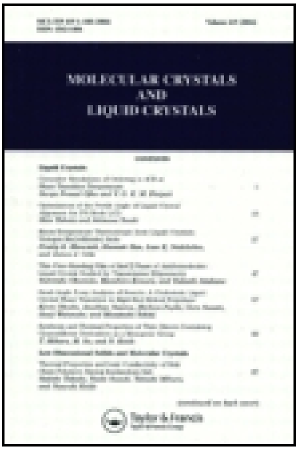


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Influence of Dissolved Dye Molecules on Liquid Crystalline Side Chain Polymers

Udo Quotschalla [a] & Wolfganu Haase [a]

[a] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr. 20, 6100, Darmstadt, F.R.G.

To cite this article: Udo Quotschalla & Wolfganu Haase (1987): Influence of Dissolved Dye Molecules on Liquid Crystalline Side Chain Polymers, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 83-97

To link to this article: http://dx.doi.org/10.1080/00268948708074527

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 83-97
Photocopying permitted by license only

Printed in the United States of America

INFLUENCE OF DISSOLVED DYE MOLECULES ON LIQUID CRYSTALLINE SIDE CHAIN POLYMERS

UDO QUOTSCHALLA AND WOLFGANG HAASE
Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr.20, 6100 Darmstadt F.R.G.

Abstract We report on the influence of dissolved dichroic dye molecules as well on the dye order parameter as on the clearing point of polymeric liquid crystalline host as a function of concentration. The investigations of several anthraquinone dyes in polyacrylic side chain polymers, using phenylebenzoate and biphenyle systems as mesogenic groups, show that the order parameter S(Dye) is constant over the concentration range under investigation for all systems. In all cases a decrease of the clearing point with increasing dye concentration could be observed. Also the influence of the dye structure, the spacer length and the mesogenic group are discussed.

INTRODUCTION

Pleochroic dye molecules dissolved in low molecular nematic liquid crystals, called guest-host-systems, had been part of many investigations in the last years. Some of the important aspects concerning these systems were the influence of the solutes on the phase transition temperatures [1-3] and the concentration dependence of the order parameters $S_{L.C.}$ and S_{Dye}. The parameter S_{Dye} in a liquid crystalline matrix depends therefore on the temperature, the structure of the dye [4-8] and the concentration of the guest [2-3].

But only little data is available concerning guest-host-systems using side chain polymers as liquid crystalline phases [9-11]. These systems could be of great technical interest because of their optical storage effect in the nematic phase[12] or their usefulness as media for non-linear optical behaviour [10,13].

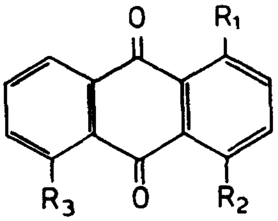
So it would be interesting to know the effect of different dye concentrations of several dye molecules on the phase behaviour as well as on the order parameter S(guest).

EXPERIMENTAL

The dyes we used for our investigations were anthraquinone derivatives. They are listed in table 1.

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, FRG. All dyes were used without further purification.

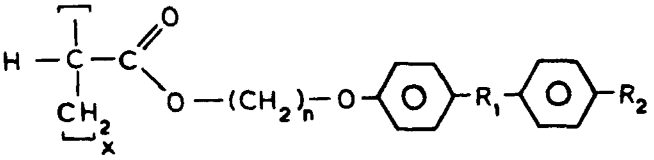


Dye	R_1	R_2	R_3
AA	NH_2	H	H
A2A	NH_2	NH_2	H
H2A	OH	OH	H
D-35	$NH-C_6H_4-C_2H_5$	H	$NH-C_6H_4-C_2H_5$
D-52M	$NH-C_6H_4-N(CH_3)_2$	H	H
D-27	$NH-C_6H_4-N(CH_3)_2$	OH	H

TABLE I Used anthraquinone dyes

The liquid crystalline side chain polymers used are listed in table II.

