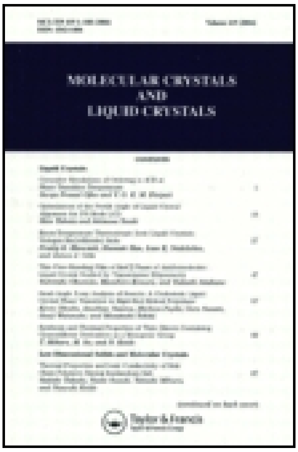

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Polar Systems with Induced A_d Phase and Selective Reflection for High Pressure Sensing

Roman Dabrowski [a], Tomasz R. Woliński [b], Marzena Brodzik [a], Jerzy Dziaduszek [a], Aleksandra Jarmolik [b], Wojciech J. Bock [c] & Stanisław Kłosowicz [a]

[a] Military University of Technology, 01-489, Warsaw, Poland
[b] Warsaw University of Technology, 00-662, Warsaw, Poland
[c] Université du Québec à Hull, Hull, Québec, J8X 3X7, Canada

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POLAR SYSTEMS WITH INDUCED A_d PHASE AND SELECTIVE REFLECTION FOR HIGH PRESSURE SENSING

ROMAN DĄBROWSKI+, TOMASZ R. WOLIŃSKI*, MARZENA BRODZIK+, JERZY DZIADUSZEK+, ALEKSANDRA JARMOLIK*, WOJCIECH J. BOCK#, STANISŁAW KŁOSOWICZ+
+Military University of Technology, 01-489 Warsaw, Poland
*Warsaw University of Technology, 00-662 Warsaw, Poland
#Université du Québec à Hull, Hull, Québec, J8X 3X7 Canada

Abstract Multicomponent mixtures composed of two group of polar nematics: one taken from tri-ring or four-ring compounds with the cyano terminal group and the second taken from biring cyano compounds were studied. In these systems the induced smectic A_d phase in the form of a nematic 'island' surrounded by a nematic 'see' occurs and after introducing a chiral component a TGB_A phase is created and a selective reflection of light with a reverse colour sequence upon temperature (from blue to red) is observed. The shape of the induced A_d phase and the concentration of the chiral components influences the properties of the selective reflection. The mixtures with the selective reflection of light were dispersed in a polymer and the obtained foils were tested as sensors of pressure.

INTRODUCTION

Recently[1,2] in our laboratory we have discovered that in bicomponent mixtures comprising nematic polar compounds with the cyano terminal group the *smectic* A_d

phase was induced in the form of a closed area inside the nematic area (a nematic 'island' surrounded by a nematic 'see'), when the compounds were chosen accordingly to the specified following rule. One nematic component ought to be taken from tri or four ring compounds exhibiting virtual A_d properties and the second one from two-ring nematic compounds. The both groups of compounds have a dimeric structure and for members with the longer alkyl tail they have the smectic A_d phase and the first component shows the N-A_d-N_{re}-A_1 or N-A_d-N_{re} phase sequence.

In the bicomponent mixtures with the induced smectic A_d phase which were studied until now this phase was observed in a thermodynamically unstable region (below the melting points of the mixtures) so it was impossible to determine exactly the shape of the smectic island in the whole concentration and temperature range. We decided to investigate the multicomponent mixture in which the induction of the A_d phase occurs to find thermodynamically stable systems in a wide temperature region, including room or even lower temperature. Such systems are also necessary for applications.

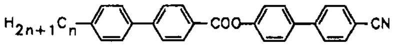
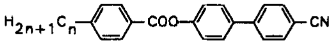
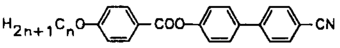
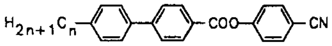
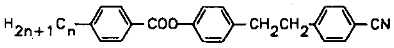
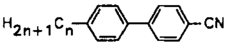
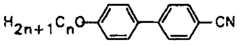
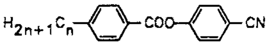
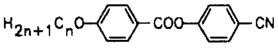
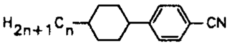
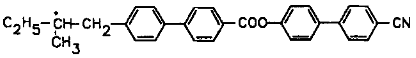
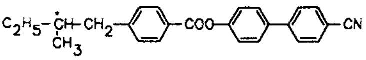
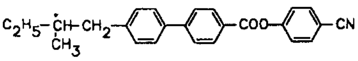
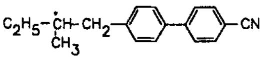
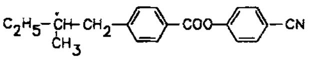
The systems with the 'nematic island' in the three-component mixtures containing two polar components and one nonpolar component were investigated by Ilian *et al.*[3] They found that those systems were sensitive to pressure. We supposed that our system with induced A_d doped with chiral compounds should exhibit a selective reflection of light and the reflective colour should be sensitive to pressure. We have been searching for such liquid crystalline material for sensing of hydrostatic pressure.[4,5]

