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Orientational ordering of dyes in the glassy state of liquid-crystalline side group polymers

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Liquid-crystalline side group copolymers containing dyes can be macroscopically oriented and the orientation can be locked-in below the glass transition temperature. The order parameters of anthraquinone dyes and a trisazo dye in nematic and smectic glasses were determined by optical absorption measurements. The dyes have higher degrees of order in the smectic glass than in the nematic glass. A comparison of order parameters of covalently bonded dyes with order parameters of monomeric dyes dissolved in the corresponding homopolymers demonstrates the influence of covalently anchoring the dye to the polymer.

1. Dye containing liquid-crystalline copolymers

Liquid-crystalline side group copolymers containing covalently attached dyes have recently been discussed [1, 2]. In these copolymers the mesogenic groups and the dichroic dyes are covalently bonded via flexible spacers to the polymer backbone. The copolymers can be compared with mixtures of dichroic dyes dissolved in low molecular weight nematic liquid crystals (guest–host mixtures) [3–5]. The covalent bonding of the mesogenic unit and the dye causes significant differences between both systems. In the case of the copolymers crystallization of the dye is sufficiently hindered so that upon cooling, orientational order can be locked-in below the glass transition temperature resulting in a dichroic polymer film. This is not normally possible in low molecular weight guest–host mixtures, where the liquid-crystalline order is destroyed by crystallization upon cooling (i.e. the macroscopic orientation cannot be transferred into the solid state). Higher dye concentrations are obtainable in copolymers and the dye content is independent of temperature and type of the mesophase.

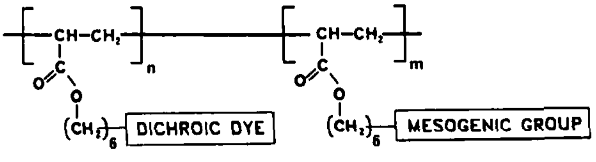
In this paper we report the orientational order of dichroic dyes in the nematic and smectic glass of liquid-crystalline copolymers. A comparison of order parameters of dyes covalently bonded in copolymers with the same dyes dissolved as monomers in the corresponding homopolymers will also be discussed.

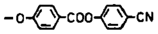
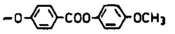
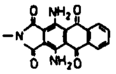
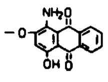
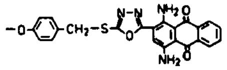
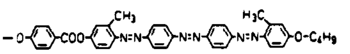
2. Experimental part

2.1. *Materials*

The random copolymers were synthesized by free radical copolymerization of mesogenic monomers with monomeric dyes (1 mol% AIBN in dioxane 70°C) [1, 6]. The chemical structures and the phase transition temperatures of the investigated dye

Table 1. Chemical structures and phase transition temperatures (°C) of the dye containing cyanophenyl benzoate copolymers **1a**–**1d** and methoxyphenyl benzoate copolymers **2a**–**2d**. Dye content based on the monomer unit is 2 per cent by weight for all copolymers.



DICHROIC DYE	MESOGENIC GROUP 			
	**1a**	g 29 n 120 i	**2a**	g 23 s_A 86 n 106 i
	**1b**	g 27 n 119 i	**2b**	g 25 s_A 90 n 112 i
	**1c**	g 25 n 109 i	**2c**	g 20 s_A 79 n 99 i
	**1d**	g 28 n 124 i	**2d**	g 26 s_A 92 n 121 i

g: glassy, s_A : smectic A, n: nematic, i: isotropic

containing liquid-crystalline polyacrylates (**1a**–**1d** and **2a**–**2d**) are given in table 1. The dye content is 2 per cent by weight for all copolymers, based on the monomeric dye unit. The copolymers with cyanophenyl benzoate as the mesogenic side group form a nematic phase, whereas the methoxyphenyl benzoate copolymers form a nematic and a smectic A phase. Table 2 shows the chemical structures of the liquid-crystalline homopolymers (**3**, **4**) used as hosts to dissolve the dichroic dye monomers (**5**–**7**). Mixtures (**8a**–**8c**, **9a**–**9c**) with a dye monomer content of 0·3 per cent by weight were prepared by dissolving both components in an organic solvent.

