Organic-dye films for optical recording

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Like the tellurium alloys described in the previous article, some organic dyes have optical, thermal and mechanical properties that enable them to satisfy the requirements made on optical recording materials. The use of organic-dye films can have advantages: they are easy to prepare, permit high writing speeds, and both digital and analog (video) information can be recorded. Although the search for suitable dyes is by no means at an end, interesting results have already been achieved with a number of dyes and with the recording characteristics of films prepared from them.

Introduction

Organic dyes consist in general of unsaturated conjugated hydrocarbon compounds in which heteroatoms (e.g. nitrogen, oxygen, sulphur) are incorporated. The 'pi electrons' of the delocalized double bonds are excited with relatively little energy. Depending on the type of compound, the first absorption band, corresponding to the lowest excitation energy, may be situated in the near infrared, in the visible wavelength range or in the near ultraviolet.

To be useful as a material for optical recording with an AlGaAs laser the dyes must adequately absorb infrared light at 820 nm. Most organic dyes, however, give strong absorption only at shorter wavelengths and are therefore ruled out. A number of the dyes that absorb well at 820 nm have been investigated with a view to their use for optical recording. Experiments have included single-dye films \(^{[1]}\), polymer films containing dyes \(^{[2]}\) and combinations of dye films and tellurium films \(^{[3]}\). Various studies have shown that with some organic dyes it is possible to prepare films that have good recording properties. These dyes not only have an intense narrow-band absorption at about 820 nm, but also have a low melting point and low thermal conductivity. Pits are formed in such films with a laser beam of relatively low energy. The films can also give strong reflection at 820 nm, thus readily allowing tracking and read-out of information written into the film. Some dyes in addition possess sufficient physical and chemical stability, thus ensuring the durability of the discs and the information stored in them.

Organic-dye films may offer advantages over tellurium alloys \(^{[4]}\). In many cases smooth homogeneous films can be applied by means of a 'spin-coating' process. The threshold energy for the formation of pits is low, enabling high writing speeds to be achieved. Provisions can also be made for the storage of analog video information, by varying the length of the pits and the spacing between them, and for increasing the information density (packing density) by varying the depth of the pits.

In the investigation described in this article, aimed at finding a suitable dye, a provisional selection was

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\(^{[4]}\) L. Vriens and B. A. J. Jacobs, this issue, pp. 313-324.
first made on the basis of general understanding of the physical and chemical properties of organic dyes. Use was also made of data from the literature concerning the advantages and disadvantages of dyes as recording materials. In view of the coating method adopted, it was necessary to determine whether the dyes are sufficiently soluble in certain organic solvents, while at the same time insoluble in water to ensure stability.

The dyes investigated were applied in the form of films of different thicknesses on substrates of glass, with and without a pregrooved 2p lacquer layer \[^{[4]}\] and polymethyl methacrylate (PMMA). The reflectance and transmittance were measured as a function of the thickness and morphology of the films. During the writing of information in the films the intensity and duration of the laser pulse were varied. During the read-out of written information the signal-to-noise ratio was measured. The geometry of the pits generated and the mechanism of pit formation were also studied, as well as the ageing behaviour of the films and the information stored in them. The investigation extended to the effects of high temperature, frequent temperature alternations at high humidity, prolonged irradiation with light and repeated read-out with a laser beam.

The investigation showed that there are a number of dyes that satisfactorily meet the requirements for optical recording. This article will deal mainly with the optical recording. If insufficient stability of the dye film is a problem, then with a given number of vinyl units, the length of the conjugated system is fairly large. Since the oscillator strength of the first absorption band increases strongly with the length of the conjugated system, each new vinyl unit gives a wavelength shift of about 100 nm. The effect of R is considerable: with a given number of vinyl units, \( \lambda_{\text{max}} \) for type B is almost 300 nm longer than for type A.

As fig. 1 shows, type B with two vinyl units meets the requirement of maximum absorption at about 820 nm. This requirement is also met by polymethine dyes with other end groups and a specific number of vinyl units. In all these cases the total length of the conjugated system is fairly large. Since the oscillator strength of the first absorption band increases linearly with this length \[^{[6]}\], the absorption can be high.

The choice of dye is also limited by the requirements for the stability of the recording layer. In general, polymethine dyes are less stable as the conjugated system becomes longer. This means that although certain dyes with a long conjugated system have a high absorption at 820 nm, they are not stable enough for optical recording. Insufficient stability of the dye film may also be the result of solubility in water. Among the ionogenic dyes this rules out the chlorides.

