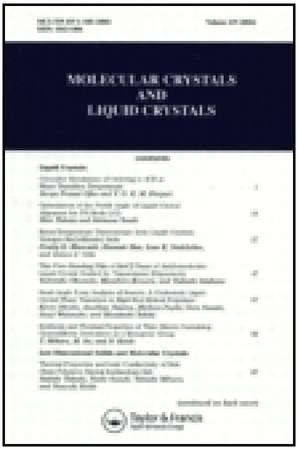

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The Effect of Rhodamine 6G on Phase Transitions in Cholesteryl Ester Mixtures

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The Effect of Rhodamine 6G on Phase Transitions in Cholesteryl Ester Mixtures

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1 INTRODUCTION

Compensated cholesteric mixtures were the subject of a whole range of studies.[1–6] Due to their characteristic properties (the existence of a temperature at which compensation occurs and the dependence of the critical field on temperature), the orientation of guest molecules by compensated cholesteric hosts[7] shows some particular features in comparison to the orienting mechanisms acting within nematic liquid crystals[8–15] or within chiral nematic mixtures.[16,17] When the colour of sample varies due to the influence of the electric field and temperature the guest dye contributes to it as well the compensated cholesteric host.

In this paper we report the modification of compensated cholesteric mixture properties due to the introduction of Rhodamine 6G as guest.

2 EXPERIMENT

The following binary cholesteric mixtures were prepared as hosts: M I–cholesteryl chloride + cholesteryl oleyl carbonate 75:25% (molar); M II–cholesteryl chloride + cholesteryl caprylate 70:30% (molar); M III–cholesteryl chloride + cholesteryl laurate 74:26% (molar); M IV–cholesteryl chloride + cholesteryl nonanoate 70:30% (molar).[4]

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† In order to obtain compensated mixtures at the lowest possible temperatures the corresponding concentrations have been calculated from the diagrams submitted by G. Meier *et al.*[8]

Rhodamine 6G was introduced into the hosts listed above using the following molar guest-host ratios: 1:200; 1:100; 1:50.

The purity of the substances was ensured by thin layer chromatography. The mixtures were dissolved in appropriate solvents, homogenized through stir-up and heated until solvents were fully evaporated. The mixtures were sandwiched by means of a capillarity procedures between two SnO_2 transparent electrodes and separated by mylar spacers while the thickness of each cell was optically measured with accuracy of 1 μm. The size of the active surface was 0.5×0.5 cm^2.

For thermal stability and heating an electrically controlled oven was used; the accuracy of the temperature control was ± 0.1°C. Optical measurements in integral light were carried out with the thermostated cells laid on a polarizing microscope-table IOR-MC5 equipped with a photo-cell and an automatic recorder. It was possible to simultaneously perform micro-structural observations and the recording of the transmission function of temperature and the applied electric field.

Spectral measurements have been carried on an experimental arrangement of the type shown in Figure 1, which consisted of: a tungsten lamp (30 w) with stabilized supply, a thermostated cell located between polaroids, a monochromator (SPM2), a photo-multiplier EMI-9558 QB, a linear d.c. amplifier and a Sephram type graphyspot for the automatic recording of the transmitted signal.

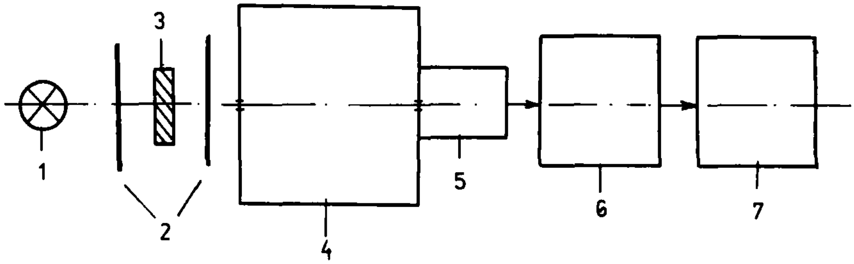


FIGURE 1 Experimental arrangement for measuring light transmission in liquid crystal cells. 1-tungsten lamp; 2-polaroids; 3-termostated sample; 4-monochromator SPM 2; 5-foto-multiplier tube; 6-amplifier; 7-recorder.

3 TRANSITION TEMPERATURES

Using the technique of transmitted light intensity depolarisation (T.L.I.D.) and direct micro-structural observations, the monotrope or enantiotrope character was determined for each mixture and the temperatures corresponding to transitions between their phases were recorded, viz.: solid crystal (C), liquid crystal (LC), isotropic liquid (L) (Table I).

TABLE I

Transition temperatures

Mixture	T_{C-LC} (°C)	T_{C-L} (°C)	T_{LC-L} (°C)	T_{L-LC} (°C)
M I	52		55	54
M I 1:200	50		51	47
M I 1:100		54		52
M I 1:50		52		51
M II		97		71
M II 1:200		91		56
M II 1:100		79		60
M II 1:50		69		60
M III		87		69
M III 1:200	53		65	63
M III 1:100		70		54
M III 1:50		67		45
M IV	51		68	58
M IV 1:200		59		57
M IV 1:100	57		61	60
M IV 1:50	52		61	57

The following mixtures show a monotropic character: M I 1:100; M I 1:50; M II; M II 1:200; M II 1:100; M II 1:50; M III; M III 1:100; M III 1:50; M IV 1:200, the others exhibiting a mesophase state during heating as well as during cooling. Obviously the introduction of Rhodamine 6G has caused some modifications of the transition temperatures between phases.

Combinations with cholesteryl caprylate crystallized very quickly. The other three mixtures have shown super-cooled isotrope phases. (Ex.: M I 1:200; M IV; M IV 1:50). These mixtures are supercooled in the liquid crystal phase as well, but not indefinitely.

4 THE CHOLESTERIC-NEMATIC PHASE TRANSITION

Mixtures were nematized as increasing voltages were applied at the rate of 1 V/s at room temperature.[1] We became particularly interested in the compositions M III and M III 1:100 because they supercooled during the liquid crystal phase for a long period (a few months). Also the times of their response to the application and to the removal of the electric field were shorter than for the other mixtures; furthermore, on M III 1:100 a net effect of colour variation with the temperature and the applied electric field has been ascertained.

The nematization process was investigated for both mixtures between parallel polarizers as well (A || *P*) in the experimental arrangement described in Figure 1. The transmission was measured for several temperatures (Figures 2,3) at a wavelength of $\lambda = 530$ nm corresponding to the peak of Rhodamine 6G absorption range (Figure 4b). The voltage applied varied in 2.5 V steps, each value of the transmission being recorded after the corresponding signal had been stabilized.

