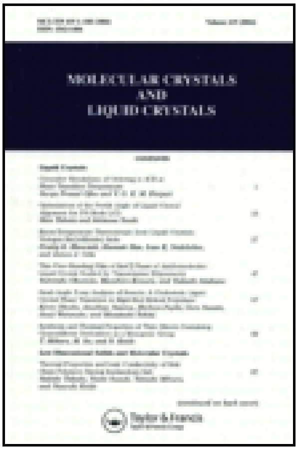

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# Guest-Host Systems: a Comparison of low Molecular and Polymeric Systems

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# GUEST-HOST SYSTEMS: A COMPARISON OF LOW MOLECULAR AND POLYMERIC SYSTEMS

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Abstract Some properties of low molecular and polymeric guest-host systems are compared. Central points are the dependence of the order parameter S(Dye), measured by absorption spectroscopy, as a function of the dye concentration and its influence on the phase behaviour. The systems used were anthraquinone dyes dissolved in phases containing cyano biphenyl derivatives as mesogenic groups. Some few statements concerning copolymeric guest-host systems were given.

## INTRODUCTION

In the recent years many investigations had been done concerning low molecular guest-host systems. The main problems were to get systems possessing dyes with high order parameters and high extinction coefficients[1-4] and for example high dye solubilities[5-8]. Concentration effects of the dye molecules were usually neglected. Only little data are available[9-12] about the following points of interest: Change of order parameter $S_{Dye}$ with increasing concentration and the accompanied influence on the clearing point as well for low molecular as for polymeric systems.

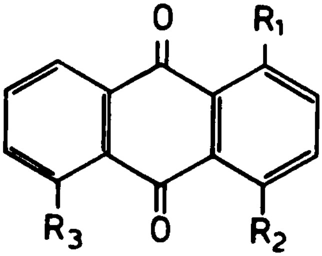
This contribution is concerned with some properties of the same dyes dissolved as well in a low molecular as in a polymeric cyano biphenyl containing phase.

The third possibility to get guest-host systems is to attach the mesogenic group and the dye molecule via flexible spacers to a polymer main chain[13-14]. The advantage of these systems is that they have temperature independent solubilities and a high dye amount can be reached (up to 40-50% per weight). Since almost no data are listed to compare these systems with the other two mentioned above, this paper contributes to it.

## EXPERIMENTAL

The dyes used for our investigations were listed in table I.

D-35, D-27 and D-52M were obtained from BDH Chemical Ltd, Poole, UK, and the dyes AA, A2A and H2A from Aldrich-Chemie, Steinheim, F.R.G. All dyes were used without further purification.



| Dye | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| AA | $NH_2$ | H | H |
| A2A | $NH_2$ | $NH_2$ | H |
| H2A | OH | OH | H |
| D-52M | $NH-C_6H_4-N(CH_3)_2$ | H | H |
| D-27 | $NH-C_6H_4-N(CH_3)_2$ | OH | H |
| D-35 | $NH-C_6H_4-C_2H_5$ | H | $NH-C_6H_4-C_2H_5$ |

TABLE I Used anthraquinone dyes

The low molecular liquid crystal used, 4-cyano-4'-pentyl-biphenyl (K-15), was a gift from E.Merck company, Darmstadt. As the polymeric liquid crystalline phase we used the side chain derivative listed in fig.I.

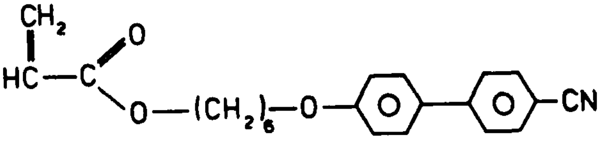


FIGURE I Used mesogenic monomer (PB6CN)

The synthesis of this polymer is described elsewhere[14].

The dye containing monomer, given in fig. II, was a gift of Dr. Etzbach, BASF AG, Ludwigshafen. The copolymerisation and purification were done in the same way as for the homopolymers[12].

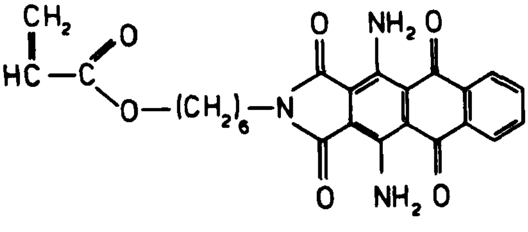


FIGURE II Dye containing monomer used for copolymerisation

The methods we used for the determination of the phase transition temperatures and the order parameter $S_{Dye}$ and the preparation of the dye/polymeric liquid crystal mixtures were discussed elsewhere[11-12].

