



3.1 Temperature Dependence of the Cholesteric Pitch

The helical pitch was measured in the temperature range of 90° to 132.7°C for all the concentrations of cholesteric mixtures. The cholesteric pitch was found to be temperature independent. This can be clearly seen from the series of photographs of the same sample of PAA/CP (0.5 %) shown in Fig. 12 a) to 12d), covering the temperature range 100°C to 132.1°C . The mesophase of PAA being in the temperature range $117.5^{\circ}\text{C} - 135^{\circ}\text{C}$, the photograph in Fig. 12a) shows a "supercool" state of the sample. The supercool state was easily obtained upon decreasing the temperature of the sample from mesophase. The easy formation of the supercool state is probably due to the confining geometry of the thin film sample constrained between two glass surfaces, making "freezing" into a solid state of higher order rather difficult. But this super-state was never obtained upon heating the sample from the solid state. The photograph in Fig. 12d) shows sharper stripes than the others. It was taken at a temperature which is nearer the transition temperature of 134°C and was taken after intervening heating cycles. The change in the stripe pattern illustrates the hysteresis in the creation of the stripes.

While the helical pitch in our systems with low concentration of cholesteric material was found to be independent of temperature, it has to be pointed out that the cholesteric structure in many pure cholesteric systems is highly temperature sensitive²⁸. This strong temperature

²⁸P.N. Keating, Mol. Cryst. Liquid Cryst. 8, (1969), 315.

dependence has been explained by Keating²⁸ with the postulation of anharmonicity in the force resisting the relative twist of neighboring planes of molecules. This pitch dilation was viewed as the rotational analog of thermal expansion in a solid. In the systems studied in the present investigation, the concentration of cholesteric was so low that even if there was anharmonicity in the restoring force it would not be sufficient to create an untwisting in the big helices of nematic and cholesteric molecules - and hence causing an increase in the pitch.

3.2 Variation of Cholesteric Pitch with Cholesteric Concentration

The photographs of low concentration of cholesteric in PAA and MBBA are shown in Figs. 13 and 14. The variation of pitch with concentration is clearly demonstrated in the photographs. The graph of helical pitch plotted against inverse concentration ($\frac{1}{c}$) is a linear curve, shown in Fig. 15. This linearity confirms that the stripe pattern was indeed due to the helical structure induced by the helix-forming tendency of the cholesterics in the predominantly nematic material.

3.3 Variation of Cholesteric Pitch with Magnetic Field Strength

The systems PAA/CP (0.2, 0.3, 0.4, 0.5 and 0.75 %) were studied in magnetic field to measure the pitch variation with the magnetic field strength. The experimental data are shown against the theoretical curve of de Gennes²⁰ in Fig. 16. It can be seen that our experimental results

agree well with the theoretical result of de Gennes. The logarithmic divergence is clearly demonstrated. Discrepancy between theory and experiment is less than 3 %. It is attributed to experimental errors associated primarily with pitch measurement, particularly errors arising from the hysteresis of stripe formation. Errors associated with magnetic field strength measurement, done with a commercial Hall probe, is considered to be unimportant.

From plots such as Fig. 16, a "critical field" can be defined as the field given by the asymptote for the logarithmic divergence. The asymptote is drawn from the experimental points considering the position of the asymptote vis-a-vis de Gennes' theoretical curve. The critical field is, therefore, determined indirectly.

Having obtained the value of the critical field, the parameter ratio $\frac{k_{22}}{\chi_a}$ can be obtained directly from Eq. (1.24).

For systems with CP concentrations of 0.2, 0.3, 0.4, 0.5 and 0.75 %, at 130°C, the values of 1.40, 1.29, 1.40, 1.26 and 1.22 respectively were obtained for $(\frac{k_{22}}{\chi_a})^{1/2}$. These values compare with the result of 1.50 at 129°C obtained by Fredericksz²⁹ using a different method based on the magnetic distortion of a pure nematic PAA sample and of 1.65 at 129°C obtained by Durand et al²³ for PAA doped with low concentration of CP, CN, CD, or CA.

Since the magnetic anisotropy χ_a for PAA is known²⁹ to be

²⁹V. Fredericksz and V. Zwetkoff, Physik. Z. Sowjetunion 6(1934), 490.