A further selection of dyes depends on the method of application adopted, in which the dye is first dissolved in an organic solvent that does not react with the substrate (glass or plastic). Suitable solvents include acetonitrile (CH\(_3\)CN), n-propanol (CH\(_3\)CH\(_2\)CH\(_2\)OH) and ethyl acetate (CH\(_3\)COOC\(_2\)H\(_5\)). The dye must be readily soluble in at least one of these solvents. In
some cases the solubility of a dye in an organic solvent is appreciably increased by the application of space-filling substituents such as tertiary butyl groups \((\text{CH}_3)_3\text{C}^-\). Such groups have the effect of increasing the stacking distance in the crystal lattice, thus reducing the intermolecular interaction energy so that the dye dissolves more readily.

Two dyes that easily meet the requirements for infrared absorption, stability and solubility are shown in fig. 2. The non-ionogenic dye referred to as SQS consists of a squarylium nucleus with thiopyrylium end-groups. These ensure that the strong absorption that is characteristic of squarylium dyes is at a maximum in the neighbourhood of 820 nm. Because of the presence of the four tertiary butyl groups, this dye dissolves readily in solvents such as \(n\)-propanol. The other dye, tetradimethyl aminophenyl pentamethine perchlorate (TPMP) is one of the many ionogenic polymethine dyes. This also absorbs strongly at 820 nm. Unlike the chloride form of this pentamethine, TPMP is insoluble in water, so that waterproof films can be obtained.

Method of application and film properties

The spin-coating process is a suitable method for applying thin SQS and TPMP films. A solution of the dye is poured on to a substrate fixed to a turntable in a clean room. The substrate is then rotated at a frequency of 3 to 30 Hz, so that the solution spreads out over the surface. During the spinning the liquid film becomes steadily thinner as most of the solution is flung off the surface and the solvent evaporates. After a short time a thin amorphous dye film remains. The thickness of the film depends on factors such as the frequency of rotation, the solvent and the initial concentration of the dye in the solution. A film thickness of between 40 and 200 nm is generally obtained.

To obtain a smooth homogeneous layer the solubility of the dye in the solvent should preferably be at least 10 g/l and the solvent should have the correct viscosity and volatility. The surface tension of the solvent should also be lower than that of the substrate, to permit effective wetting. In addition the solvent must not react with the substrate and must leave no vaporization residues. For the application of SQS and TPMP films the solvents acetonitrile, \(n\)-propanol and ethyl acetate mentioned above meet these requirements reasonably well. The spin coating can be carried out at normal pressure and temperature. Dust and other contaminants can be removed from the solution beforehand, e.g. by filtration, and highly homogeneous films can thus be obtained.

Fig. 1. Wavelength \(\lambda_{\text{max}}\) of the maximum of the first absorption band as a function of the number of vinyl units \(m\), for two types of polymethine dyes with the general formula \(R'(-\text{CH} = \text{CH})_m\text{CH} = R\) for one resonance structure. For both types \(\lambda_{\text{max}}\) increases by about 100 nm per vinyl unit. At a given value of \(m\) it can be seen that \(\lambda_{\text{max}}\) for type B is about 300 nm longer than for type A. At \(m = 2\), the maximum absorption with type B is found at about 820 nm.

Fig. 2. Structural formulae of SQS and TPMP, two organic dyes suitable for optical recording. Only one resonance structure is given for each of the two dyes.
An important difference compared with films deposited by vacuum evaporation or sputtering is encountered when the films are applied to a grooved substrate, as used in the manufacture of digital optical recording discs. In this case the substrate has a pre-grooved layer of lacquer or pregrooved PMMA. When the film is deposited on such a substrate by vacuum evaporation or sputtering the pattern of grooves is followed exactly, so that the film acquires virtually the same surface structure and the thickness is virtually constant over the entire surface. In the spin-coating process for dyes, on the other hand, the grooves in the substrate are filled up with dye solution and the final result is a film with a completely smooth surface.

The films of SQS and TPMP, applied by the spin-coating process have strong absorption and acceptable reflection in the near infrared. Fig. 3 shows the measured reflectance and transmittance of a 75-nm SQS film on a glass substrate, with the light incident from the substrate side. At a wavelength of 820 nm the reflectance is about 20% and the transmittance about 10%.