EXPERIMENTAL

Liquid crystal compounds and mixtures

Liquid crystal compounds used to formulate multicomponent mixture are listed in Table 1. These compounds were prepared and purified in our laboratory. The methods of preparation and mesogenic properties are very well known from the literature. Only some chiral analogues, compounds 11, 12, 13 are new compounds prepared specially for the purpose of this work.

TABLE I Nematic components of mixtures

Multiring components with virtual smectic A_d properties	Biring components with dimeric structure
A	B
1  a) n=7 Cr 123 S_{AI} 136 N 350 I b) n=6 Cr 141.5 S_{AI} 158.7 N 360 I c) n=5 Cr 139.5 S_{AI} 168 N 380 I 2  a) n=7 Cr 90 N 222 I b) n=6 Cr 93 (S_{AI} 41.8) N 231 I c) n=5 Cr 109 (S_{AI} 60) N 240 I 3  a) n=7 Cr 89 (S_{AI} 52) N 246.5 I 4  a) n=7 Cr 105 N 211.5 I 5  a) n=7 Cr 89.8 N 148.5 I	6  a) n=7 Cr 30 N 43.9 I b) n=5 Cr 22.5 N 35.7 I 7  a) n=7 Cr 54 N 75.5 I b) n=5 Cr 50 N 69 I 8  a) n=8 Cr 45 N 53 I b) n=7 Cr 29 N 57 I c) n=5Cr 61.1 (N 57.8) I 9  a) n=8 Cr 75.4 N 84.3 I 10  a) n=7 Cr 30.2 N 57.8 I
Chiral analogues	
Ch_A	Ch_B
11  Cr 148 N* ~400 I[*] 12  Cr 96.5 N* 210.5 I[*] 13  Cr 101 S_A 194 I[*]	14  Cr 4 (N* -30) I 15  Cr 35.3 (N* -1) I[*]

[*] - this work

Four base mixtures A, A_1, B and B_1 of the composition listed in Table II were prepared.

TABLE II The composition of base mixtures A, A_1, B and B_1

A	wt%	A_1	wt%
1a	13	1a	7.0
1b	18	1b	10.0
1c	14.8	1c	8.0
2a	28.8	2a	20.0
3a	25.4	2b	10.0
		2c	10.0
		3a	20.0
		4a	10.0
		5a	5.0
B	**wt%**	**B_1**	**wt%**
6a	33.94	6a	10.0
7a	13.55	6b	30.0
8a	11.42	7a	10.0
9a	4.80	7b	10.0
10a	36.29	8b	10.0
		8c	10.0
		10a	20.0

Mixture A, A_1 and B were doped with chiral compounds. The following chiral nematic mixtures were formulated:

a) B:Ch_{B1} with weight ratio 3:1, 1:1, 1:3, 1:4 (Ch_{B1} is compound 14)

b) B:Ch_{B2} with weight ratio 1:1 (Ch_{B2} is compound 15)

c) A+Ch_{A1}, A contains 10wt% of 11

A+$Ch_{A1,2}$, A contains 10wt% of 11 and 10% of 12

A+$Ch_{A1,2,3}$, A contains 10wt% of 11, 10% of 12 and 10% of 13c

d) A_1+Ch_{A1}, A_1 contains 10wt% of 11

$A_1+Ch_{A1,2}$, A_1 contains 10wt% of 11 and 10% of 12

$A_1+Ch_{A1,2,3}$, A_1 contains 10wt% of 11, 10% of 12 and 10% of 13

The phase diagrams were obtained by the single concentration method. The reflective colors were observed with naked eye. Microscopic slides with a liquid crystalline mixture between them were placed on blacken surface of a heater.