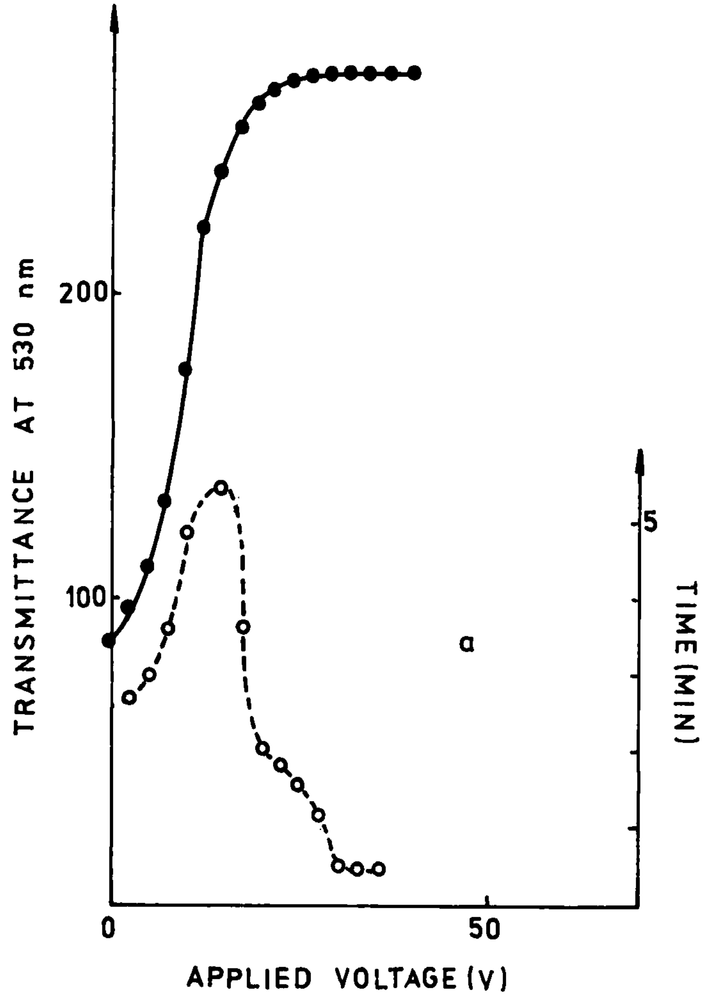
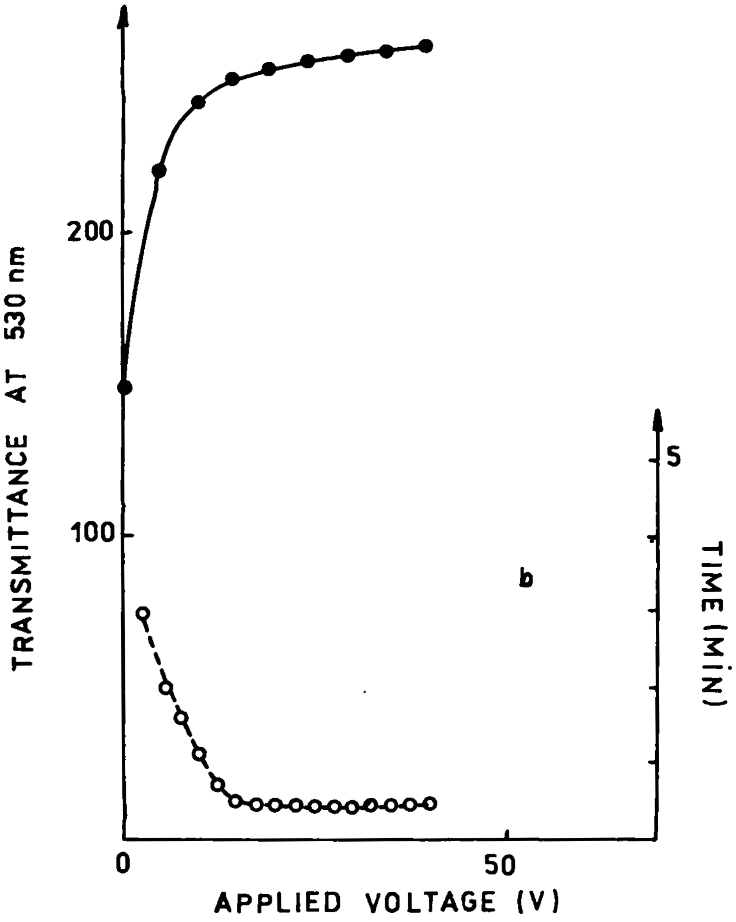
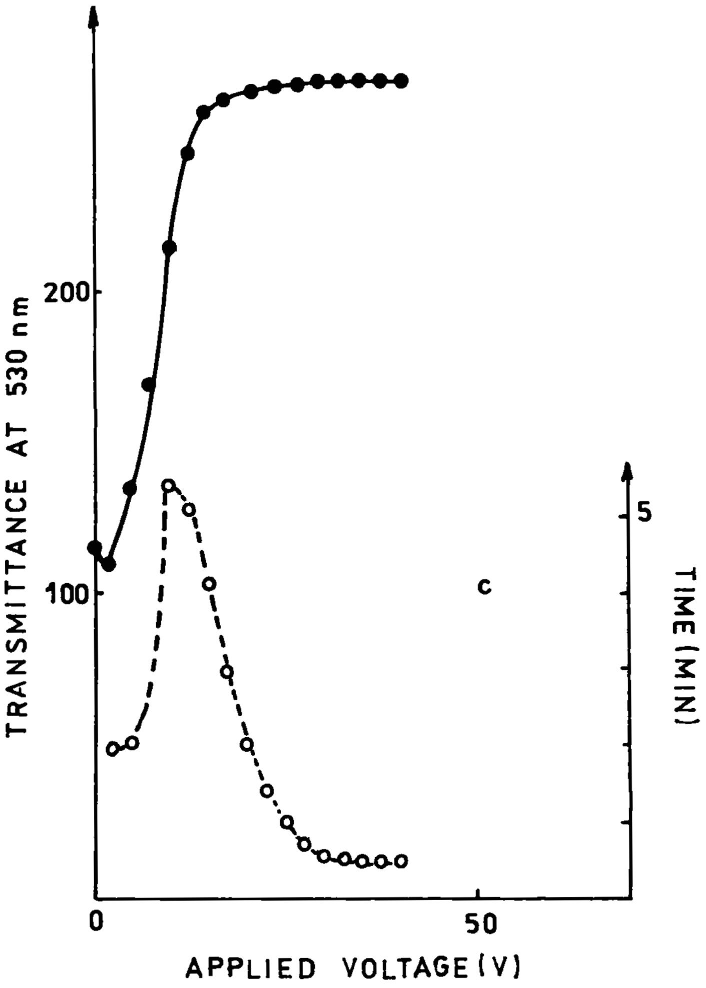
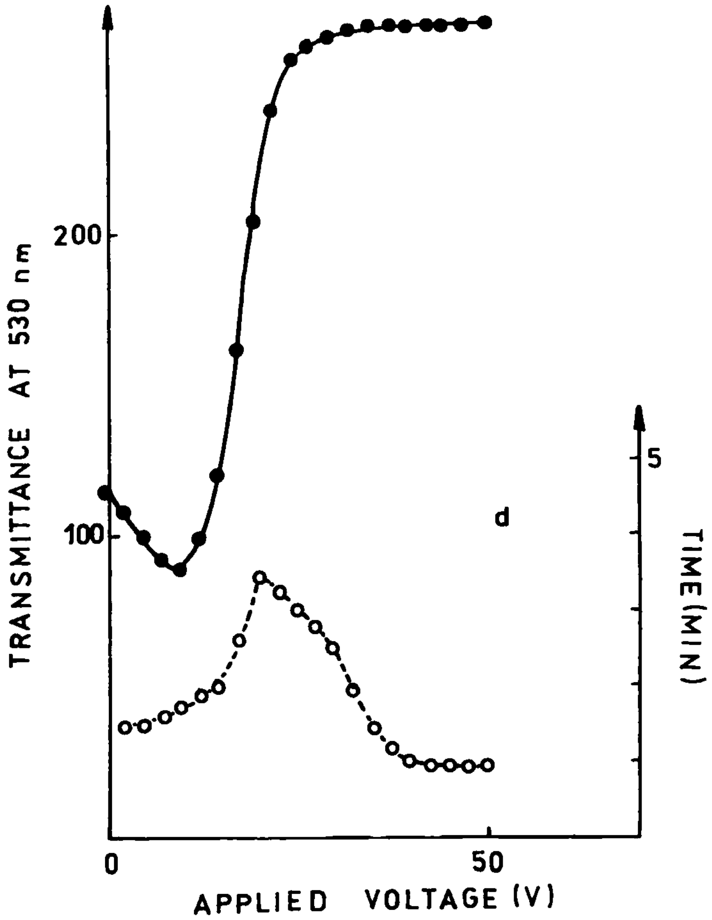
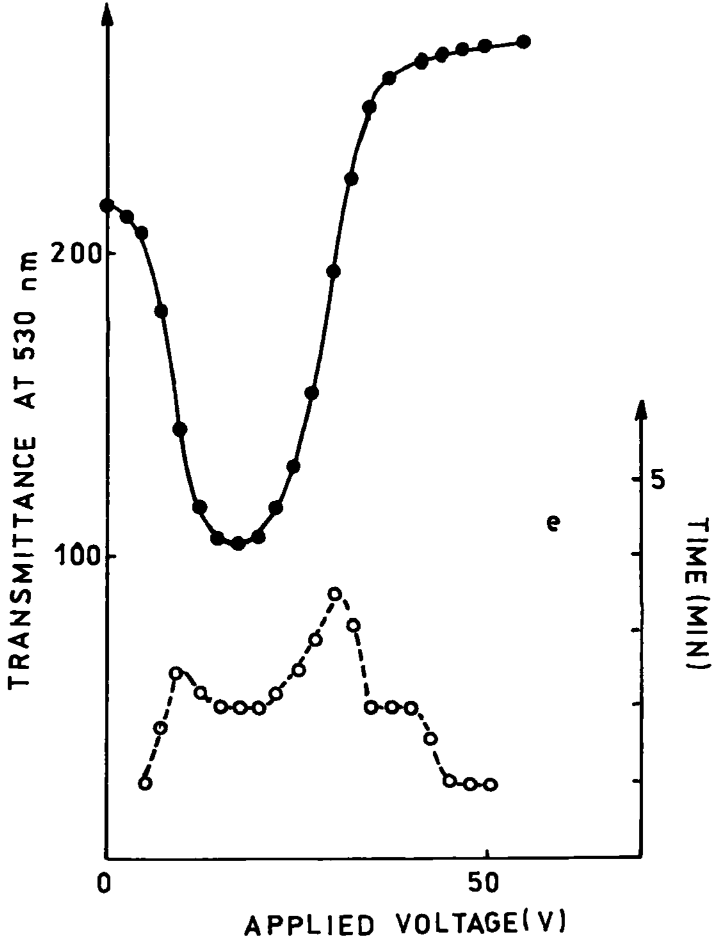


FIGURE 2 Transmittance versus applied voltage and stabilisation time of signal, M III mixture, $\lambda = 530$ nm; *A*||P (untreated electrodes); a-*t* = 20, 5°C; b-t = 25°C; c-*t* = 31°C; d-*t* = 40°C; e-*t* = 49°C; f-*t* = 56.5°C (thickness cell — 30μm).


