Azo Dyes as Side Chains in Liquid Crystalline Oligomers for Holographic Application

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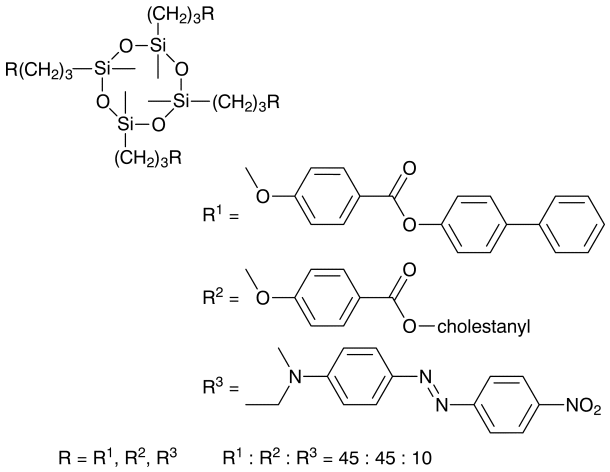
In a systematic study on materials for holographic data storage, a wide variety of azo dyes of different shapes and optical properties were covalently bound to cholesteric liquid crystalline oligosiloxanes; some of these materials exhibit high holographic efficiency and/or sensitivity but no general correlation between the holographic writing efficiency and/or the sensitivity with the structure was found.

Most promising materials for optical storage are nematic or cholesteric liquid crystalline polymers that possess arylazo groups as side chains.[2] The general structure of our liquid crystalline materials is shown in Scheme 1 with a simple azo dye as an example. They are composed of an octacyclosiloxane backbone with diphenyl- and cholestanyl-*p*-hydroxybenzoates and the azo dyes as side chains. They were made by palladium-catalysed hydrosilylation of the appropriate alkenes with the oligosiloxane.[5]



Scheme 1

A HeCd laser (442 nm) and a NdYAG laser (with frequency doubled emission at 532 nm) were used in the holographic experiments as the writing beam. The holographic efficiency was measured with a HeNe laser (633 nm, reading beam).

The structural variations of the azo dyes were carried out for the following reasons: (1) To tune the position of the long wavelength absorption band by variation of the strength of the electron-acceptor group.[6] (2) To generate a hypsochromic shift of the long wavelength absorption band by donor–donor substitution, by acceptor–acceptor substitution and by steric hindrance of the azo bridge.[6] (3) So as to investigate the influence of the length of the spacer on the liquid crystalline properties. (4) To study the effect of side-on instead of end-on binding on the mesogenic properties. (5) To get some information on the effect of the length of the photomechanically switched molecular part: the efficiency of the writing process should be higher the more the liquid crystalline order is disturbed, *i.e.* the longer the free part of the switching azo molecule is at the photochemical isomerization.

Simple azo dyes were made by the usual methods.[8] Styryl and arylethynyl groups were introduced into the azo dyes by palladium-catalysed cross-coupling reactions.[9]

The results of the optical measurements, the long wavelength absorption bands, the optical densities (OD) of the siloxane films, the efficiencies (Eff) and the sensitivities (S) of the holographic writing process at 442 and 532 nm are given in Table 1.

Some of these materials exhibit high holographic efficiency and/or sensitivity. But for a given azo dye/oligosiloxane system no prediction of the holographic optical storage properties can be made: as expected, the systems absorbing at short wavelengths have low ODs at 532 nm

Table 1 Optical properties of the arylazo dyes[a]

Dye	λ_{max} (nm, sol.)	OD_{442}	OD_{532}	Eff_{442}	Eff_{532}	S_{442}	S_{532}
5c	464	>4	4	24	26	1	2.1
5d	476	>4	4	21	16	1.3	1.2
5e	486	2.6	2.7	22	29	1.2	6
5f	446	>4	0.9	17	40	0.8	1.4
5g	458	>4	4	9	23	1	1.7
6a	442	>4	2.7	16	30	0.5	0.3
6b	424	>4	0.8	5	9	0.2	0.2
6c	408	>4	0.25	11	12	0.3	0.03
7c	438	0.9	0.05	23	1	1.1	0.01
7d	438	0.5	0.02	24	0.2	2	0.05
7e	436	0.8	0.08	28	0.2	1.4	0.01
7f	436	0.33	0.03	10	0.2	0.3	0.03
7g	464	1.9	0.4	25	31	0.5	0.7
7h	470	0.35	0.13	21	15	0.8	0.4
7i	448	0.5	0.08	17	10	1.9	0.3
7j	446	0.6	0.08	20	15	3.3	0.6
7k	442	0.2	0.05	7	0.4	0.11	0.01
7l	458	0.2	0.08	4	7	0.07	0.06
8a	464	1.8	0.2	0.1	0.1	0.01	0.01
9a	436	4	0.55	21	18	1.9	1.3
9e	464	3.6	1.9	15	34	3.2	2.7
9f	464	4	3.2	22	32	2.8	3.2
9h	454	4	1.2	26	24	3.2	5.5
10a	450	>4	2.5	30	34	3.4	6.6
10b	450	>4	2.4	25	35	3	6.1
11c	380	3.8	0.12	15	5	1.8	0.06
13a	438	>4	0.9	18	26	3.1	3.5
13b	438	>4	0.06	19	0.1	1.6	0.01
13c	420	>4	0.07	31	17	1.4	0.1
13d	438	>4	0.2	34	20	1.4	0.4
13f	420	>4	0.05	15	0.1	1	0.01

[a]Absorption wavelengths in solution, all other measurements in an oligosiloxane matrix.

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(connected with low efficiencies and sensitivities). Nevertheless some of these compounds exhibit high values. No further relationship seems to exist between the structure or the properties of the azo dye moieties and the Eff or S. It is noteworthy that completely different molecules, *i.e.* extended arylazostilbenes and arylazoimines and a simple azo dye, exhibit the best values.

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Techniques used: IR, UV–VIS, ^{1}H and ^{13}C NMR, EI and FAB mass spectrometry

References: 17

Schemes: 2

Fig. 1: Absorption spectra of **5e**, in methylcyclohexane (□), at $\lambda_{max} = 452$ nm normalized to OD = 1; after irradiation for 5 min with a xenon lamp 250 W cm^{-2}, Schott filter GG 385 nm (△); in siloxane matrix (○), at $\lambda_{max} \approx 483$ nm normalized to OD = 1. The strong absorption below 350 nm is owing to the oligosiloxane moiety

Fig. 2: Dependency of the efficiency (Eff) on the optical density. Eff of **7c–f**, **k**; **8a**; **13b**, **f** < 1

Fig. 3: Dependency of the sensitivity (S) on the optical density. S of **6a–c**; **7c–f**, **h**, **j–l**; **11c**; **13b–d**, **f** ⩽ 0.6

Fig. 4: Correlation of the sensitivity (S) with the efficiency (Eff) of oligosiloxanes with arylazo dye side chains

Table 2: Method of preparation and analytical data of the arylazo compounds **5a–i**, **6a–c**, **7a–l** and **8a**,**b**

Table 3: Method of preparation and analytical data of the (*E*)-arylazo stilbenes **9a–k**, **11a–c** and arylazoimines **10a**,**b**

Table 4: Method of preparation and analytical data of the benzothiophenes **12a**,**b** and the arylazo compounds **13a–f**

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