For pressure sensing the mixtures were dispersed in a polymer. The method used was described in ref. 5 and the measurement set-up is described in the paper presented at this conference.[6]

RESULTS

The nematic mixture A and B comprise mainly the nematic compounds being the closest members of compounds with A_d phase in a homologous series. The mixtures obtained by mixing mixtures A and B are liquids to -20 °C and show the induced A_d phase in a large range of the temperature and concentration range, see Figure 1a. Diluting mixture A or B with components with shorter alkyl tails (mixture A_1 and B_1) diminishes of the smectic A_d island (system A_1-B or A-B_1, figure 1a and 1c) or cancels the induction of the A_d phase at all (system A_1-B_1) when both mixtures comprising a large amount of components with shorter alkyls are combined together.

After the doping of mixture A_1 with 10wt% of compound 11, which is chiral analogous compounds 1 we observed that the smectic A_d island is increased, see Figure 1b and 2a. The steric hindrance resulting from the presence of the methyl group in the alkyl chain do not disturb the creation of A_d phase, but reinforces it. The ability of this compounds to inject the smectic A_d phase is much higher than for the compound with the unbranched alkyl tail of the same length.

The introduction of further chiral compounds: 12 and 13 changes the shape of the A_d island, the areas of the smectic phase decreases. It results from the fact that their virtual A_d-N transition temperatures are lower. Systems shown in Figure 2 still do not show a selective reflection.

Systems with the selective reflection of light are shown in Figure 3-6. In Figure 3 the systems containing mixture A and mixture B diluted with chiral compound 14 in

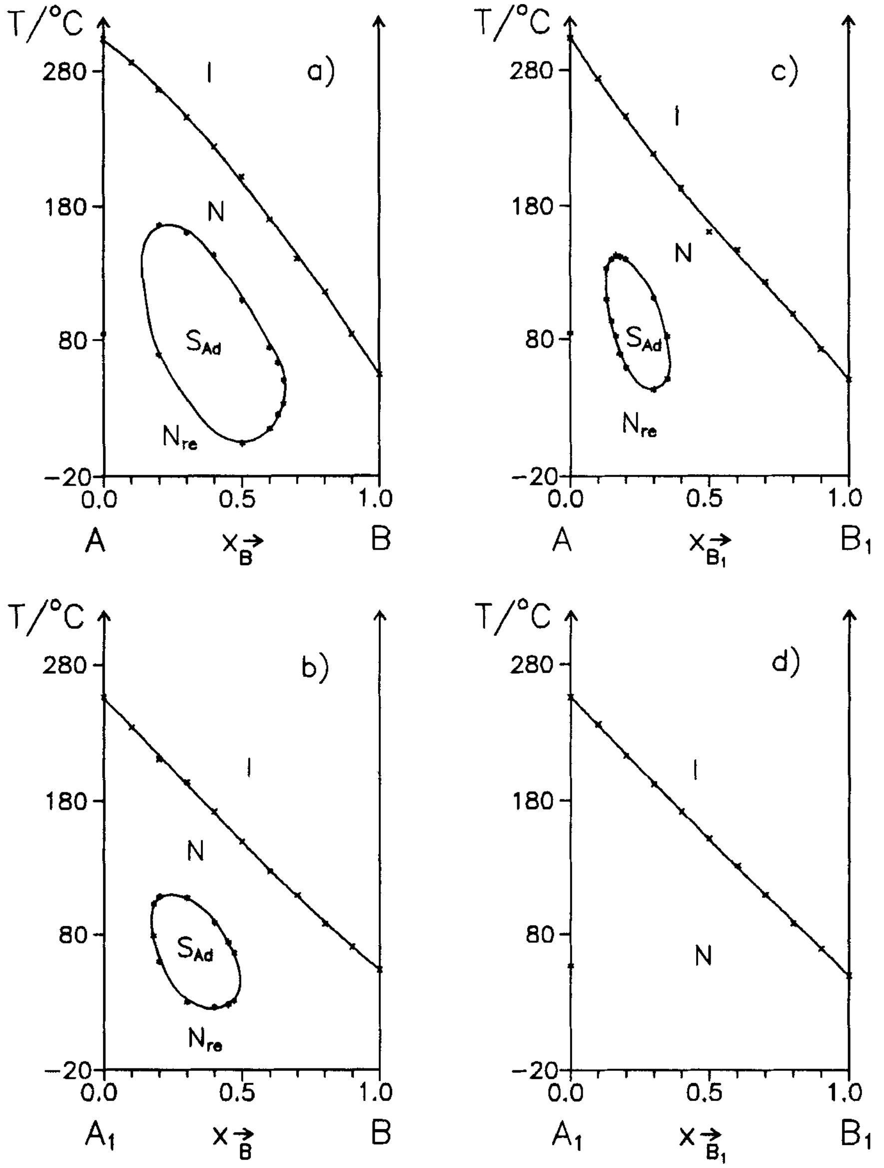


FIGURE 1 Phase diagram of the binary system: component A, B, A_1, B_1 are the multicomponent nematic mixtures with the composition listed in the text. Concentration is in wt. ratio.