TRANSMITTANCE AT 530 nm
200
100
0
50
APPLIED VOLTAGE (V)
TIME (MIN)
5
b


TRANSMITTANCE AT 530 nm
200
100
0
50
APPLIED VOLTAGE (V)
TIME (MIN)
5
c


TRANSMITTANCE AT 530 nm
200
100
0
50
APPLIED VOLTAGE (V)
5
TIME (MIN)
d


TRANSMITTANCE AT 530 nm
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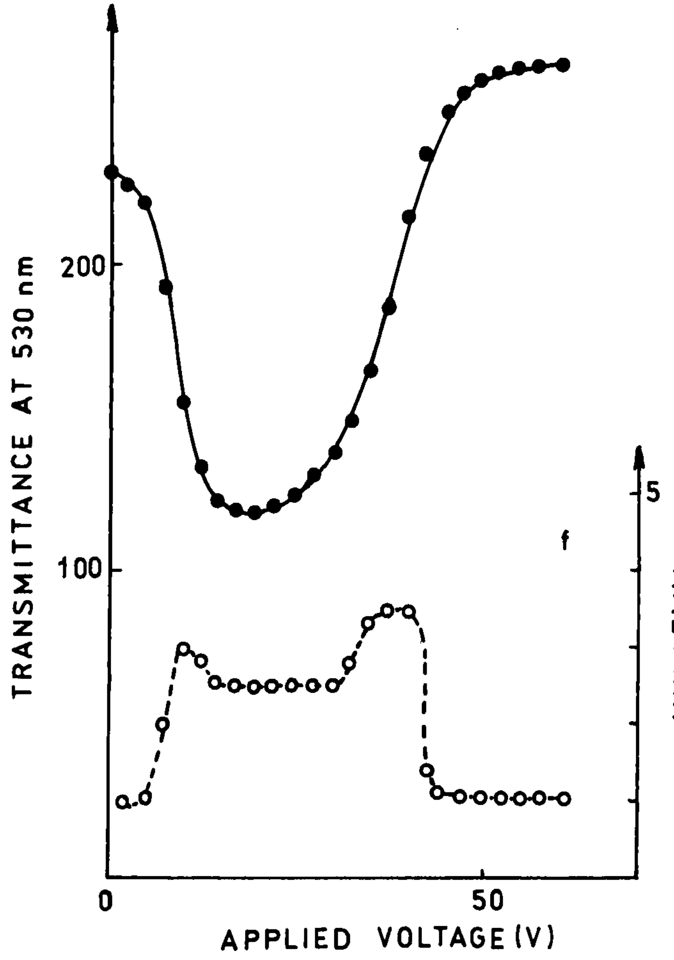
100
0
50
APPLIED VOLTAGE(V)
5
TIME (MIN)
e



At 20.5°C and 25°C (Figure 2 a,b) during the nematization process of the host mixture M III, the value of transmission increases when the field increases, while at 31°C; 40°C; 49°C and 56.5°C (Fig. 2 c,d,e,f) the nematization is achieved quite differently. The transmission first decreases when the field increases, and then it increases as in the previous case, when the nematization process takes place properly. Direct microstructural observation has revealed a "finger print" homeotropic structure before the field is applied, (at 20.5° and 20°C); at 25°C, M III is close to nematization (the pitch directly measured on the finger print texture was about 3 μm). At 31°C, 40°C, 49°C and 56°C, the texture was planar or focal conic. Relying

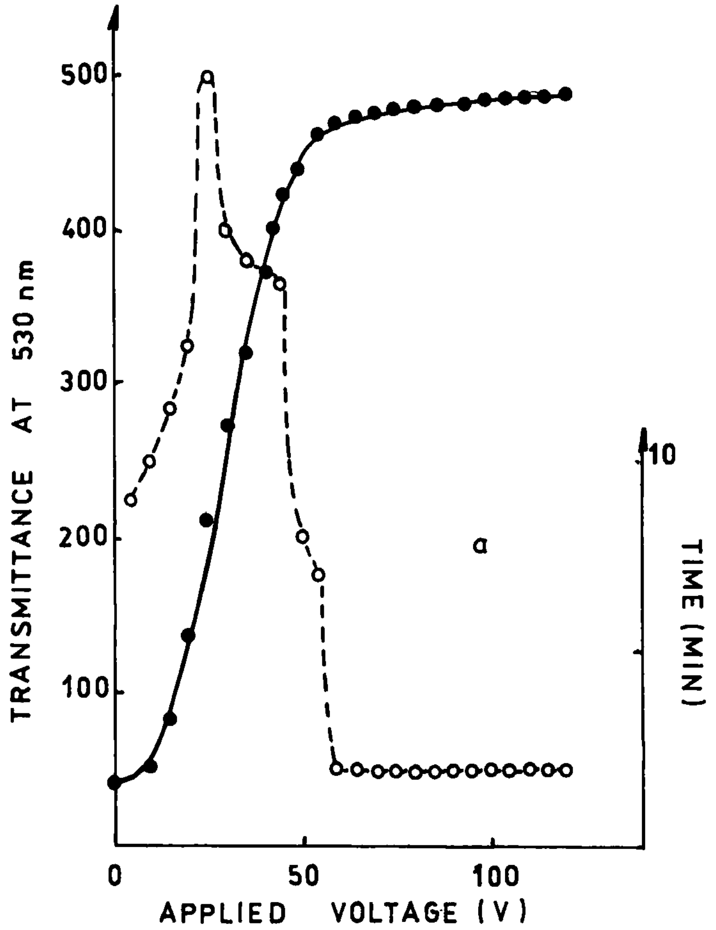
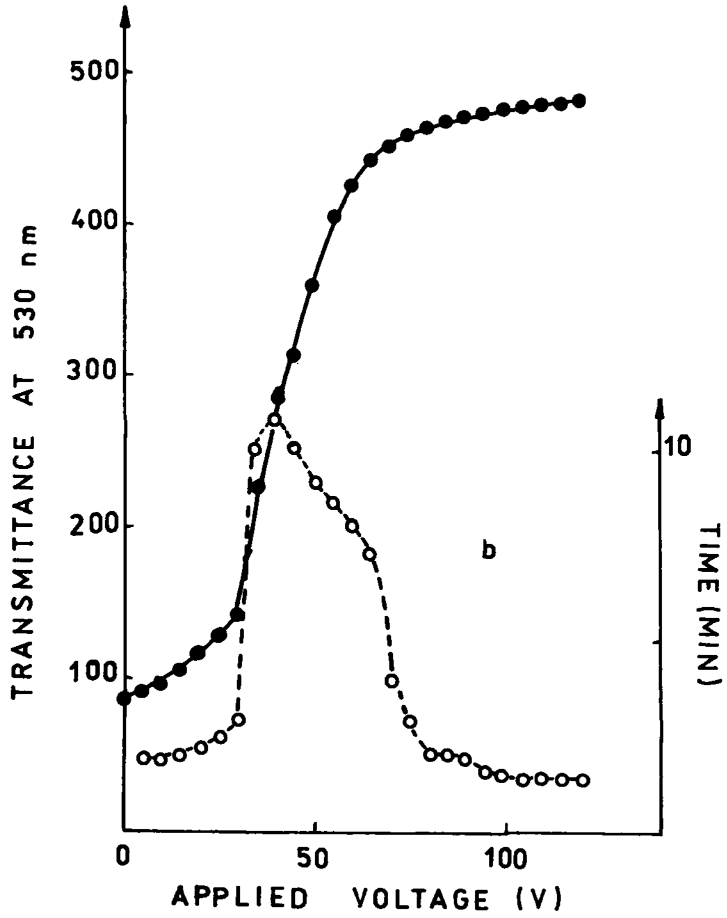
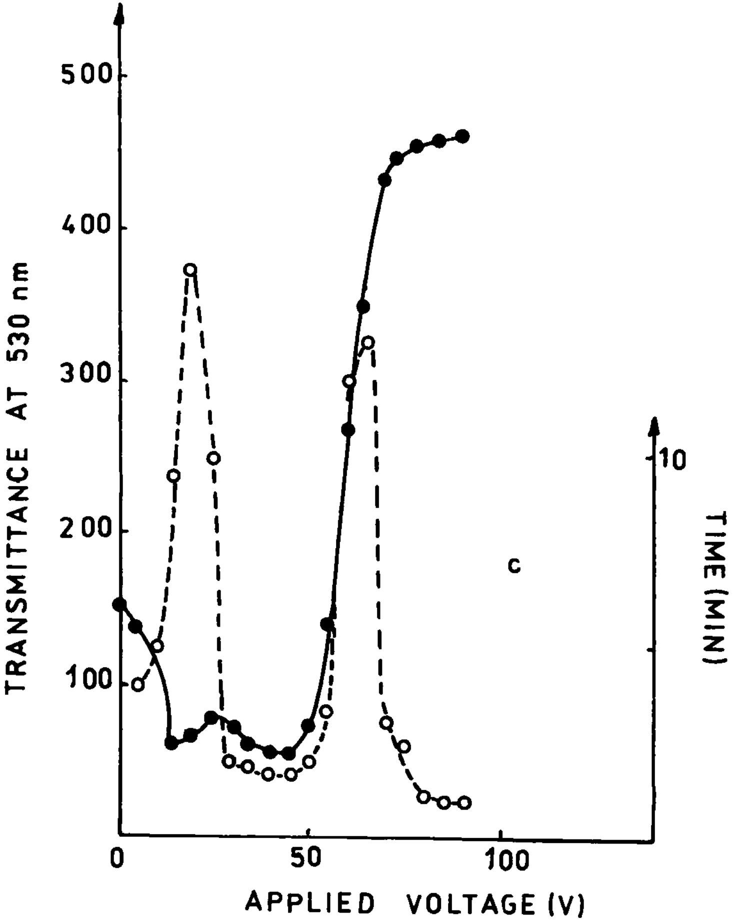


