEIGHT %. SAMPLE THICKNESS IS 700 MICRONS.

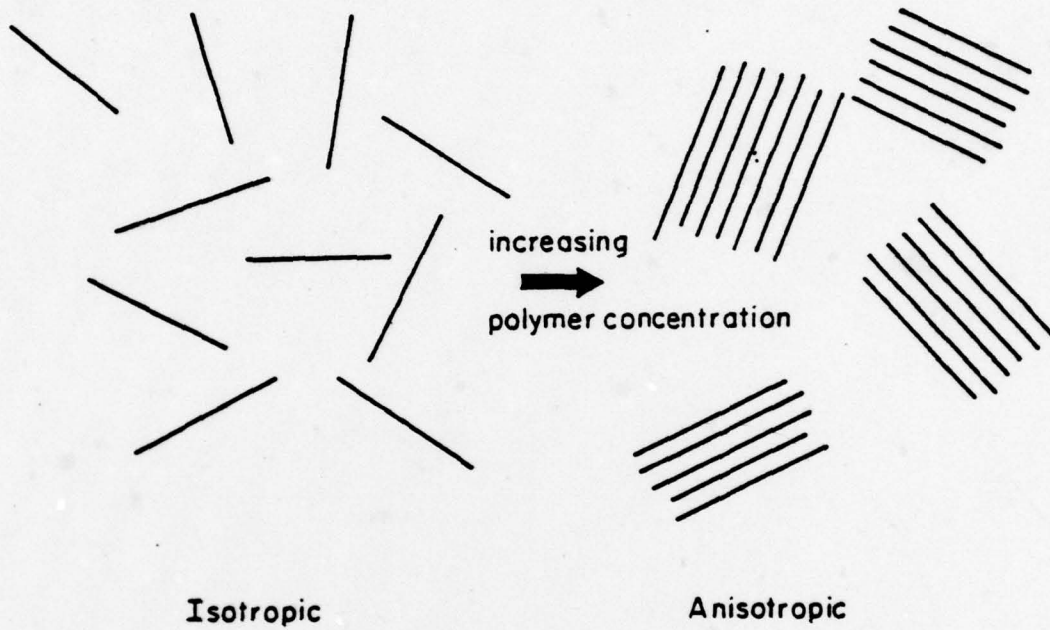
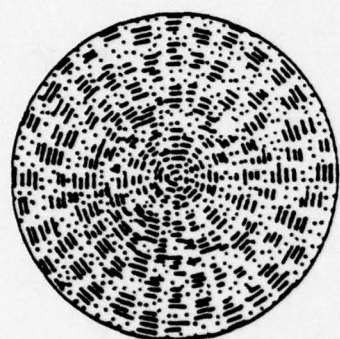
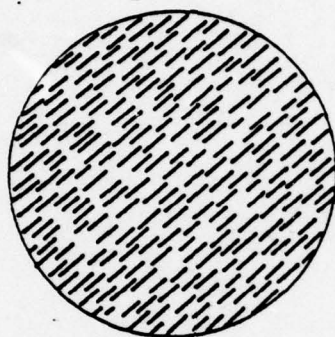


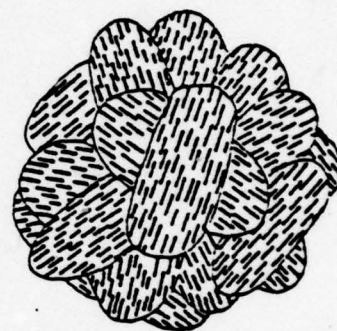
FIGURE 5. SIMPLE MECHANISM OF MESOPHASE FORMATION AS POLYMER CONCENTRATION INCREASES.



A



B



C

FIGURE 6. SCHEMATIC REPRESENTATION OF AGGREGATES OF MESOPHASE STRUCTURES.