SQS film on a glass substrate as a function of the wavelength of the incident light. In the reflection measurements the light is incident from the substrate side, as it is in the writing and reading of optical recording discs. At 820 nm the reflectance is about 20% and the transmittance about 10%, so that the absorption is about 70%. Roughly the same values are found with TPMP films.

The measured reflectance and transmittance at a given wavelength and the measured film thicknesses can be used to calculate the complex refractive index of the dye films. This is equal to $n - jk$, where $n$ is the real refractive index, and the absorption index $k$ is related to the linear absorption coefficient $\alpha$ at the wavelength $\lambda$; the relation is $k = \alpha\lambda/4\pi$. As would be expected, the complex refractive index of SQS and TPMP films depends strongly on the wavelength. Fig. 4 shows as an example the values of $n$ and $k$ calculated for a TPMP film plotted against wavelength. The maximum value of $k$, which is about 1.3, is obtained at 830 nm, when $n$ is about 2.1.

The calculated values of $n$ and $k$ can now be used to predict the reflectance and transmittance at a given wavelength as a function of the thickness of the dye film. Fig. 5 gives the results of such calculations for SQS layers at a wavelength of 800 nm, where $n = 1.9$ and $k = 1.5$. The experimental values of the reflectance and transmittance of films of different thickness agree reasonably well with the predicted curves. The reflectance of SQS and TPMP films has a maximum at a thickness of about 90 nm.
Recording characteristics

The recording characteristics of a dye film can be determined by focusing the beam from a krypton-ion laser emitting at 799 nm on to a disc coated with the film. The laser beam is incident on the substrate side, and is focused by an objective with a numerical aperture of 0.5, giving a light spot with an effective diameter of about 1 µm. During the exposure the disc rotates at a frequency of say 25 Hz, giving a tangential velocity of 10 to 20 m/s. The 'writing' is done by a pulsed laser beam with a repetition frequency of 5.7 MHz, which is equivalent to recording a 'carrier' \[11\] at this frequency. During the writing the energy is varied from 0.08 to 1.2 nJ per pulse by varying the power of the laser beam at the recording layer from 1 to 15 mW, with a pulse duration of 80 ns. For focusing, tracking and read-out the laser beam on the film has a continuous power of about 0.5 mW.

The carrier-to-noise ratio, CNR, on read-out is highly dependent on the laser energy used in writing the carrier into the dye film. In fig. 6 the carrier-to-noise ratio (at a bandwidth of 30 kHz) measured for SQS and TPMP films on a pregrooved PMMA sub-

![Fig. 6. Carrier-to-noise ratio CNR on read-out as a function of the writing energy E, for recording in 80-nm SQS and TPMP films on a pregrooved PMMA substrate. The measurements were made at a bandwidth of 30 kHz and a rotation frequency of 25 Hz. For writing the pulse rate is 5.7 MHz and the pulse duration 80 ns. In both cases a measurable signal is only obtained after a threshold energy (about 0.15 nJ) is exceeded. Above this threshold the CNR-value increases steeply with E. With the SQS film a saturation value of 63 dB is reached at 0.6 nJ.](image)


![Fig. 7. Micrographs made with the SEM (scanning electron microscope) of pits in an SQS film, formed at a writing energy of 0.23 nJ (a), 0.27 nJ (b) and 0.42 nJ (c); the scale divisions are 1 µm. At a higher writing energy deeper and broader pits are produced. During writing, the disc rotates at a frequency of 8 Hz and the tangential velocity at the writing positions is about 5 m/s. During a laser pulse of duration 80 ns the write locations hardly move at all, so that circular pits are produced. For video recording the rotation frequency is higher (e.g. 25 Hz) and elongated pits are formed.](image)
strate is plotted as a function of writing energy. The threshold energy for obtaining a measurable signal is relatively low in both cases: about 0.15 nJ. Above the threshold energy the CNR-value rises steeply with the writing energy. At a writing energy higher than 0.6 nJ a CNR-value of 63 dB is reached with the SQS film. Slightly lower values are found with the TPMP film. Values are high enough for recording video information as well, which requires a minimum of 57 dB. This was confirmed by initial experiments with video recording on SQS films.

From micrographs made with the scanning electron microscope (SEM) it can be concluded that writing on SQS and TPMP films produces pits with a ring at the surface. In TPMP films this ring is relatively thick.