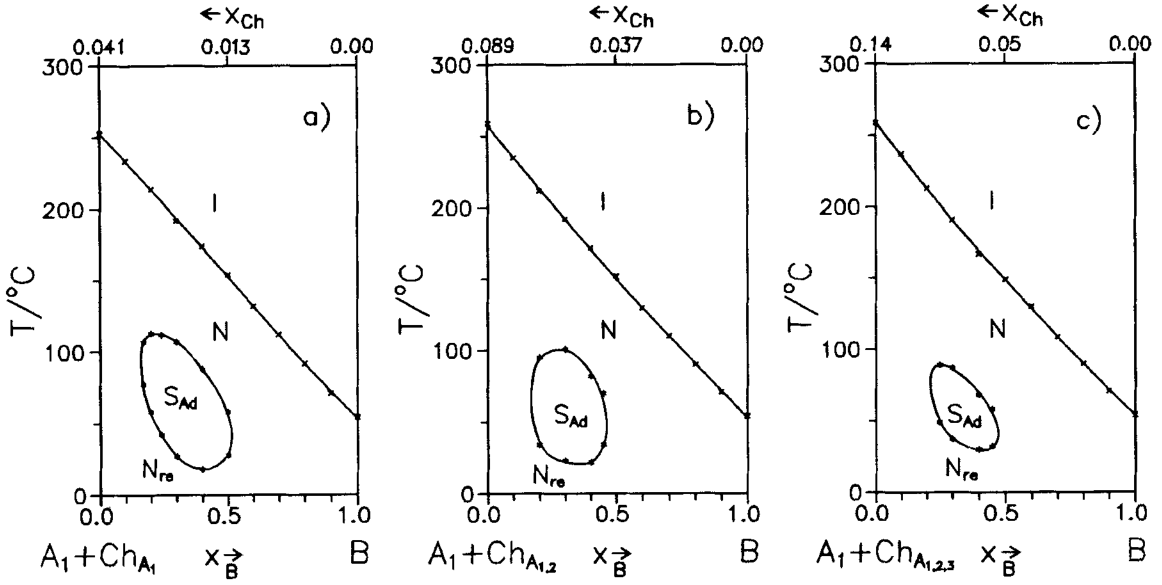


FIGURE 2 Change of the shape of the induced smectic A_d islands after doping chiral compounds showing A_d properties. x_{Ch} - concentration of the chiral compounds in mole ratio.