1.18×10^{-7} cgs and is not expected to vary much for samples with cholesteric concentrations in the range 0.2 - 0.75 %, the ratio of $(k_{22}/\chi_a)^{1/2}$ of 1.40 will give the value of k_{22} of $(1.40)^2 \times 1.18 \times 10^{-7} = 2.31 \times 10^{-7}$ cgs. This compares with $k_{22} = 2.9 \times 10^{-7}$ cgs given in the literature².

Using the values of pitch read from the graph of Fig. 13a) and the values of critical field read from the graph of Fig. 19, we found that the values of $\frac{k_{22}}{\chi_a} = 2.00 \times 10^{-7}$ computed with the help of Eq. (1.24) as shown in Table 6.

Table 6 Values of $\frac{k_{22}}{\chi_a}$ calculated from average values of pitch and critical field.

c(% of CP)	Pitch(μm)	H_c (kG)	k_{22}/χ_a
0.2	66.5	2.1	2.00
0.4	33.3	4.2	2.00
0.6	22.2	6.3	2.00

Thus the parameter ratio $\frac{k_{22}}{\chi_a}$ is independent of cholesteric concentration. This contrasts with the fluctuation of 1.7 - 2.0 for the value of the parameter ratio when the pitch and critical field values for each concentration were used to compute the ratio. The fluctuation thus reflects the range of experimental errors associated with our measurements. This insensitivity of the ratio $\frac{k_{22}}{\chi_a}$ to cholesteric concentration is perhaps reflecting the fact that the individual values of k_{22} and χ_a are not sensitive to doping by cholesteric. In the low

doping range studied, the values of k_{22} and χ_a should be those of the base material, namely PAA.

The observation that the $\frac{k_{22}}{\chi_a}$ values remain strictly constant at cholesteric concentrations of 0.2, 0.4, 0.6 % as shown in Table 6, constitutes a powerful confirmation of the validity of de Gennes' analysis of which Eq. (1.24) is one specific result.

3.4 Critical Field Dependence on Cholesteric Concentration

The results of the investigation of critical field dependence on cholesteric concentration are shown in Fig. 19. The graph shows a linear dependence of the critical field on the cholesteric concentration. This contrasts with the earlier results that the cholesteric pitch varies inversely with cholesteric concentration. It is to be noted that, according to Eq. (1.24) the critical field varies inversely as the helical pitch distance. The linear dependence of critical field H_c on cholesteric concentration supports the idea that the stripe structure observed was really due to twisting of the molecules of the mixture system into helices by the cholesteric dopant. H_c , interpreted as the field strength required to "untwist" the helices, should depend on how much cholesteric was present to "twist" the molecules into helices.

3.5 Critical Field Dependence on Sample Film Thickness

Because of the sensitivity of molecular orientation to the glass boundaries which necessitated the employment of Châtelain's²⁷ rubbing technique for the glass slides used to contain the sample, it

was decided to examine whether the helical pitch would be affected by sample film thickness, particularly for small values of film thickness. Pitch distance of PAA/CP (0.5 %) was measured in samples of the following thicknesses : 30, 50, 75, 100, 125, 150, 200, 250, 300 μm . It was found that the cholesteric pitch was independent of sample thickness in the range examined. It is to be pointed out that, even for the smallest value of 30 μm , the sample thickness is still $10^3 - 10^4$ times the length of a PAA molecule. For typical magnetic coherence length of 5 μm , this means that the bulk of the liquid crystal molecules can be regarded as being quite isolated from the glass boundaries.

It was also decided to examine whether the critical field would depend on sample film thickness. The results for PAA/CP (0.5 %) for sample film thickness of 30, 50, 75, 100, 125, 150, 200, 250, 300 μm are shown in Fig. 20. A linear graph with a slight negative slope was obtained. The effect of sample film thickness on the critical field was thus observed to be small and negative, meaning there is a slight reduction in critical field at greater values of sample film thickness. This perhaps reflects the presence of a modest boundary effect of the glass walls which may have a slight restraining effect on the orientation of the molecules forming the helices thereby increasing H_c at smaller film thicknesses. For larger film thickness, the portion of molecules suffering from the restraining effects of the glass boundaries become smaller, allowing freer "stretching" or "unwinding" of the helices and resulting in the slight reduction of the critical field.

For most experiments in the present investigation, a sample film thickness of 150 μm was used.