(A) SPHERULITIC

(B) NEMATIC GLOBULAR

(C) RANDOM AGGREGATE OF NEMATIC STRUCTURES

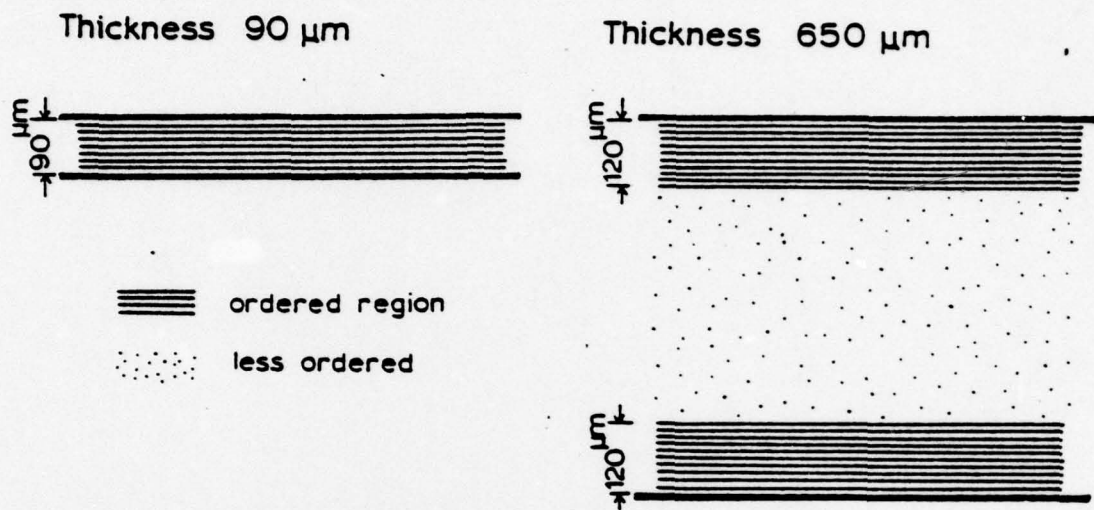


FIGURE 7. STRUCTURAL ARRANGEMENTS EXPLAINING SAMPLE SIZE EFFECTS IN HPC SOLUTIONS.

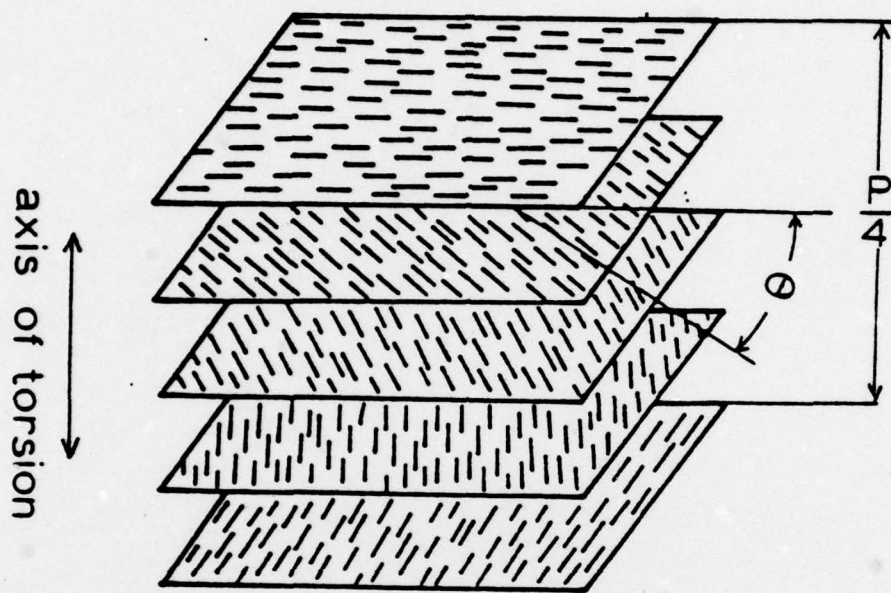


FIGURE 8. SCHEMATIC REPRESENTATION OF POLYMER CHAIN ORIENTATION FOR CHOLESTERIC LIQUID CRYSTALS, AFTER ROBINSON (11).