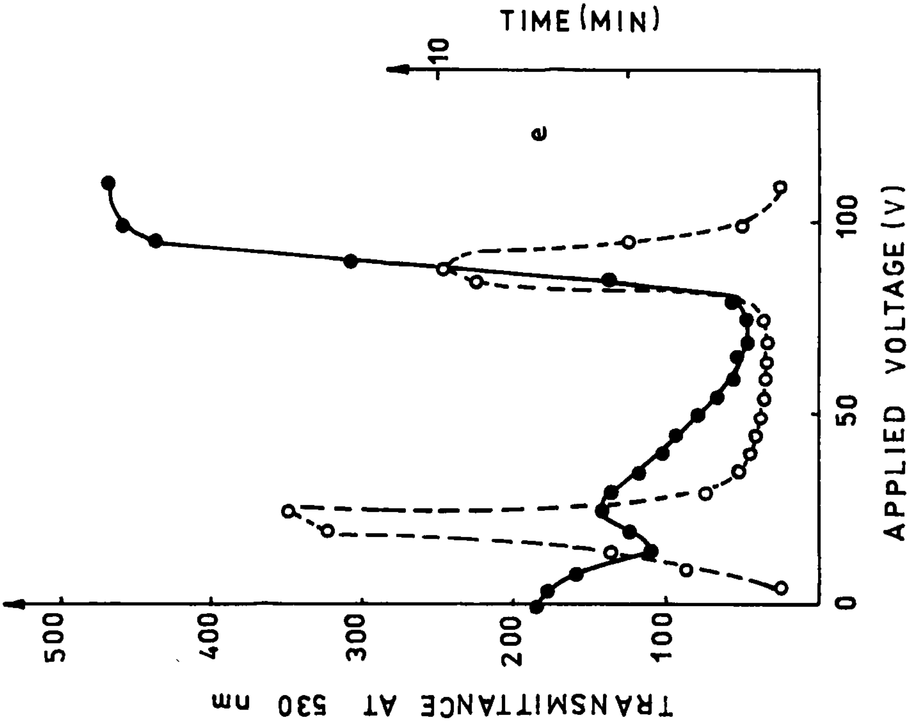
FIGURE 3 Transmittance versus applied voltage and stabilisation time of signal; M III: 100 mixture; $\lambda = 530$ nm, $A \| P$, (untreated electrodes); a-$t = 21$°C; b-$t = 24$°C; c-$t = 31$°C; d-$t = 35.5$°C; e-$t = 40$°C; f-$t = 49$°C (thickness cell — 30 μm).

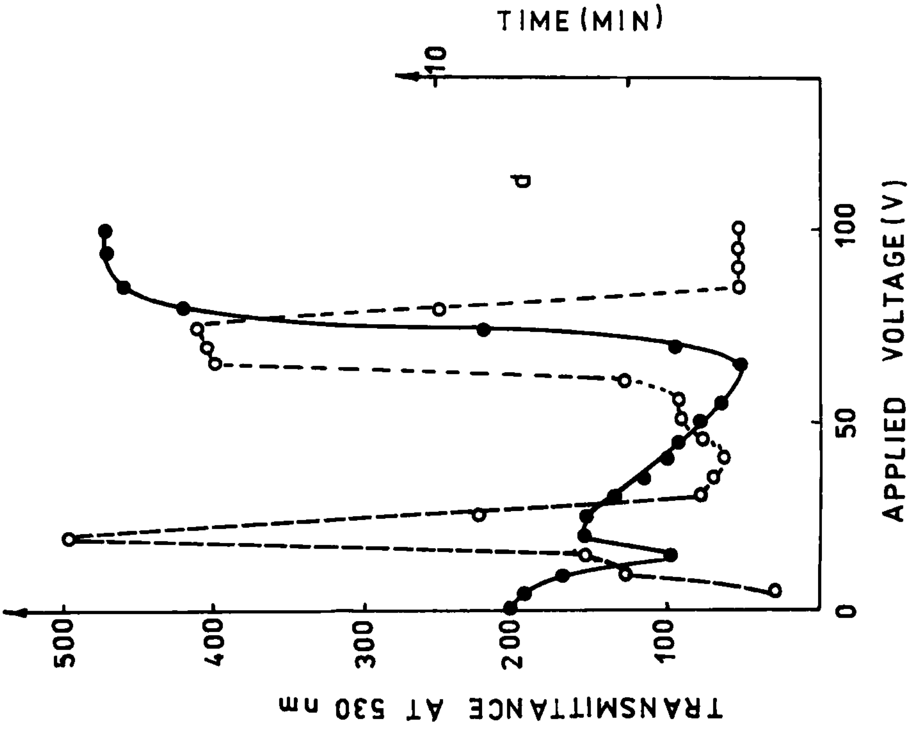
on the results of these measurements we estimated that the temperature around which the mixture M III is compensated ranges from 25°C to 31°C. In Figure 2 we have also shown the time during which the signal was stabilized for each applied field. It is noticed that, for the fields when nematization occurs as well as for those where the cholesteric axis tilts (according to transmission minima)[5] longer times were necessary for stabilization.