3.6 Temperature Dependence of the Critical Field

The temperature dependence of the critical field for PAA/CP (0.2, 0.3, 0.4, 0.5, 0.75 %) in the temperature range $90^{\circ} - 135^{\circ}\text{C}$ is shown in Fig. 21. The discontinuity at the isotropic transition temperature reflecting the first-order nature of the transition is clearly shown for all the curves. There is also a clear change in the slope in each curve at the temperature corresponding to the melting point (m.p.) of the liquid crystal systems. Helical pitch and critical field continued to be observable and measurable in the supercool region from below the m.p. of PAA till the temperatures at which the samples actually froze over.

The negative slope of the curves reflects the fact that, as temperature increases, increased thermal fluctuation allows easier "stretching" of the helix by the applied magnetic field causing the lowering of the critical field. The slope is less steep in the supercool region. This can perhaps be understood as being caused by increased viscosity and greater density of the liquid in the supercool state causing a more gradual change in the relaxing of cholesteric-induced helix.

The temperature dependence of H_c yields the temperature dependence of the ratio k_{22}/χ_a through Eq. (1.24) which gives

$$\frac{k_{22}}{\chi_a} = \frac{(H_c z_0)^2}{\pi^4}$$

In the temperature range of mesophase, the values of the ratio k_{22}/χ_a are given in Table 7.

Table 7 Values of $\frac{k_{22}}{\chi_a}$ of PAA/CP at different temperature.

T(°C)	T/T _c	c = 0.5 %, z _o = 26.3 μm		c = 0.75%, z _o = 17.5 μm	
		H _c (kG)	k ₂₂ /χ _a	H _c (kG)	k ₂₂ /χ _a
117.7	0.960	5.750	2.351	8.737	2.400
120	0.966	5.656	2.274	8.534	2.290
125	0.978	5.302	1.999	7.676	1.853
130	0.990	4.747	1.602	6.868	1.483
132.5	0.996	4.363	1.353	6.514	1.334

The temperature dependence of k_{22}/χ_a is plotted in Fig. 22 for PAA PAA/CP systems with cholesteric contraction of 0.5 % and 0.75 % respectively.

The temperature dependence of k_{22}/χ_a may be related to the temperature dependence of the order parameter S^{15,30}.