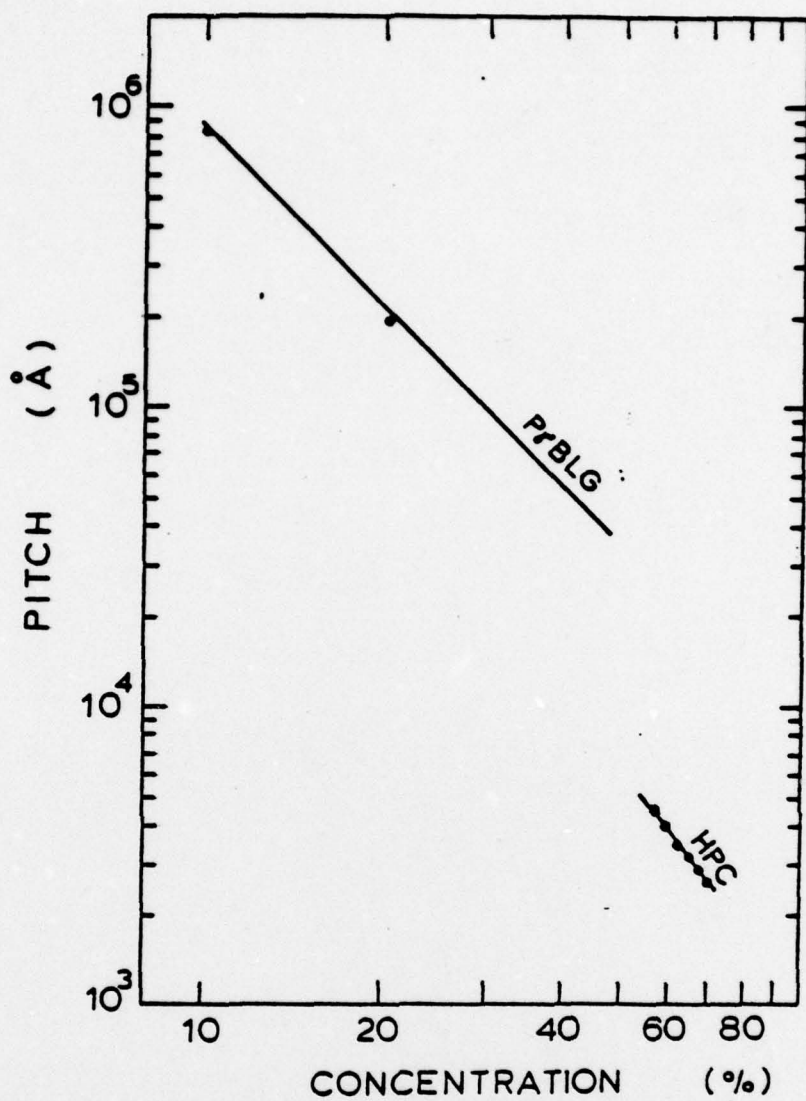
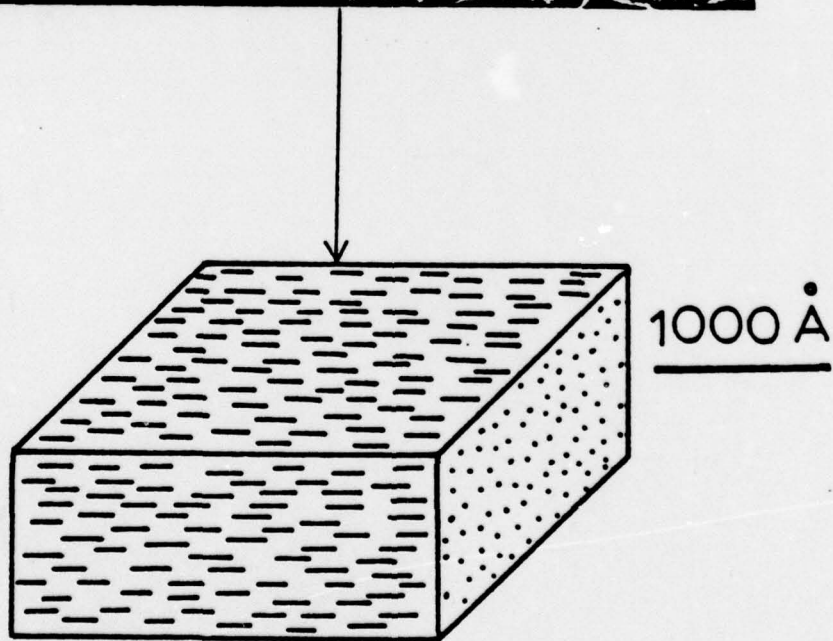


FIGURE 9. HELICOIDAL PITCH AS A FUNCTION OF CONCENTRATIONS
PYBLG DATA FROM ROBINSON (13)

thread like structure



←→
optical axis

FIGURE 10. SCHEMATIC REPRESENTATION OF THREADLIKE SUPERSTRUCTURE AND POLYMER CHAIN ORIENTATION FOR NEMATIC PPD-T AND CL-PPD-T.