2.2. *Sample preparation*

The macroscopically oriented dichroic polymer films were prepared with the aid of surface treatment and a magnetic field. Homogeneous planar alignment was obtained by using rubbed, polyimide coated glass plates and cooling the samples in a magnetic field (2·1 T) from the isotropic melt through the nematic and/or smectic phase into the corresponding anisotropic glass.

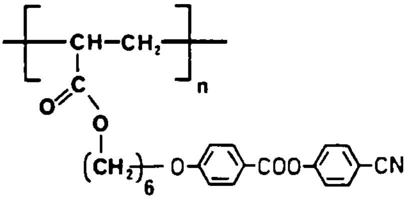
2.3. *Determination of the order parameter*

The optical absorbance was measured both parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the director of the homogeneous planar liquid crystal layer. The dichroic ratio R and the order parameter S_D, characterizing the orientational ordering of the transition moment of the dye, is deduced according to the expressions [4]

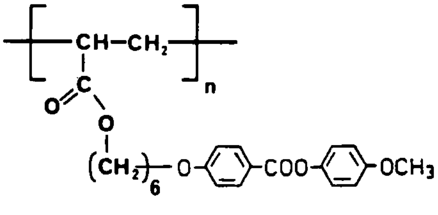
$$R = \frac{A_\parallel}{A_\perp}, \quad S_D = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}.$$

Table 2. Chemical structures and phase transition temperatures of the liquid-crystalline homopolymers (3, 4) used as hosts to dissolve the dye monomers (5–7). (* Virtual clearing point above decomposition and polymerization temperature.)

HOMOPOLYMERS:

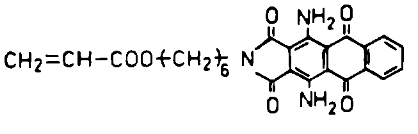


3 g 30 n 119 i

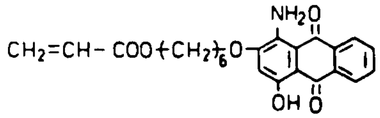


4 g 22 s_A 89 n 112 i

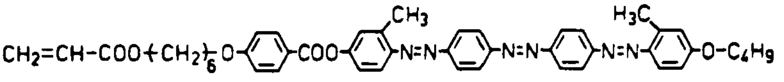
DYE MONOMERS:



5 c 162 i



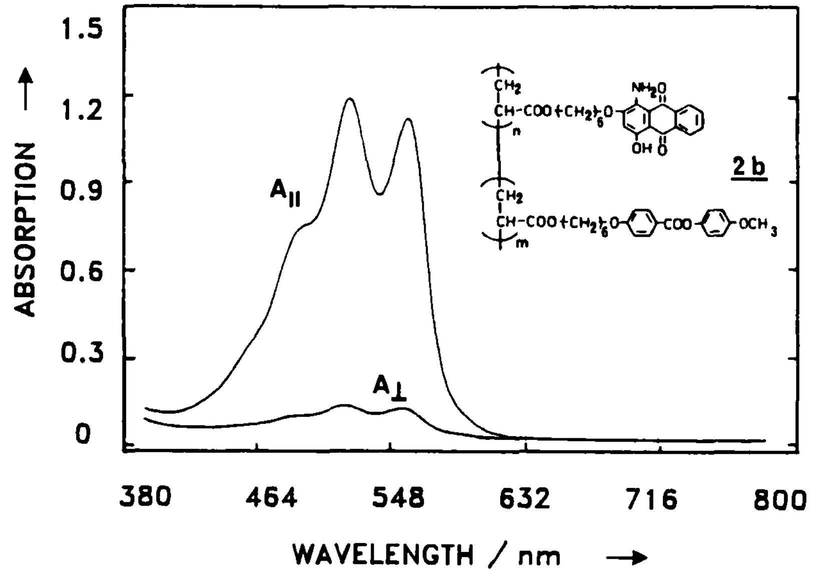
6 c 119 i



7 c 114 n >230 i*

No correction was made for the anisotropy of the polarization field. The optical absorbance was determined with a Perkin Elmer 330 double beam spectrophotometer equipped with HN 32 polarizers in both beams; no reference cell was used. After adjusting the light polarization direction parallel to the alignment direction of the cell, $A_\parallel$ was measured. $A_\perp$ was determined by means of a 90° rotation of both polarizers. As an example, the absorption spectra $A_\parallel$ and $A_\perp$ for the 1-amino-2-alkoxy-4-hydroxy-anthraquinone dye in the smectic glass of copolymer **2b** are shown in the figure. By choosing a suitable cell thickness (typical 10–30 μm), $A_\parallel < 2{\cdot}0$ and $A_\perp > 0{\cdot}1$, the experimental error is minimized. In combination with good sample quality this guarantees a reproducibility of the order parameters S_D with maximal deviations of 0·02 for different samples.