PB6CN, PB4CN and PPB6CN were synthesized in our laboratory in accordance with known preparation schemes [14-15]. The starting chemicals which were necessary for PB6CN and PB4CN were a gift from E.Merck company, Darmstadt. The monomer of PPB5CN was a gift from O.Röhm company, Darmstadt. The polymers were obtained by solution polymerisation at 70°C in dioxane. They were purified by GPC with THF as eluent.



substance index	R_1	R_2	n
PB6CN	-	CN	6
PB4CN	-	CN	4
PPB6CN	COO	CN	6
PPB5CN	COO	CN	5

TABLE II Polymeric liquid crystalline host phases

The dye/polymeric liquid crystal mixtures were prepared by mixing different ratios of dye molecules dissolved in trichlormethane and polymeric liquid crystals also dissolved in trichlormethane. The solvent was evaporated and dried at 70°C for several days.

The methods we used for the determination of the phase transition temperatures and the order parameter S_{Dye} were discussed elsewhere [2].

RESULTS AND DISCUSSION

ORDER PARAMETERS

The dye order parameter S_{Dye} of the different anthraquinone dyes (see table I) were determined as a function of their concentration in four polymeric hosts (see table II). All these phases show only a nematic phase except PB6CN (sequence $g-n_{re}-s_A-n-i$). But in this case no discontinuities in the order parameter as a function of temperature were observed so that all phases are comparable. Table III shows the well investigated effect of dye D-35 in PPB6CN as an example:

c[mmole/l]	11	18	30	35	51	90
S_{Dye}	0.68	0.67	0.67	0.67	0.66	0.67

TABLE III Dye order parameter of D-35 as a function of its concentration in PPB6CN at $T_{red}=0.75$ (Reduced temperature: $T_{red}=T/T_K$; T_K: clearing point of the mixture)

This example shows, that the order parameter S_{Dye}

is within the experimental error (S= 0.01) constant over the whole concentration range under investigation. It can be prooved, that this effect is a general one for the investigated systems. To show this figure I presents the dependence of the order parameter of some other dyes in various polymeric liquid crystals as a function of their concentrations at the same reduced temperatures.

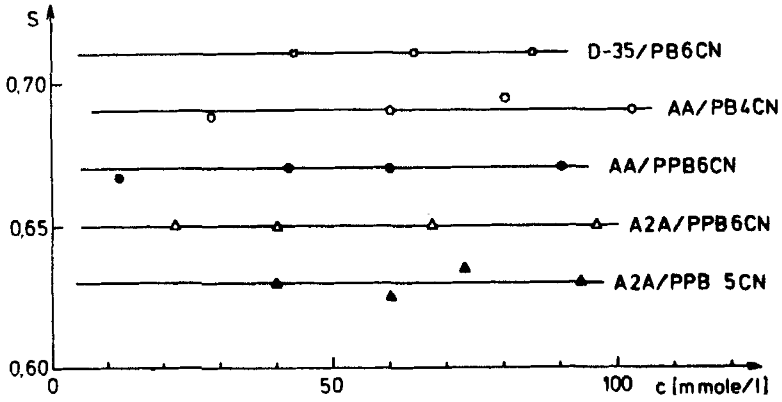


FIGURE I Concentration dependence of different dye/polymeric liquid crystal mixtures

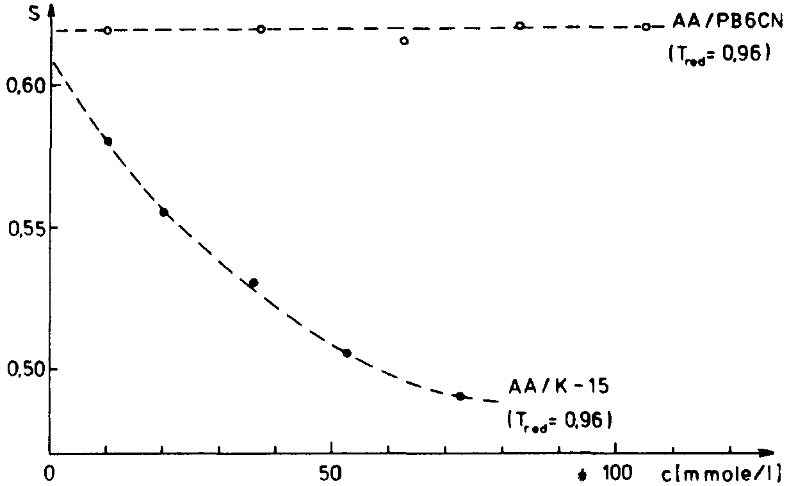


FIGURE II Comparison of the dependence of order parameter S_{Dye} on dye concentration between the systems AA/K-15 and AA/PB6CN