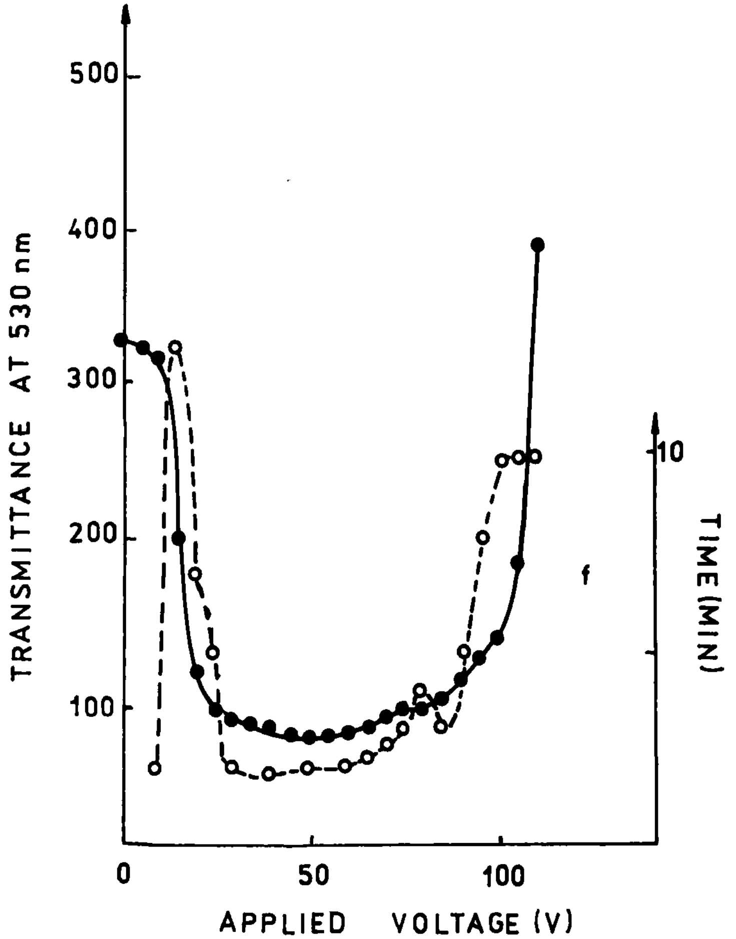
In Figures 3 a,b,c,d,e,f we have presented the same types of measurements carried out for M III 1:100. At 21°C and 24°C (Figures 3 a,b), the transmission increases when the applied field increases (M III). At 31°C, 35.5°C, 40°C, 49°C (Figures 3 c,d,e,f) a certain phenomena occur, namely, (1) the decrease of


TRANSMITTANCE AT 530 nm
500
400
300
200
100
b
10
TIME (MIN)
0
50
100
APPLIED VOLTAGE (V)


TRANSMITTANCE AT 530 nm
500
400
300
200
100
c
10
TIME (MIN)
0
50
100
APPLIED VOLTAGE (V)


e
TIME (MIN)
10
TRANSMITTANCE AT 530 nm
500
400
300
200
100
0
50
100
APPLIED VOLTAGE (V)


d
TIME (MIN)
10
TRANSMITTANCE AT 530 nm
500
400
300
200
100
0
50
100
APPLIED VOLTAGE (V)



the transmission with the growth of the field; (2) the transmission tends to rise for values of the electrical field at which the host mixture begins to nematize; (3) a decrease of the transmission to a value that is inferior to that reached in 1; (4) an increase of the transmission which corresponds to nematization.

In comparison with the host mixture (Figure 2) the voltage range for which transmission is near to the minimal value is larger and the nematizations occur for greater values of the fields. When the transmission is a minimum the texture is focal conic and intensely coloured.†

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† The thickness of the cells for which these measurements were carried out (Figs. 2 and 3) were identical, i.e. 30 μm.

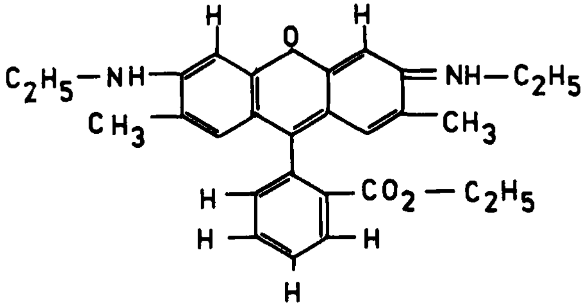

FIGURE 4a Rhodamine's 6G molecule (a) and its absorption spectrum (b).

The stabilization time of the transmission for each applied field was longer for M III 1:100 than that for M III (Figure 3).

Figure 5 presents the diagrams of the critical field value versus temperature for M III and M III 1:100. The critical field values have been obtained obtained by determining the concavity change points (when begins the nematisation for the curves in Figures 2 and 3. On the same Figure 5 we have also marked the values of the critical fields that were determined by method of T.L.I.D.[19-21] T.L.I.D. traces were obtained by applying to isotropic mixtures the corresponding electric field and by cooling the samples at the rate of 3°C/min (Figures 6 and 7).

The Bragg diffraction images recorded in a He-Ne laser beam at various temperatures during cooling from the isotropic phase are shown in Figure 8. The diameter of the diffraction ring decreases with the temperature (Figure 8 a,b,c) consequently the pitch increases.[22] Around 29°C (Figure 8 d), the diffraction image becomes a point. This corresponds to the hemeotropic nematic phase of the compensated mixture.[22] For temperatures below 29°C (Figure 8 e) a second diffraction ring appears. The direction of the laser beam polarization plane slightly rotates counterclockwise for $t > 29$°C while for $t < 29$°C rotation is clockwise.†

Because of the scattering of the central spot of the laser beam it was not possible to evidence the difference between the compensation temperatures by analysing the diffraction patterns recorded around 29°C for both M III and M III 1:100, although this difference normally exists.

In Figures 9,10,11 we have shown the transmission spectra for different temperatures and different applied electric fields, for the host M III as well as for M III 1:100. The samples were lighted at a normal incidence. The

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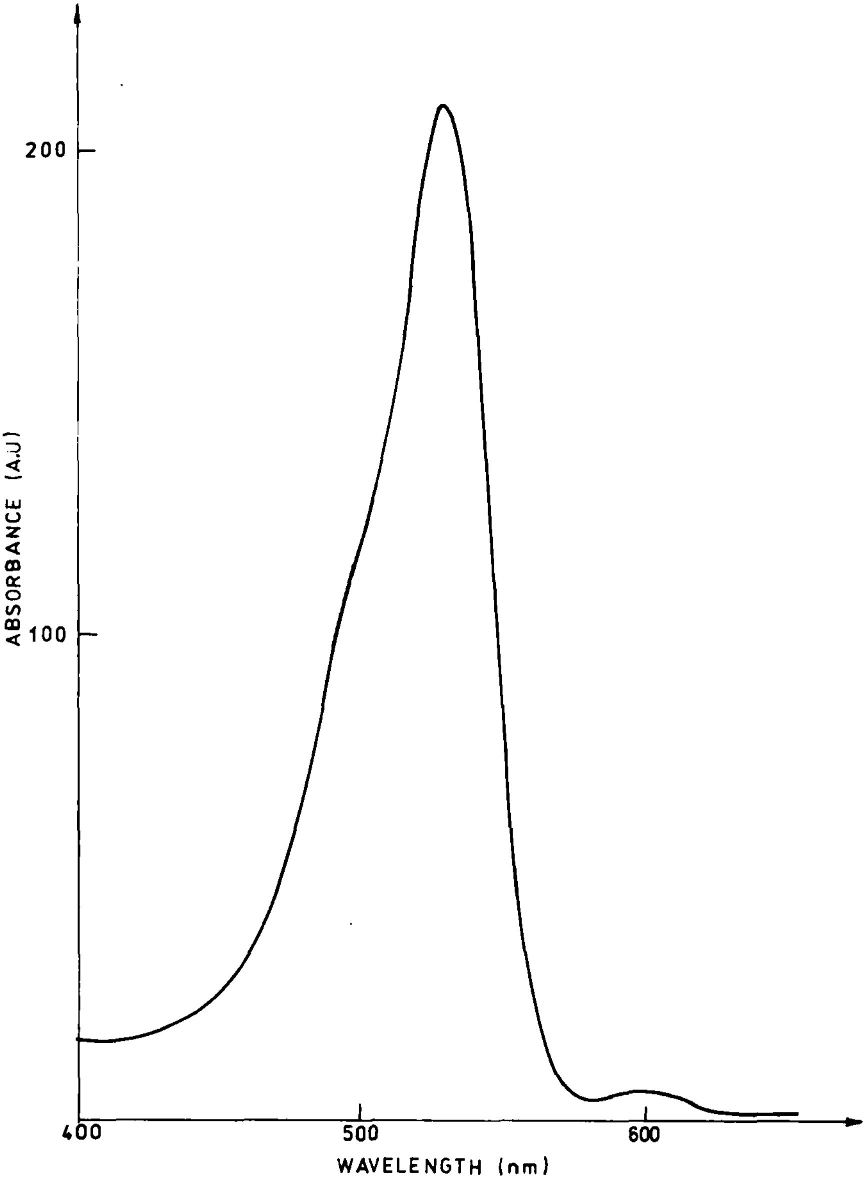
† In the absence of the sample, the laser beam is polarized in a vertical plane; the photoplates onto which the diffraction figures were recorded were displayed in the same position with respect to the beam.



(b)

transmission spectra depending on the applied field, recorded for a M III sample placed between parallel polarizers (Figure 9) are all shifted upwards when field variation is similar to the variation of the transmission for $\lambda = 530$ nm, for temperatures higher than 29°C (Figure 2).