## RESULTS AND DISCUSSION

### INFLUENCE ON THE CLEARING POINT

### A) Low molecular systems

The change of the clearing point ($T_C$) as a function of concentration of the various anthraquinone dyes in the low molecular liquid crystal K-15 is shown in figure III.

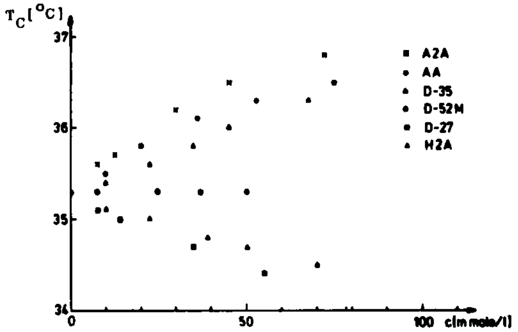


FIGURE III Concentration dependence of $T_C$ for the different anthraquinone dyes in

The data of D-35 are in good agreement with these in ref. 11.

Taking into account these facts some first empirical rules could be interpreted:

- free amino groups cause an increase of the clearing point,

as it is shown for the dyes AA and A2A. It seems that the number of these free $NH_2$-groups has also an effect because of the fact that the slope of A2A is greater than the of AA.

- free hydroxy groups destabilize the liquid crystalline phase.

This is shown for the dyes H2A and D-27. The difference between D-27 and D-52M is the additional OH-group in the 4-position at D-27. This additional group causes a decrease in comparison to D-52M where the clearing point is constant over the investigated concentration range.

- molecules possessing a large molecule length axis (>20Å) stabilize the liquid crystalline phase of K-15.

Dye D-35 with a length axis of 25Å obtained from X-ray data[15] shows an increase of the clearing point. Also this effect was found in a former work[10] for dye D-16. The length of the molecule axis in D-16 is about 29Å and a slight increase of the clearing point was found (sequence D-35> D-16> D-52M), overcompensating the effect of the free OH-group in the 4-position.

The conclusion is that steric effects like the molecule length as well as interactions due to the substituents influence the phase behaviour.

### B) Polymeric systems

The same dye molecules used for low molecular liquid crystals were dissolved in the comparable polymeric liquid crystalline phase PB6CN. Their influence on the clearing point was shown in an earlier work[12].

We found always a decrease of the clearing point due to changing the polymer properties by adding dye impurities. The sequence A2A> AA> D-35> D-52M> H2A> D-27 was observed for all studied systems[12]. This is identical with the sequence found in the low molecular liquid crystal K-15.

### C) Copolymeric systems

The values for the concentration dependence of our investigated copolymer are listed in table II.

| dye content [ mmole/l ] | $T_C$[°C] |
|---|---|
| 0 | 125.0 |
| 22 | 124.4 |
| 46 | 123.9 |
| 65 | 123.5 |

TABLE II Variation of $T_C$ with increasing dye amount

Also, it seems that copolymeric systems show a slight decrease of the clearing point in a comparable concentration range. More detailed studies will be discussed elsewhere.

The comparison with the most familar dye A2A dissolved in PB6CN shows nearly the same concentration dependence in the identical range.

## ORDER PARAMETERS

### A) Low molecular systems

At first we present the results of the different anthraquinone dyes dissolved in the low molecular liquid crystal K-15. All investigated systems show a strong dependence of the dye order parameter $S_{Dye}$ especilly in the range of low concentrations[11]. As an example we present the system AA/K-15 in figure V. $S_{Dye}$ as a function of $\sqrt{c}$ leads to correlation coefficients that were nearly always greater than 0.99 and in the most cases greater than 0.999. For all systems a linear dependence of S on $\sqrt{c}$ in the investigated concentration range was found. The resulting fit parameters $S^{\infty}$, which are the dye order parameter at absolute dilution, are listed in table IV. The following seems to be applicable:

$$S = S^{\infty} - b\sqrt{c}$$

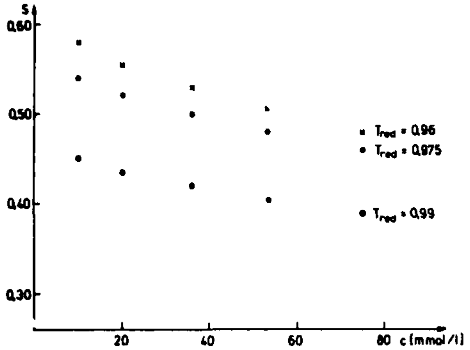


FIGURE V Concentration dependence of 1-aminoanthraquinone in K-15 for three different reduced temperatures ($T_{red}$)

| system | $T_{red}$ | $S^{\infty}$ |
|---|---|---|
| AA/K-15 | .96 | .64 |
| | .975 | .59 |
| | .99 | .49 |
| A2A/K-15 | .96 | .61 |
| | .975 | .58 |
| | .99 | .50 |
| H2A/K-15 | .96 | .53 |
| | .975 | .48 |
| | .99 | .39 |
| D-52M/K-15 | .96 | .56 |
| | .975 | .52 |
| | .99 | .45 |
| D-27/K-15 | .96 | .53 |
| | .975 | .50 |
| | .99 | .43 |
| D-35/K-15 | .96 | .63 |
| | .975 | .60 |
| | .99 | .53 |

TABLE III Resulting $S^{\infty}$ parameters of the dye/ liquid crystal systems as a function of $T_c$

From the value $S^{\infty}$ some interesting aspects can be derived, comparing the calculated values $S^{\infty}$ at $T_{red}=0.96$ shown in table III with the order parameter of pure K-15 which is about 0.56 at this reduced temperature[16]. Therefore all dyes with $S^{\infty} > 0.56$ should stabilize the liquid crystalline phase, which is shown in an increase of the clearing point, whereas for the systems possesing $S^{\infty}<0.56$ a destabilization should be observed. This effect is shown by comparison of the $S^{\infty}$ values and the clearing point influences, presented in the last chapter. D-35, AA and A2A cause an increase of the clearing point, D-27 and H2A a decrease. D-52M has a constant clearing point in the investigated concentration range and the $S^{\infty}$ value is the same as found for pure K-15. The strong concentration effect on $S_{Dye}$ could be interpreted in terms of specific guest-host interactions in the liquid crystalline state. A dye molecule at great dilution should have his own ordering scheme via the given host matrix, which is undisturbed by other dye molecules. An increasing dye amount conteracts the ordering scheme of the liquid crystalline host and vice versa. Since this effect was observed in K-15 and comparable liquid crystalline hosts a possible reason therefore could be the cyano-phenyl - associations[17] in the liquid crystalline state. A theoretical explanation will be given elsewhere[18].Experiments using liquid crystalline phases possessing no oligomerizations are center of our present studies in order to verify this assumption.

B) Polymeric systems

The same dye molecules dissolved in the polymeric liquid crystal PB6CN show some remarkable results. As we presented elsewhere[12], a constant value for $S_{Dye}$ over the whole investigated concentration range was found. The interesting values are listed in table IV.

The comparison of the values $S_{Dye}$ at $T_{red}=0.96$ with those found for $S^{\infty}$ in K-15 (see table III) shows the same value for every dye within the experimental error.

This is a very interesting fact. It seems that the order parameter in a low molecular liquid crystal at great dilution and in a polymeric liquid crystal with the same mesogenic side chain has nearly the same value.

The effect that the order parameter is constant could be explained with the less tendency of oligomerization in contrast to low molecular K-15. This fact was found from X-ray studies for

| dye | $S_{Dye}(T_{red}=0.75)$ | $S_{Dye}(T_{red}=0.96)$ |
|---|---|---|
| AA | 0.70 | 0.62 |
| A2A | 0.69 | 0.61 |
| H2A | 0.60 | 0.52 |
| D-52M | 0.64 | 0.55 |
| D-27 | 0.60 | 0.52 |
| D-35 | 0.71 | 0.63 |

TABLE IV Order parameter values at two different reduced temperatures

the pure homopolymer[19]. So the small part of oligomers doesn't influence the $S_{Dye}$ and a constant value is observed.

### C) Copolymers

The order parameters of the investigated copolymeric system have been determined. The result is a constant value of 0.68 at a reduced temperature of 0.80. This is in good agreement with the same copolymer of one similar dye content[14].

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