Williams and Cladis related $\frac{k_{22}}{\chi_a}$ to S through the relation

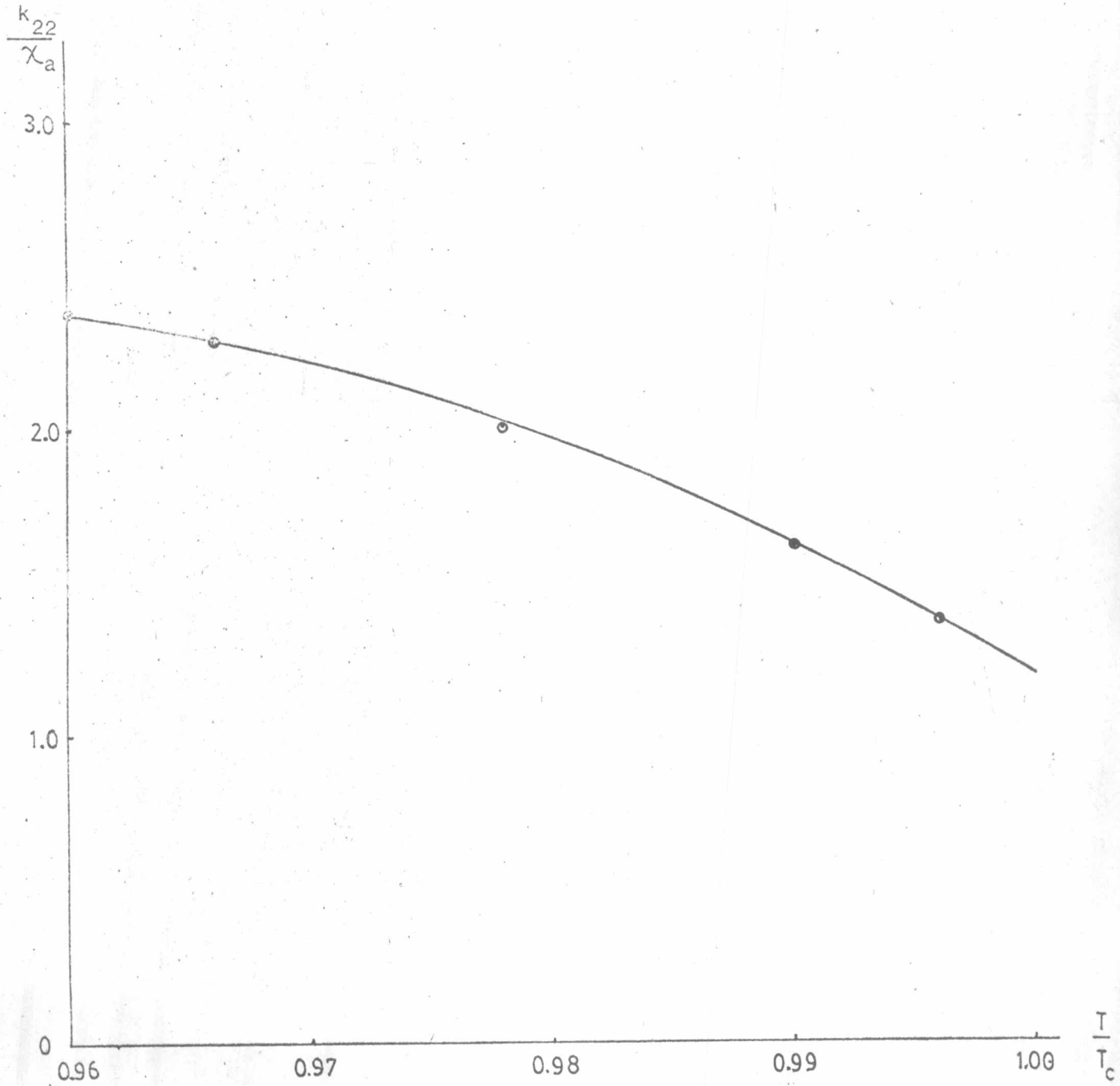
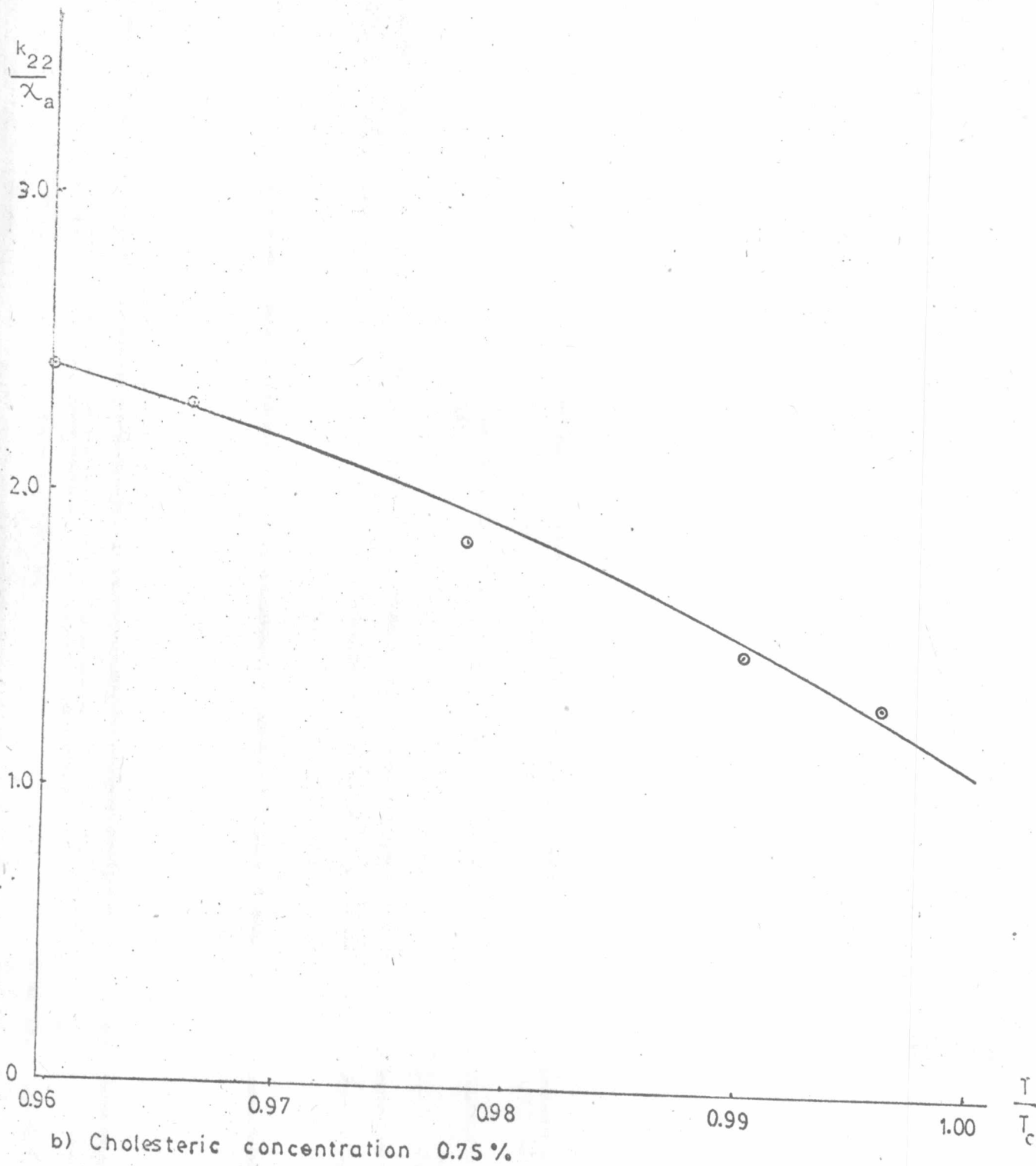