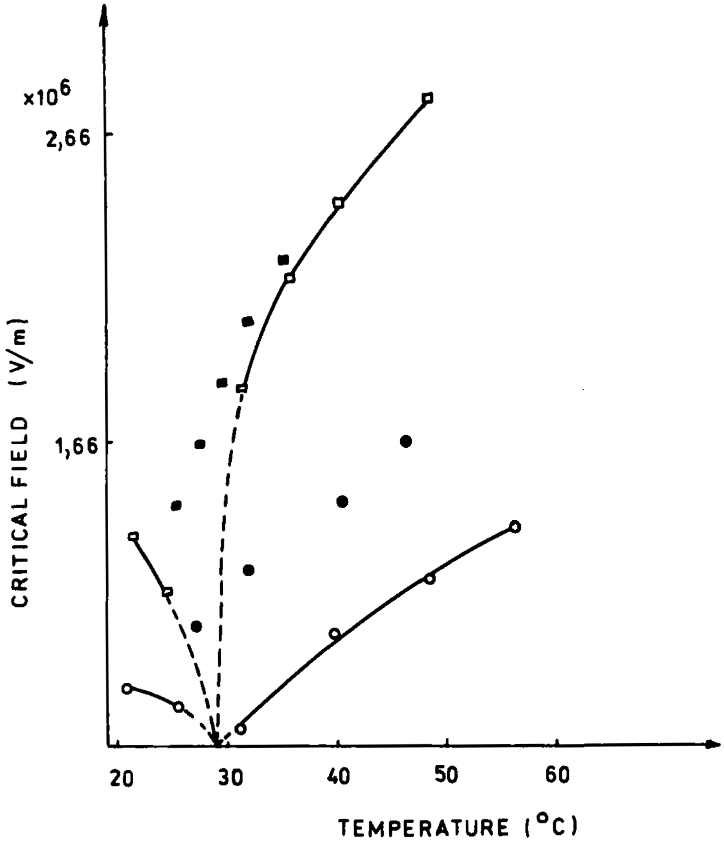


FIGURE 5 Critical field versus temperature diagram—M III mixture (calculated values from dependences represented in Figure 2)—M III 1 : 100 mixture (calculated values from dependences represented in Figure 3)—M III mixture (calculated values from depolarized light intensity measurements—Figure 6).—M III 1:100 mixture (calculated values from depolarized light intensity measurements—Figure 7).

At first the transmission decreases than it rises towards nematization.

Figure 10 shows the transmission spectra during sample cooling, in a non-polarized light, for M III 1:100.

The variation of transmission spectra function of the applied field, in non-polarized light at the temperature of 37.5°C for M III 1:100 has been presented in Figure 11. Inside the spectra obtained for M III 1:100 for different temperatures and applied electric fields an absorption range appears around $\lambda = 530$ nm wavelength corresponding to the absorption band of the guest Rhodamine 6G.

The value of the contrast ratio at different temperatures, calculated as the ratio between the transmittance value in the nematic state and the minimum

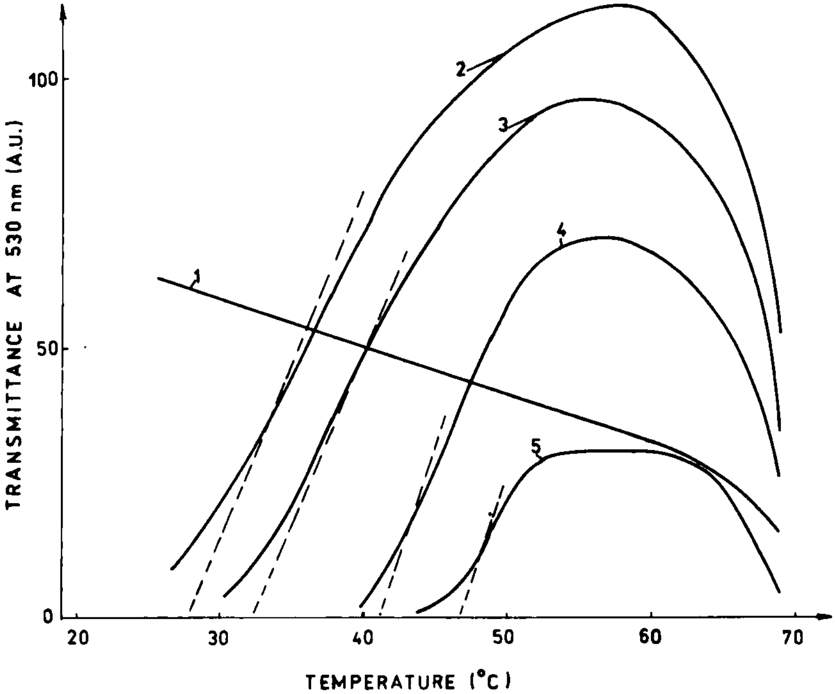


FIGURE 6 Depolarized light intensity in electric field; M III mixture—λ = 530 nm ($A \perp P$); 1-0 V; 2-20 V; 3-30 V; 4-40 V; 5-50 V.

value of transmittance in the cholesteric state, at λ = 530 nm, (Figure 12) for both mixtures studied. A decrease of the contrast can be noticed in the vicinity of the nematization temperature, followed by an increase when the temperature rises, after which the peak is reached at 37.5°C. The contrast will decrease when the temperature increases. The shape is similar for both mixtures, but the value of the contrast in M III 1:100 is three times larger than in M III at the temperature of 37.5°C. For this reason, we have drawn the transmission spectra for different fields for M III 1:100 (Figure 11), at this temperature.

5 DISCUSSION AND CONCLUSIONS

The study carried out has revealed several modifications of the compensated properties of the binary mixtures in the presence of the Rhodamine 6G guest.

The variation of transition temperatures was ascertained for all combinations, i.e. the guest has caused a decrease of these temperatures; moreover,

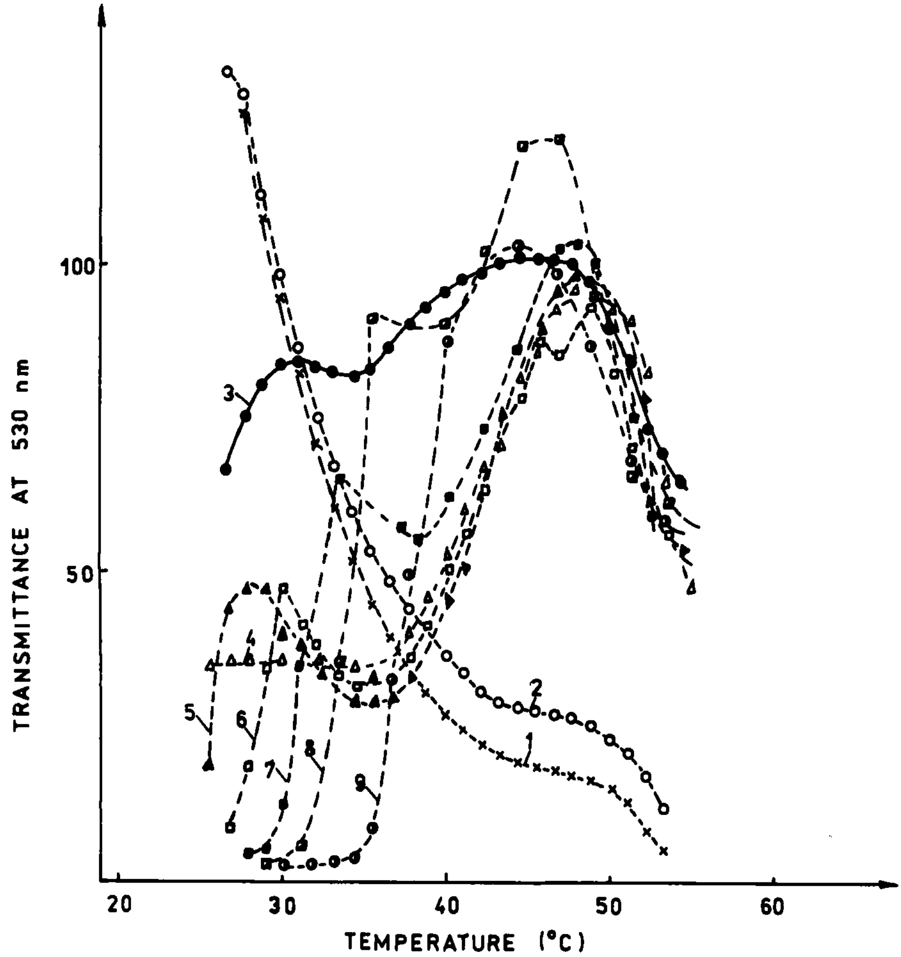


FIGURE 7 Depolarized light intensity in electric field; M III 1:100 mixture; $\lambda = 530$ nm ($A \perp P$) 1-0 V; 2-10 V; 3-20 V; 4-30 V; 5-40 V; 6-50 V; 7-60 V; 8-70 V; 9-80 V.

the time they remain in a supercooled state in the mesophase is much longer for the mixtures containing Rhodamine 6G.