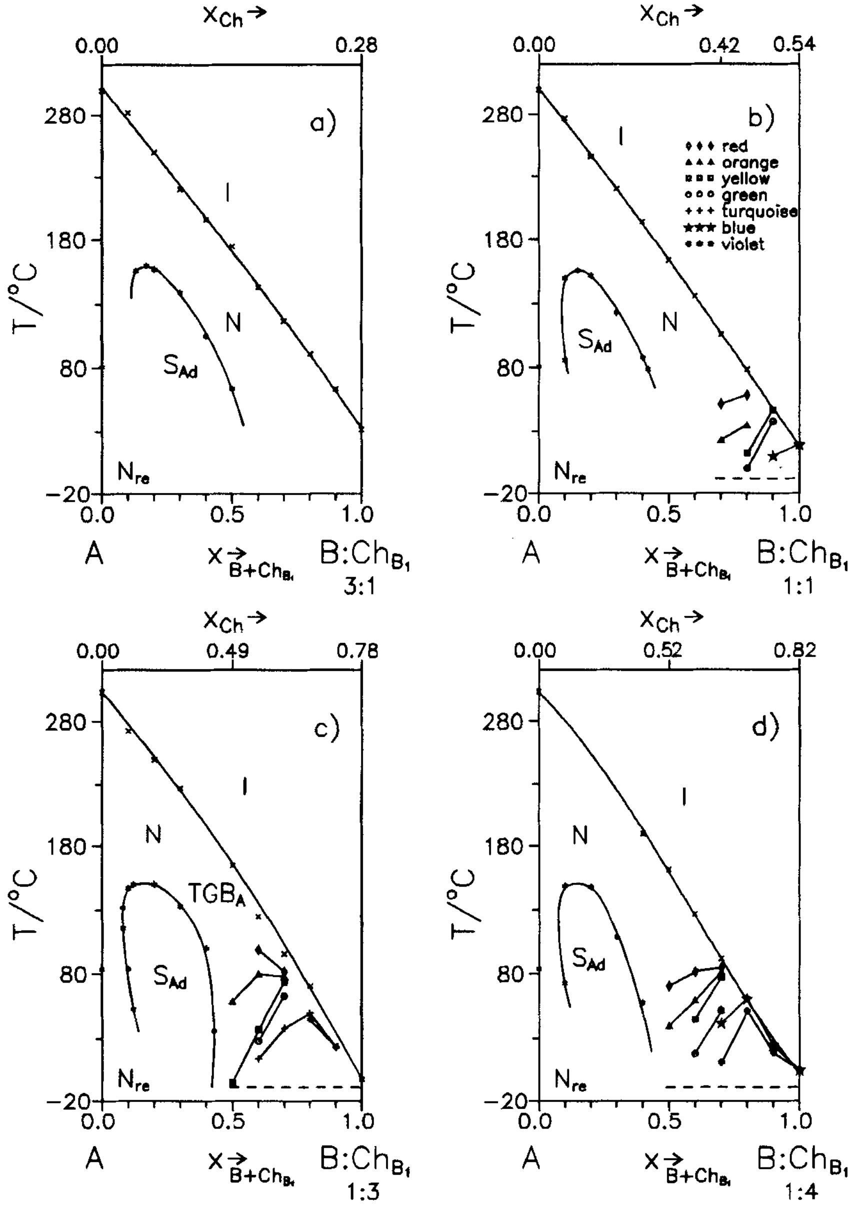


FIGURE 3 Change of the selective reflection of the light upon concentration of the chiral compounds (x_{Ch} - mole ratio).

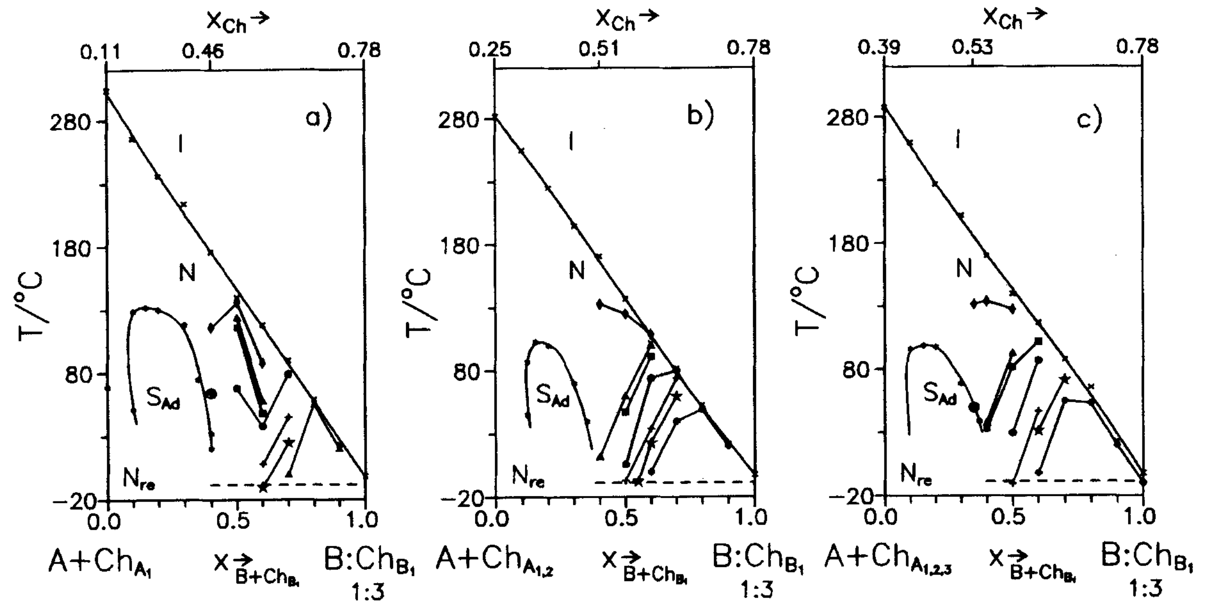


FIGURE 4 Change of the selective reflection of the light upon concentration of the chiral dopants (x_{Ch} - mole ratio).