Fig. 22 Temperature dependence of k_{22}/χ_a for PAA/CP

a) Cholesteric concentration 0.5 %



$$S(t) = \alpha \frac{k_{22}}{\chi_a}$$

for MBBA doped with 0.365 % cholesteryl propionate ($z_0 \sim 15 \mu\text{m}$) and obtained $\alpha = 0.206$.

By using $S = 0.52$ at 120°C for PAA²⁶ and doing a scaling of our result at this temperature, we obtain $\alpha = 0.229$ for PAA/CP(0.5 %) and $\alpha = 0.227$ for PAA/CP (0.75 %).

3.7 Summary

In the present investigation, an experimental set up has been constructed for studying the magnetic field effects of liquid crystals. The cholesteric-nematic transition caused by magnetic field in the nematic p-azoxyanisole (PAA) doped with small amounts of cholesteryl palmitate (CP) was studied in detail.

The nematic-cholesteric mixtures were found to exhibit stripe patterns which were linked to the helical structure induced by the cholesteric in the predominantly nematic systems. The formation of stripe pattern shows hysteresis and depends on temperature and magnetic field strength to which the sample is subjected. It is believed that the axes of the helices lie in the plane of the thin film sample and that the axes are oriented at random in plane. The axes tended to orient perpendicular to the direction of applied magnetic field with the samples in mesophase. This tendency became stronger the alignment of the helical axes becomes more complete when the magnetic field cycling was done with the liquid

crystal system in an isotropic state and the sample is then cooled down into mesophase in a strong magnetic field.

The helical pitch was found to be independent of temperature and sample film thickness but varied inversely with the cholesteric concentration reflecting the tendency that the helices are more tightly wound when there is more helix inducing cholesteric in the sample.

The helical pitch was found to diverge as the strength of the applied magnetic field in the manner predicted by de Gennes. The logarithmic divergence as a "critical field" is approached was clearly demonstrated. The measurement of the value of the critical field allowed the determination of the ratio $\frac{k_{22}}{\chi_a}$.

The critical field was studied for its dependence on sample film thickness, cholesteric concentration and temperature. The critical field depended linearly but very weakly and negatively on sample film thickness in the thickness range studied namely from 30 μm to 300 μm . The smallest thickness was some $10^3 - 10^4$ times the length of a PAA molecule and 2 - 3 times the cholesteric pitch and it was concluded that boundary effects of the glass slides were neither very strong nor very long range.

The critical field was found to depend linearly on cholesteric concentration thus giving additional support to the attribution of the stripe pattern to helices of nematic molecules induced by the cholesteric dopant.

The observed critical field dependence on temperature showed clearly the first order nature of the nematic-isotropic transition. It also revealed the existence of a supercool state in the systems investigated..

The critical field dependence on temperature also gave the temperature dependence of the ratio $\frac{k_{22}}{\chi_a}$ which in turn was related to the temperature dependence of the order parameter S. The experimental result agreed well with the results of the self consistent field calculation by Saupe and Maier.³⁰