The analysis of the first nematization processes[7] has enabled us to notice the difference in the way these processes develop, viz.: for host mixtures and for those that have a guest. The 90° tilt of the cholesteric helix which corresponds to the minimum of the transmittance ($A \| P$), especially for mixtures with a Rodamine concentration 1:100, took place over a larger voltage range than for host mixtures. More detailed studies carried out on M III and M III 1:100 led to more precise information concerning the evolution of these

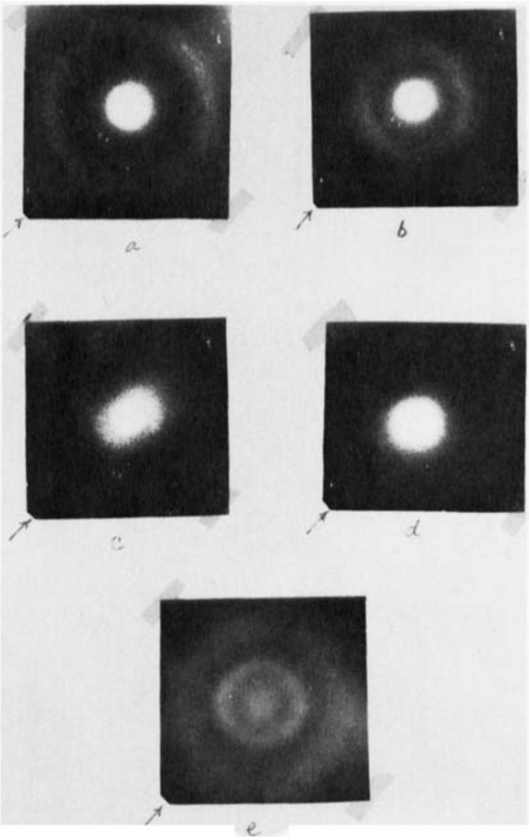


FIGURE 8 Light diffraction patterns; M III 1 : 100 mixture a-t = 42°C; b-t = 35°C; c-t = 32°C; d-t = 29°C; e-t = 23°C.

nematization processes. We consider that the measurement of transmittance as a function of the applied field at various temperatures, the signal being recorded after the stabilization of the value for each applied field, gives very useful and adequate information for the plotting of the diagrams for $E_c = f(T)$. At the same time, this type of measurement provides the temperature around which the cholesteric helix is reversed and indirectly the right-or left-handed character of the mixture is subject to that temperature.† These conclusions agree with those obtained interpreting the diffraction patterns recorded in a laser beam at various temperatures. Both mixtures have a

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† We refer all signs of rotation to an observer who looks in the direction of the incident light with the same convention as B. H. de Vries.[23]

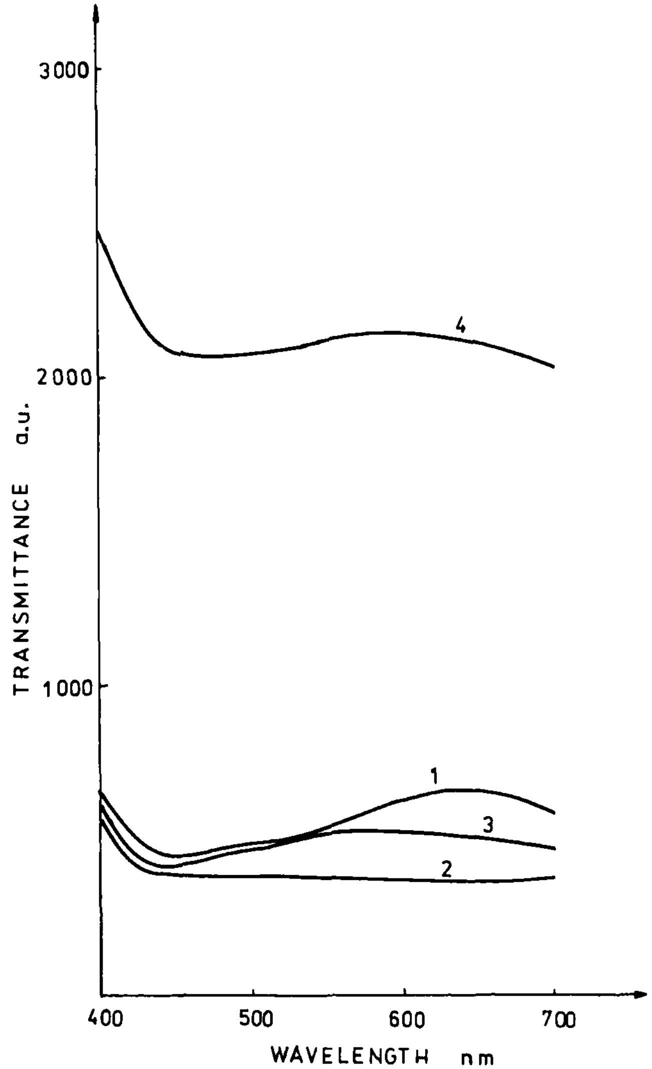

FIGURE 9 Transmittance spectrum; M III mixture ($A \parallel P$), $t = 33°C$; 1-0 V; 2-10 V; 3-20 V; 4-30 V.

right-handed character and a positive pitch for $t < 29°C$ and a left-handed character with negative pitch at higher temperature.

The critical field determined by means of the T.L.I.D. procedure (Figures 5, 6 and 7) has greater values at the same temperature than the critical fields determined by processing the transmission plot dependency of Figures 2 and 3, because the T.L.I.D. measurements were carried out for varying temperatures.

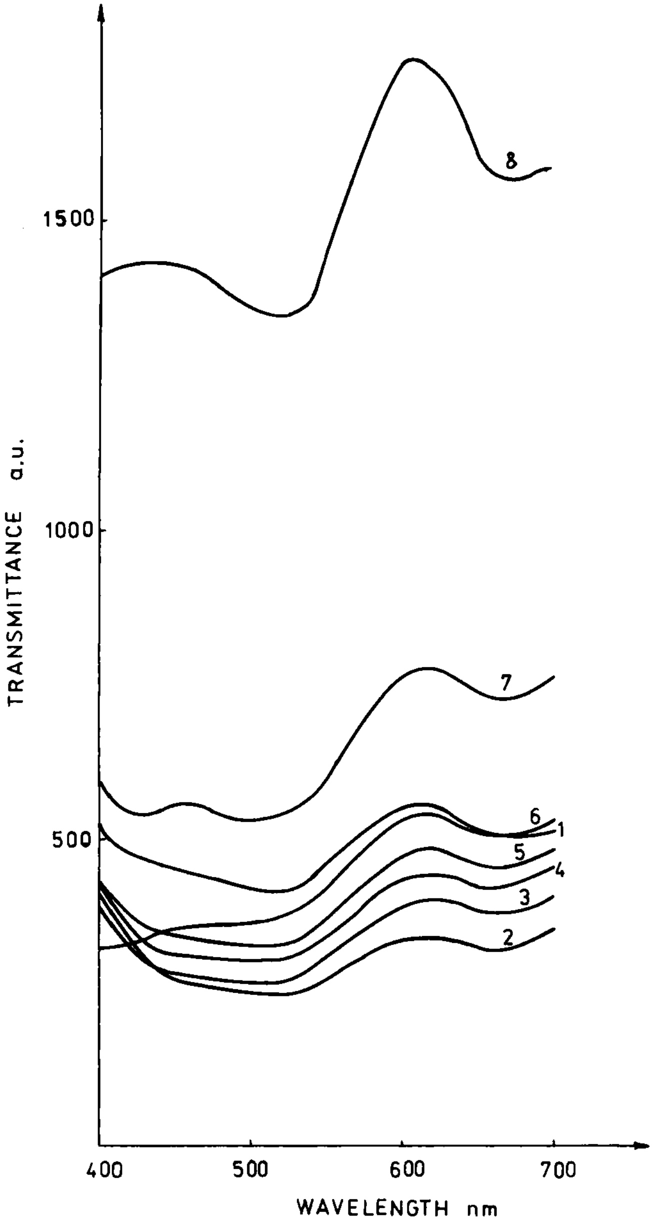

FIGURE 10 Transmittance spectrum versus temperature; M III 1:100 mixture, unpolarised light (at cooling) 1-t = 29°C; 4-t = 37.5°C; 7-t = 60°C; 2-t = 32°C; 5-t = 45°C; 8-t = 65°C; 3-t = 35°C; 6-t = 52.5°C.