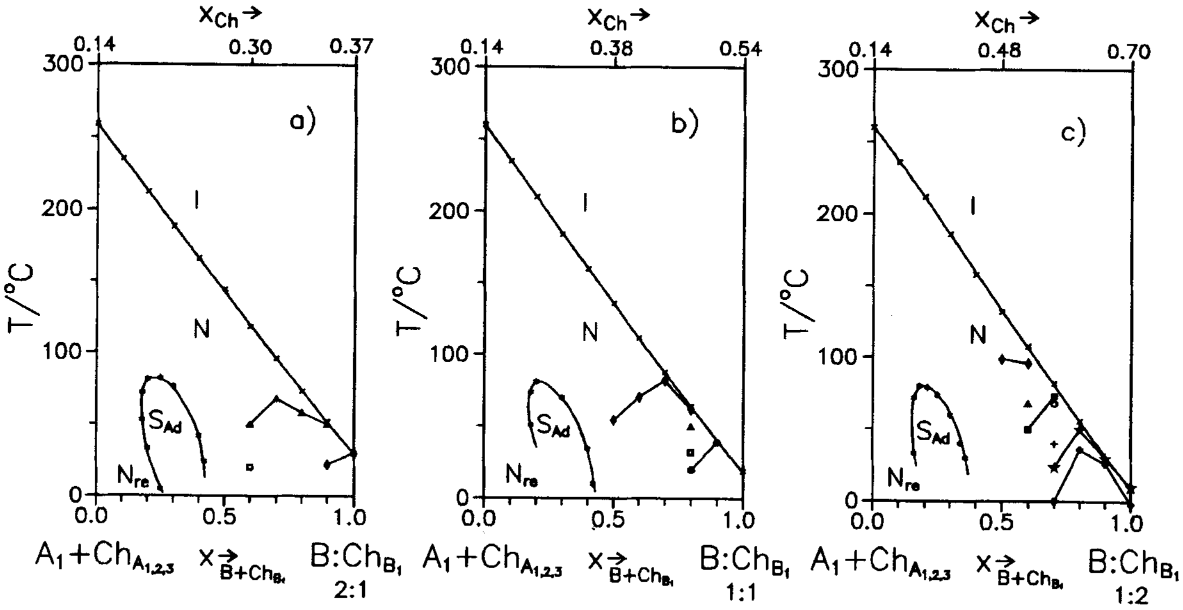


FIGURE 5 Evolution of the selective reflection of the light upon concentration of the chiral dopants and of the shape of the A_d islands.