Therefore results that the order parameter S_{Dye} for the investigated systems - dye dissolved in liquid crystalline side chain polymers - isn't influenced by dye concentration. This is in contrast to similar dye/low molecular liquid crystal systems, where a noteworthy dependence on dissolved dye amount has been found $^{2-3}$. To illustrate this difference figure II shows the order parameter behaviour of dye AA in the low molecular K-

15 [3] (p-cyano-p'-pentyl-biphenyle) and in PB6CN. The dye order parameters of all investigated systems are listed in table IV.

	PB6CN	PB4CN	PPB6CN	PPB5CN
A2A	0.69	0.67	0.65	0.63
AA	0.70	0.69	0.67	0.64
D-35	0.71	0.69	0.67	0.65
D-52M	0.64	0.61	0.60	0.57
D-27	0.60	0.57	0.56	0.53
H2A	0.60	0.58	0.55	0.53

TABLE IV Order parameters of the different guest-host-systems at $T_{red}=0.75$

INFLUENCE ON THE CLEARING POINT OF THE HOST

The influence of the different anthraquinone dyes on the clearing points of the different dye/polymeric liquid crystal mixtures is shown in figure III a-d.

In all cases there is a linear decrease of the clearing point with increasing dye concentration. An increase how it was found for some similar dye molecules in low molecular liquid crystals like

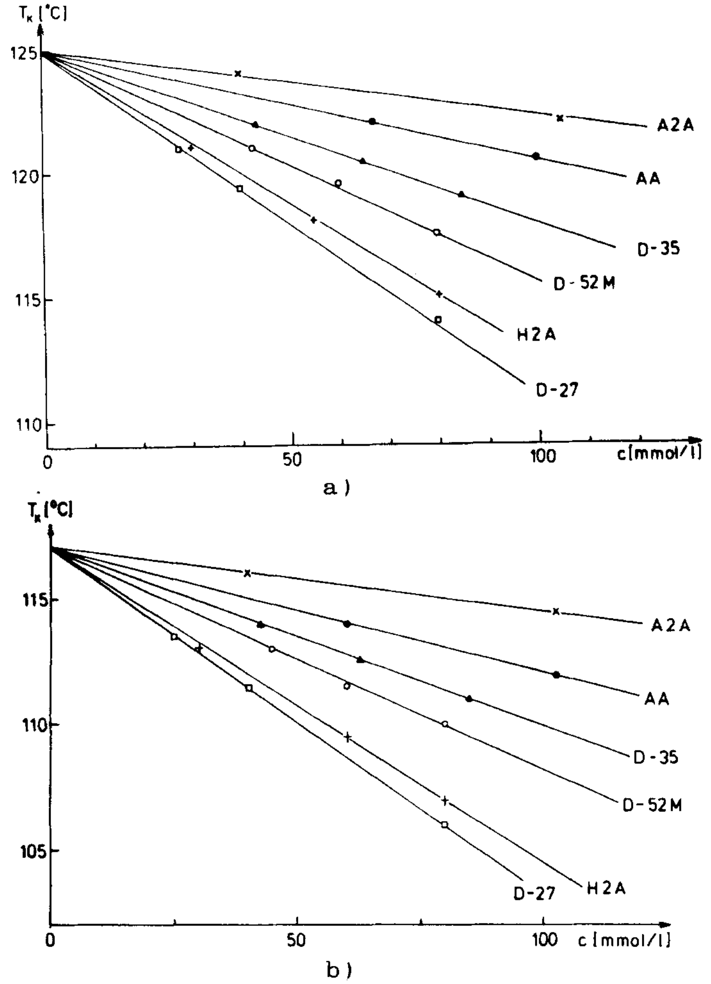
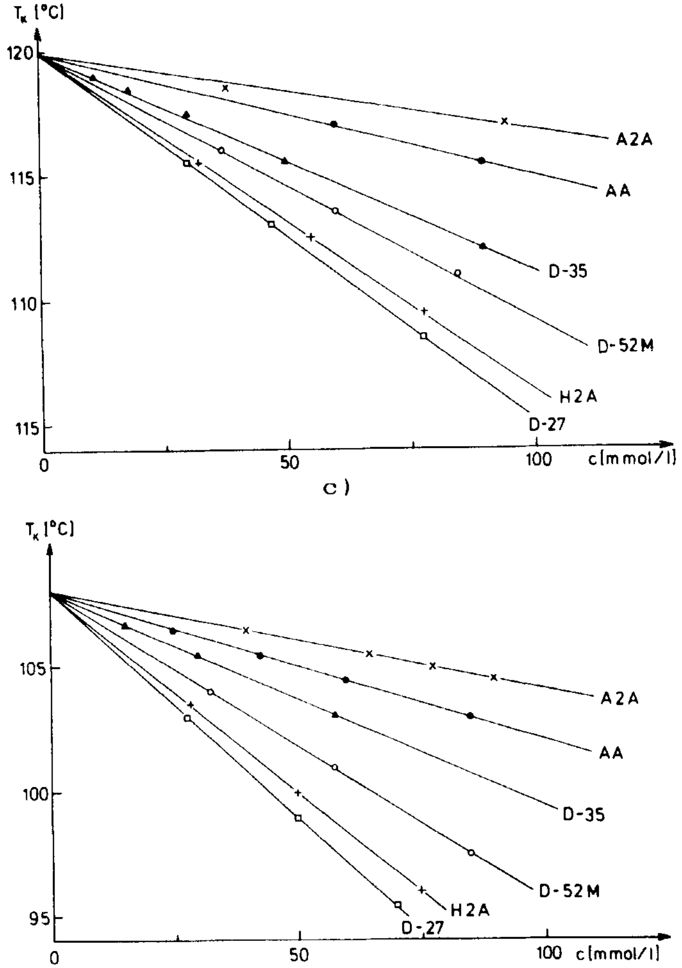