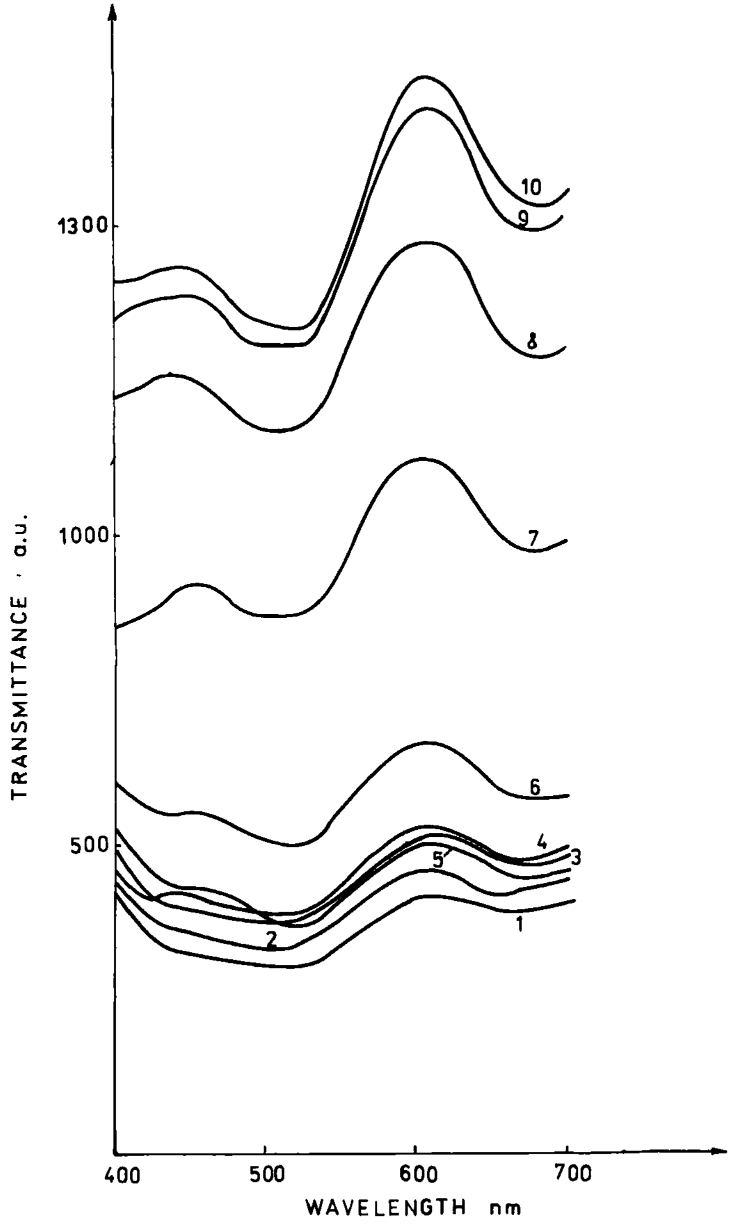

FIGURE 11 Transmittance spectrum versus applied voltage; M III 1 : 100 mixture, unpolarised light, $t = 37.5°C$; 1-$U = 10$ V; 5-$U = 50$ V; 9-$U = 90$ V; 2-$U = 20$ V; 6-$U = 60$ V; 10-$U = 100$ V; 3-$U = 30$ V; 7-$U = 70$ V; 4-$U = 40$ V; 8-$U = 80$ V.

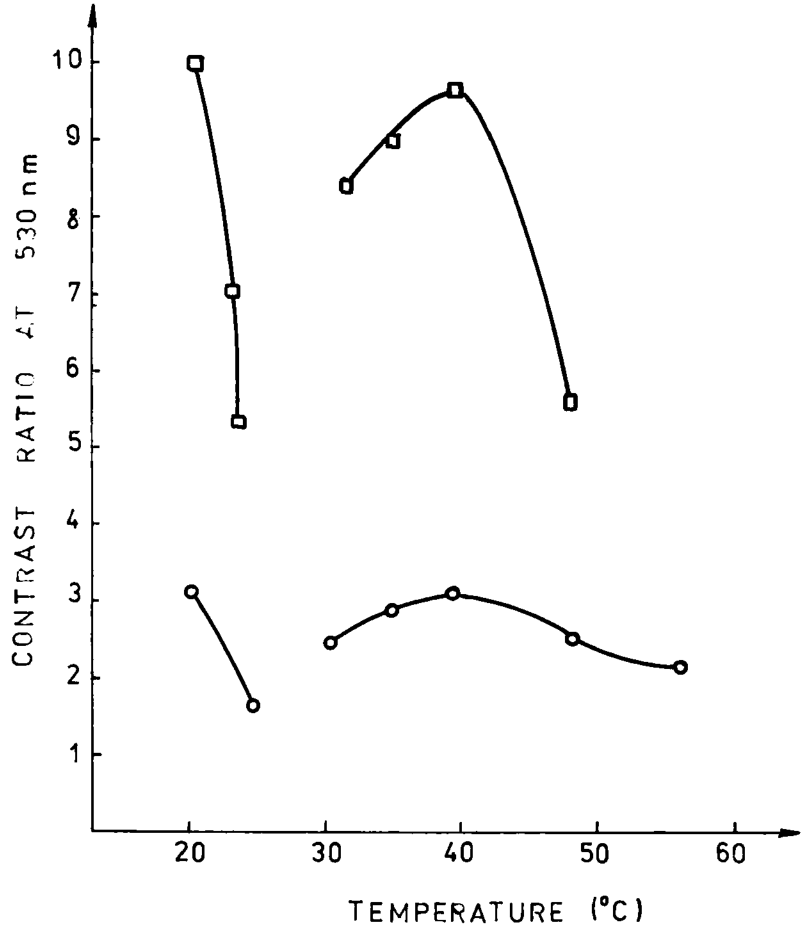

FIGURE 12 Contrast ratio versus temperature; 0–M III mixture; □–M III 1:100 mixture.

As a matter of fact, in a previous report[21] it has been shown that this method could not be used at all for small nematization fields, at temperatures in the vicinity of the compensation temperature. This conclusion is valid for the present case too. The critical fields determined by means of the T.L.I.D. procedure may produce nematization instantaneously at the corresponding temperature; those that were determined by means of measurements carried under steady-state conditions represent the lowest values of the fields for which nematization may take place at that temperature. The T.L.I.D. plots for M III 1:100 (Figure 7) show the decrease of the transmittance (A ⊥ *P*) occurring before the nematization. The minima under discussion agree with the peaks that arise in *A*||*P* (Figure 3 d,e,f). The differences between the temperatures and the fields at which minima appear in $A \perp P$ and those at which maxima appear in $A \| P$ are obviously explained by the fact that the heat conditions of the measurements were different, i.e. a temperature decrease rate of 3°C/min was used in the first case and in the second the temperature was kept constant all during the time interval at the end of which the stabilized value of the signal was recorded.

It may be stated that the evolution of spectra for M III 1:100 investigated at different temperatures and values of the applied electric field are first of all determined by the behaviour of the host mixture. At every temperature, exceeding the compensation one, when the value of the field increases, starting from zero there are at first values which produce a tilt of the cholesteric helix in M III. After this, the transmission grows a little (Figure 3 d,e,f), showing the nematizing tendency of the host. Further the transmission decreases again and, finally, it increases due to the nematization.

We consider that the guest Rhodamine 6G which, due to the modification of its orientation, increases the light absorption thus extending the voltage range in which absorption takes place before nematization.

It may be noticed that the maximum absorption inside such types of devices takes place around a certain value of the applied field which depends on the temperature. Above this value, when the field increases, the transmission grows too. Therefore, the behaviour of these devices differ from other types of devices which operate by means of the "guest-host" interaction which is coloured or colourless when the field is missing; but when the field is applied, they are discoloured or coloured, respectively.[13–15] The contrast ratio, in M III 1:100 was of about 3 (three) times greater than in M III, which proves the advantage of introducing Rhodamine into the chosen host.

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