All measurements were made at room temperature in the glassy state of the polymer. The reduced temperature (T_{red}) for the glassy state of the liquid-crystalline polymers is defined by the ratio of the glass transition temperature (K) to the nematic–isotropic transition temperature (K). The transition temperatures were determined by D.S.C. measurements.



Absorption spectra taken both parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the alignment direction for copolymer **2b** in the smectic glass.

3. Results and discussion

The order parameters of dichroic dyes in low molecular weight guest–host mixtures strongly depend on the molecular structure of the dye [3–5] and the liquid crystal host [7, 8]. The influence of the molecular structure of the dye and the influence of the type of the liquid crystal phase on the dye order parameter in liquid-crystalline side group copolymers will be discussed below. A comparison is made of the order parameters of polymer-bonded dyes and the monomeric dyes dissolved in the corresponding homopolymers.

3.1. *Order parameters of polymer-bonded dyes in liquid-crystalline copolymers*

The dye order parameters of covalently bonded anthraquinone dyes and a trisazo dye in the nematic cyanophenyl benzoate copolymers (**1a**–**1d**) are given in table 3. Additionally, the reduced temperature (T_{red}) for the glassy state, the wavelength at which the order parameter has been evaluated, and the dichroic ratio (R) are given. Since the reduced temperatures are similar for all copolymers, the order parameters can be compared.

Table 3. Dichroic ratio R and order parameter S_D in the nematic glass of the cyanophenyl benzoate copolymers **1a**–**1d**.

No.	T_{red}	λ/nm	R	S_D
1a	0·77	682	7·2	0·67
1b	0·77	516	5·7	0·61
		552	5·7	0·61
1c	0·78	603	5·3	0·59
		627	5·1	0·58
1d	0·76	500	8·6	0·72

The order parameter of the 1,4-diamino-2,3-dicarboximidoanthraquinone dye in the nematic glass of copolymer **1a** is 0·67. In low molecular weight nematic guest-host mixtures S_D is in the same range for analogously substituted 1,4-diamino-2,3-dicarboximidoanthraquinone dyes at similar reduced temperatures [9]. The order parameters of the 1-amino-2-alkoxy-4-hydroxyanthraquinone dye in copolymer **1b** and the 1,4-diaminoanthraquinone dye in copolymer **1c** are lower. An unfavourable packing of the 2-substituted anthraquinone dyes is one possible explanation. Trisazo dyes have a high ratio of length to width and show generally high degrees of order in low molecular weight liquid crystals [10]. Therefore, the fixed trisazo dye in copolymer **1d** has a higher order parameter (0·72) than the anthraquinone dyes.

Table 4. Dichroic ratio R and order parameter S_D in the smectic A glass of the methoxyphenyl copolymers **2a**–**2d**.

No.	T_{red}	λ/nm	R	S_D
2a	0·78	682	11·8	0·78
2b	0·77	517	11·0	0·77
		554	11·2	0·77
2c	0·79	600	7·2	0·67
		626	7·4	0·68
2d	0·76	500	16·4	0·84

The dye order parameters in the smectic glass of the methoxyphenyl benzoate copolymers (**2a**–**2d**) are given in table 4. The influence of the dye molecular structure on S_D is very similar in the nematic copolymers but all dyes are essentially higher ordered than those in the nematic glass. The increase of orientational ordering of dye molecules is caused by the higher ordered structure of the smectic A phase. The measured dye order parameters are in the range of 0·78 for the anthraquinone copolymers **2a** and **2b** and 0·84 for the trisazo copolymer **2d**. These results are in agreement with deuteron N.M.R. measurements [11] and E.S.R. spin probe studies [12] in the smectic glass of homopolymer **4**. The order parameter of the mesogenic group determined by deuteron N.M.R. studies is 0·85 ± 0·05 and the order parameter measured via a spin probe is about 0·92.