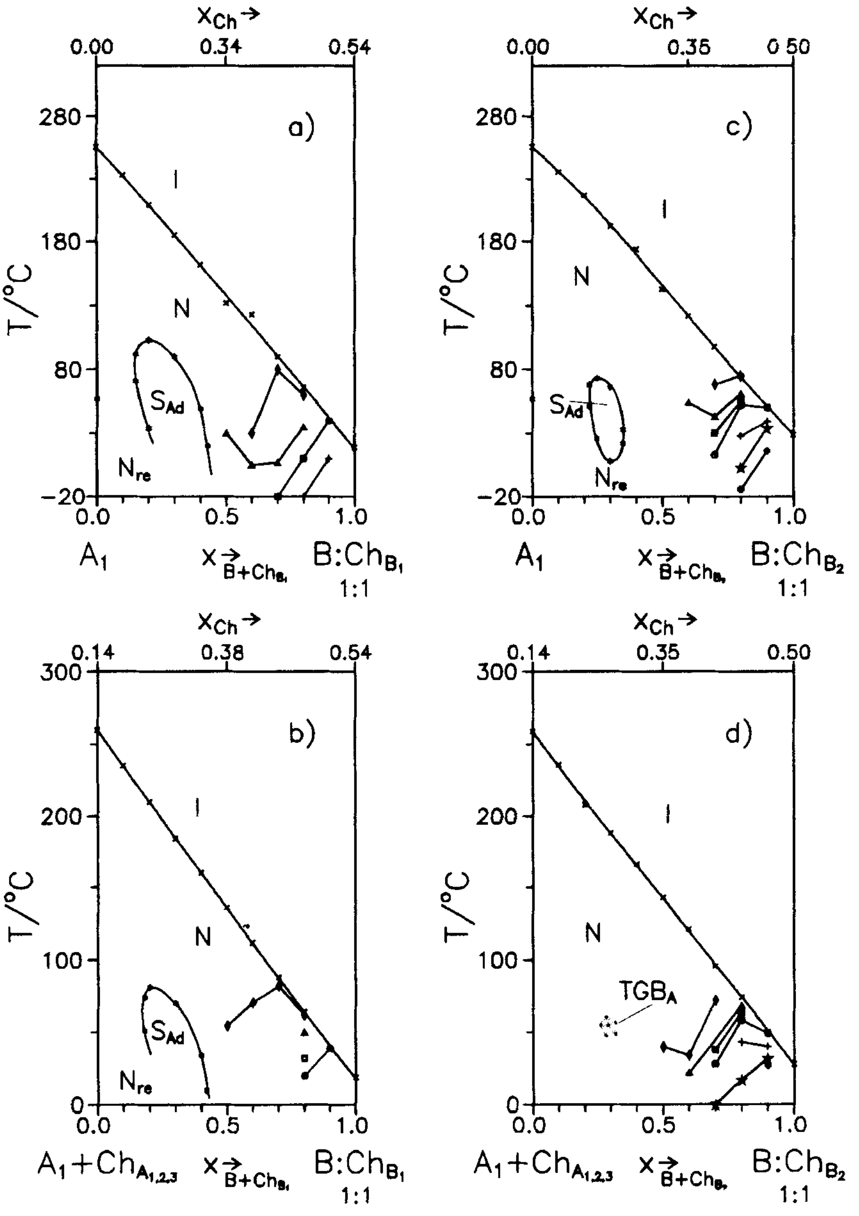


FIGURE 6 Comparison of the selective reflection of the light in the systems with different stability of the smectic A_d phase.

weight ratio 3:1, 1:1, 1:3 and 1:4 are compared. The maximal concentration of the chiral compound 14 is 0.82 mole ratio in these mixtures. The selective reflection is observed for the mole concentration of 14 $X_{Ch}=0.42$ or higher. In the all those systems which exhibit the selective reflection of light a TGB_A smectic phase is also observed in the range of two degrees and above the A_d island. The selective reflection is observed outside the region of the smectic A_d and TGB_A phases. The TGB_A phase area was only marked in Figure 3b, but it was observed in all remaining systems shown in Figures 3-6.

As an example, the exact temperature ranges of the TGB_A smectic phase upon concentration in the bicomponent systems A-(B:Ch_{B1}, 1:3) are listed in Table 2.

TABLE III The temperature ranges of the TGB_A smectic phase upon concentration in the bicomponent systems A-(B:Ch_{B1}, 1:3)

Concentration of B:Ch_{B1} [wt%]	Concentration of Ch_{B1} [mole %]	Temperatures [°C]	
		Heating	Cooling
9.78	15.42	159.8-160.9	156.8-161.1
20.00	28.25	157.4-158.2	153.8-157.8
29.91	38.36	117.4-119.9	114.6-119.5
59.97	60.15	91.7-98.4	90.8-97.1

From phase diagram shown in Figure 3 may be concluded that increasing the concentration of chiral compound 14 involves:

- great riches of colors
- enhancement of the range of violet
- shift of red to higher temperature region.

More distinctly the same relation is seen in Figure 4. The systems presented there two different types of chiral dopants are used. The selective reflection of light is not observed for concentration of chiral dopant lower than mole ratio $X_{Ch}=0.46$.

In Figure 5 and 6 the systems with lower stability of the induced smectic A_d phase are compared. The mixture showed in Figure 5a (A_1+$Ch_{A1,2,3}$) - B:Ch_{B1} (2:1) has other sequence of colour than the rest of investigated systems. The selective reflection of the light is observed for the lower concentration of dopants. It starts from X_{Ch}=0.3 ratio. The colour changes from yellow to red with growing concentration of chiral dopants in this system. The increasing of the concentration of the chiral dopants in this system by adding more chiral components to base mixture B (B:Ch_{B1} from 2:1 to 1:1 and 1:2), see Figure 5b and c, reverses the colour sequence. In the mixture A_1+$Ch_{A1,2,3}$ - B:Ch_{B1} (1:1 or 2:1) a greater variety of colors is observed when the concentration of compound 14 increases and the red colour is shifted to higher temperature region.