FIGURE III Influence of dye concentration on the following systems

a) PB6CN b) PB4CN

c) PPB6CN d) PPB5CN



c)

d)

FIGURE III continued

K-15[2-3] couldn't be observed. This decrease can be explained with a change of polymer arrangement in adding some impurities. These impurities lower M_n and are therefore accompanied by a decrease of the clearing point.

INFLUENCE OF DYE STRUCTURE

In both cases, the dependence of the order parameter S_{Dye} and the clearing point of the mixture on dye concentration, there is a noteworthy effect of dye size on the behaviour.
The comparison of the order parameter S_{Dye} of the different dye molecules (see table III) shows the same sequence in all four liquid crystalline systems, namely: D-35 > AA > A2A > D-52M > D-27 > H2A. The same sequence is also found in familiar low molecular systems [3]. One interesting aspect can be estimated from figure III: the order parameter S_{Dye} of a dye in absolute dilution ($c_{Dye} \approx 0$) in the low molecular liquid crystal K-15 seems to have nearly the same value S_{Dye} as in the comparable system PB6CN. So there seem to be some parallelities between low molecular and polymeric guest host systems, which will be discussed more detailed elsewhere [3].
The influences of the dye structure on the clea-

ring point of the host also are in good accordance with each other. In all cases the sequence A2A > AA > D-35 > D-52M > H2A > D-27 can be observed. This is also identical with the sequence found in low molecular liquid crystals [2-3]. At polymeric liquid crystalline systems this dye effect is superposed by a strong decrease due to changing the polymer properties by adding dye impurities. This effect is stronger, so that in the investigated systems a decrease is observed although in low molecular liquid crystals for some dyes an increase was found [2-3].