3.2. *Order parameters of dissolved dyes in liquid-crystalline polymers*

As in low molecular weight liquid crystals, liquid-crystalline side group polymers can be used as hosts to orient dichroic dyes [13–16]. If dichroic dyes are used as guest molecules in liquid-crystalline side group polymers, the problem of limited solubility and possible phase separation with crystallization of the dye exists in the mesophase and the isotropic phase. Therefore, mixtures of a dye monomer content of only 0·3 per cent by weight were investigated. The results of nematic mixtures **8a**–**8c** and smectic mixtures **9a**–**9c** are summarized in tables 5 and 6 and compared with order parameters of the copolymers.

The order parameter of the 1,4-diamino-2,3-dicarboximidoanthraquinone monomer **5** dissolved in the nematic homopolymer **3** and of the polymer bonded dye in copolymer **1a** are equal (table 5). In the case of the 1-amino-2-alkoxy-4-hydroxyanthraquinone dye, a higher order parameter was observed for the copolymer. This is the only example where a higher order parameter for the polymer-bonded dye was

Table 5. Comparison of dye order parameters S_D for the dissolved dye monomers **5**–**7** in the nematic homopolymer **3** (mixtures **8a**–**8c**) with S_D for the covalently bonded dyes in the corresponding copolymers **1a**, **1b** and **1d** (table 3).

	Dissolved dyes in polymer 3			Polymer-bonded dyes		
No.	Dye monomer†	T_{red}	S_D	Copolymer	T_{red}	S_D
8a	**5**	0·77	0·67	**1a**	0·77	0·67
8b	**6**	0·77	0·56	**1b**	0·77	0·61
8c	**7**	0·77	0·76	**1c**	0·76	0·72

† Mixture of 0·3 per cent by weight dye monomer in homopolymer **3**.

Table 6. Comparison of dye order parameters S_D for the dissolved dye monomers **5**–**7** in the smectic homopolymer **4** (mixtures **9a**–**9c**) with S_D for the covalently bonded dyes in the corresponding copolymers **2a**, **2b** and **2d** (table 4).

	Dissolved dyes in polymer 4			Polymer-bonded dyes		
No.	Dye monomer†	T_{red}	S_D	Copolymer	T_{red}	S_D
9a	**5**	0·77	0·84	**2a**	0·78	0·78
9b	**6**	0·77	0·79	**2b**	0·77	0·77
9c	**7**	0·77	0·87	**2c**	0·76	0·84

† Mixture of 0·3 per cent by weight dye monomer in homopolymer **4**.

found. Trisazo monomer **7** in homopolymer **3** has a S_D of 0·76 which is higher than 0·72 measured for copolymer **1c**. In comparison, Finkelmann *et al.* [13] measured a S_D of 0·42 for a fixed bisazo dye in the nematic phase of a copolysiloxane. The order parameter for the monomeric dye dissolved in the homopolymer is higher (S_D : 0·54). Lower order parameters for polymer-bonded dyes can be explained by an incomplete motional decoupling of dye and polymer backbone due to the shortness of the spacer.

The dissolved dye monomers are oriented better in the smectic mixtures **9a**–**9c** (table 6) than in the nematic mixtures **8a**–**8c**. This is in agreement with the results observed for the copolymers discussed above. The high-order parameters $S_D = 0{\cdot}84$ of anthraquinone monomer **5** and $S_D = 0{\cdot}87$ of trisazo monomer **7** in the smectic homopolymer are remarkable. In all cases, the order parameters are higher in the mixtures than in the smectic copolymers. This result suggests that, in general, the decoupling of dye from the polymer backbone is more difficult to achieve in a smectic layer structure than in a nematic phase.

In summary, the results of the investigations demonstrate that dye containing liquid-crystalline copolymers and mixtures of dyes in liquid-crystalline polymers are suitable for the preparation of dichroic polymer films with high dichroic ratios. Higher order parameters should be obtainable by optimizing the molecular structure of the dye and the mesogenic side groups. Thin and well aligned copolymer films may open interesting application possibilities in the area of display and information storage technology.

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