In Figure 6 two pairs of systems which differ in the stability of the induced smectic A_d phase are compared. The concentrations of the chiral dopants are similar. The difference in the stability results from the use of different chiral dopants, 14 and 15.

The same concentration of chiral compound 15 induces a much smaller smectic A_d island than it is observed for compound 14 at the same concentration. It is seen especially distinctly in Figure 6b and d. In the system A_1+$Ch_{A1,2,3}$ - B:Ch_{B1} (1:1) the smectic island exists in a large range of concentrations and temperatures, while in similar systems A_1+$Ch_{A1,2,3}$ - B:Ch_{B2} (1:1) the smectic island is not observed, only the TGB_A phase is observed in a small concentration and temperature region. The shape of the induced smectic A_d area influences greatly the position of the colors at the temperature scale. The red colour is shifted to lower temperature region when the smectic island decreases.

The most interesting feature is that the selective reflection occurs at nearly constant distance from A_d island for all the investigated systems and colour sequence is reverse in the most cases, that is change from violet to red with increasing temperature. This is contrary to the behavior of the systems with an injected A_1 phase[5] or other common known chiral systems with selective reflection of the light.[6,7]

Sensing of high pressure

Liquid crystal mixture: A 40 wt.% and B:Ch_{B1} (1:3) 60 wt.%, see diagram in Figure 3c, was used to make dispersions in the polymer. The selective reflection of the polymer differs from the reflection given by staring mixtures.

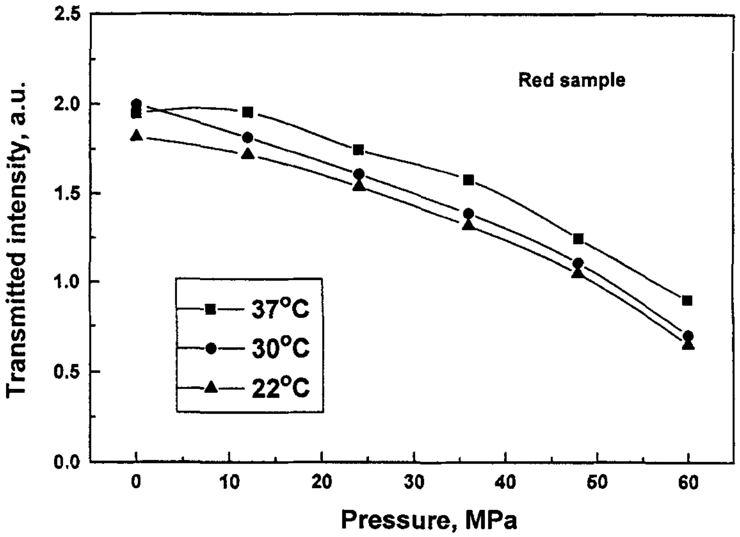


FIGURE 7 Dependence of the intensity of the transmitted light through the polymeric foil with the disspersed liquid crystal mixture: 40 wt%of A and 60 wt% of B:Ch_{BI} (1:3)

Selective reflection of the mixture before dispersing it in polymer:

turquoise green yellow orange red

-10 15.5 27.9 37.2 89.4 99.1

Selective reflection after dispersing in polymer:

red

-10 61

Under pressure the prepared foil changes the intensity of transmitted light, Figure 7. The influence of temperatures on this pressure dependance is not high. This material is not more sensitive to pressure than previously investigated systems with selective reflection.[5] Probably the mixtures chosen from the other regions of concentration may be more sensitive to pressure. It is under study.

ACKNOWLEDGEMENT

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REFERENCES

1. M. Brodzik and R. Dąbrowski, Liq. Cryst., 1994 in press.
2. M. Brodzik and R. Dąbrowski, Proceedings of XV ILCC.
3. G. Illian, H. Kneppe and F. Schneider, Ber. Bunsenges. Phys. Chem., 92, 776 (1988).
4. T. R. Woliński and W. J. Bock, Mol. Cryst. Liq. Cryst., 199, 7 (1991).
5. T. R. Woliński, R. Dąbrowski, W. J. Bock, A. Bogumił and S. Kłosowicz, Thin Solid Films, 1994 in press.
6. T. R. Woliński, R. Dąbrowski, A. Bogumił and Z. Stolarz, Proceedings of XV ILCC.
7 G. W. Gray and D. G. McDonnell, Mol. Cryst. Liq. Cryst., 48, 37 (1978)