INFLUENCE OF SPACER LENGTH

The comparison of the different dyes in the four polymeric liquid crystalline systems shows (table IV) that there are always little effects due to the spacer lengths. In both comparable systems (PB6CN-PB4CN and PPB6CN-PPB5CN) differences were only about 0.02 in S_{Dye} where the systems possessing the shorter spacer has the lower order parameter. This is in good agreement with earlier investigations of Finkelmann et al. [9] who found that the order parameter is nearly unchanged for liquid crystalline polysiloxanes with flexible spacers . Only loss in flexibility of the mesogenic group by reducing the spacer length to n=2 causes a strong decrease [16] in S_{Dye}.

The comparison of the slopes due to the decrease of the clearing point for one dye in the four polymeric liquid cristalline media show that PB6CN ≤ PB4CN and PPB6CN < PPB5CN. This means that there are only small differences in the slope and therefore in the influence of spacer length. But here also the effect can be seen that the liquid crystalline phase with the longer spacer is less influenced.

The result of these investigations is that the influence of spacer length is little in the region of flexible spacers (n>3).

INFLUENCE OF THE MESOGENIC GROUP

An important aspect is the difference of S_{Dye} between cyanobiphenyle derivatives and the cyanophenylebenzoate derivatives. From comparable low molecular systems it is known, that this difference is about 0.1 in S_{Dye} using the same dye molecule [17-19]. The comparison of PB6CN and PPB6CN always leads to difference values of about 0.03 to 0.04 in S_{Dye}. This difference is distinct smaller as found for low molecular guest host systems. The reason therefore must be a consequence of the polymeric properties. It seems that the differences in liquid crystalline side chain polymers concerning the liquid crystalline behaviour are smaller. That means that attaching the mesogens via flexile spacers to polymeric chains results in an assimilation of the liquid crystalline behaviour.

ACKNOWLEDGEMENTS

We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support. We also thank the companies E.Merck, Darmstadt and O.Röhm, Darmstadt for their support concerning the monomer preparations.

REFERENCES

1. P.Diot, J.K.Foitzik and W.Haase, Revue Phys. Appl. 20, 121(1985).
2. W.Haase, O.Trinquet, U.Quotschalla and J.K.Foitzik, Mol. Cryst. Liq. Cryst. 148, 15(1987).
3. U.Quotschalla and W.Haase, submitted.
4. B.Bahadur, R.K.Sarna und V.G.Bhide, Mol. Cryst. Liq. Cryst. 75, 121(1981).
5. Z.Salamon and D.Bauman, Mol. Cryst. Liq. Cryst. 82, 115(1982).
6. R.J.Cox, Mol. Cryst. Liq. Cryst. 55, 1(1979).
7. F.Jones and T.J.Reeves, Mol. Cryst. Liq. Cryst. 60, 99(1980).
8. F.Jones and F.A.Kirby, Mol. Cryst. Liq. Cryst. 108, 165(1984).
9. H.Finkelmann, H.Benthack and G.Rehage, J. Chim. Phys. 80, 163(1983).
10. G.R.Meredith, J.G.van Dusen and D.J.Williams, Macromol. 15, 1385(1982).
11. R.V.Talroze, V.P.Shibaev, V.V.Sinitzyn and N.A.Platé, Polym. Prep., Am. Chem. Soc. 24, 309(1983).
12. V.P.Shibaev, S.G.Kostromin, N.A.Platé, S.A.Ivanov, V.Yu.Vetrov and Y.Kovlev, Polymer Commun. 24, 364(1983).
13. D.J.Williams, Angew. Chem. 96, 637(1984).
14. M.Portugall, H.Ringsdorf and R.Zentel, Makromol. Chem. 183, 2311(1982).
15. V.P.Shibaev, S.G.Kostromin and N.A.Platé, Eur. Polym. J. 18, 651(1982).
16. K.H.Wassmer, E.Ohmes, G.Kothe, M.Portugall and H.Ringsdorf, Makromol. Chem., Rapid Commun. 10, 281(1982).
17. S.Aftergut and H.S.Coles, Mol. Cryst. Liq. Cryst. 78, 271(1981).
18. A.Bloom and P.L.K.Huong, Mol. Cryst. Liq. Cryst. 40, 213(1977).
19. A.Bloom and P.L.K.Huong, Mol. Cryst. Liq. Cryst. 44, 323(1978).