Read-out of the written information is based on the lower reflectance at the location of the pits, since the film at these locations is thinner (see fig. 5). Since relatively little energy is necessary to form readily 'readable' pits in SQS and TPMP films, the sensitivity of these films for optical recording is high. Higher writing energies produce deeper and broader pits; see fig. 7. A deeper pit gives a more marked reduction in reflectance, so that the CNR-value rises with the writing energy (fig. 6). It may also be deduced from the SEM
micrographs that writing does not give rise to any 'grain' and that the pits are regular in shape. This agrees with our earlier observation that writing is not accompanied by any additional noise. It is possible to explain why writing from the substrate side generates pits in the surface of the dye film and not in the interface with the substrate by making use of calculations of the temperature profile produced in the film; see fig. 8a. Since the absorption length (λ/4πk) of SQS and TPMP is about 50 nm, films with a thickness of this order are fairly homogeneously heated by the laser beam. Heat dissipation to the substrate produces a steep temperature gradient in the film, with the highest temperature at the surface.

Because of the temperature increase that occurs at the surface during writing, the dye film melts at the places exposed to the beam and partially vaporizes or decomposes. The evaporating dye molecules or their decomposition products cause a pronounced recoil effect, producing considerable pressure on the surface of the molten dye. This sets up radial movement of material towards the outside, so that a pit with a ring is formed.

With thicker dye films and a high writing energy, holes may be formed at the writing locations, i.e. pits extending down to the substrate. With TPMP films more than 110 nm thick a writing energy of more than 0.5 nJ is necessary to produce such holes. Near the holes some grain is usually found, probably as a result of a kind of eruption. Holes are formed in a thick film and not in a thin one because the temperature profile produced in a thick film is completely different; see fig. 8b. Since only the first 50 nm of the film is heated effectively, with poor thermal conductivity in the film and heat dissipated to the substrate, a steep temperature gradient is obtained in the film with the highest temperature on the inside. This results in considerable gas generation inside the film, caused by the evaporating dye or its decomposition products. At a high writing energy the gas pressure in the interior of the film can become so high that the 'cold' upper layer tears open, producing a hole right through the thickness of the film at the writing location.

With a film thickness of about 90 nm, the optimum for reflection at 820 nm, no holes but only pits are formed. With this thickness, however, it is not possible to produce good recording inside the groove tracks when a grooved substrate is used. This is because the film between the groove tracks would be only 20 nm thick at the normal groove depth of 70 nm \(9^{-1}\), and it would therefore not reflect sufficiently (fig. 5). Good recording is possible, however, if the information is written between the groove tracks, and if the dye film has a thickness of 90 nm there.

A special feature of the organic-dye films described here is that the dimensions of the pits can be adjusted fairly accurately by taking appropriate values for the frequency of rotation of the disc, the laser power and the pulse duration. As an example, fig. 9 shows the length of the pits as a function of pulse duration for recording on an SQS film. At a given rotation frequency and laser power the pit length can be seen to increase linearly with the pulse duration.

Because the pit dimensions are adjustable, organic-dye films widen the scope for optical recording. For instance, in addition to digital recording, which is a matter of generating or not generating pits, they can also be used for analog recording in which the length of the pits and the spacing between them are varied. This means that video information can also be recorded. Fig. 10 shows an SEM micrograph of an SQS
film with a pattern generated by the writing of video information. As remarked earlier, the available signal-to-noise ratio is high enough to ensure reliable video recording. Another capability is the storage of information by writing pits of different depths. In this way the information density can be considerably increased. The practicability of the various potential applications will depend largely on the ageing behaviour of the dye films.

Ageing behaviour

In view of the different potential applications of organic dye films for optical recording, only a few general stability tests have so far been made on unprotected dye films. To study the effect of heat on ageing, we kept the films for some time in an oven at 90 °C. We also subjected films to rapid alternations in temperature at high humidity as specified in the Z/AD test \[12\]. For this test the films were stored in an environmental test chamber in which the temperature is cycled between 25 and 65 °C at a relative humidity of about 93%. Measurements were also made of the light-fastness of the films by subjecting them to prolonged irradiation from an intense light source and a large number of laser irradiations under read-out conditions.

During most of the tests SQS films gave unwanted crystallization. This can be prevented by the addition of a small amount of certain polymers, without in any way affecting the recording characteristics.

Transmittance measurements before and after ageing showed that TPMP films stand up well to high temperatures. After 200 days in an oven at 90 °C the transmittance only went up from 20 to 22%. SQS films, however, are adversely affected by storage at high temperatures. The transmittance of an SQS film on a PMMA substrate doubles after 20 days at 90 °C. At room temperature, on the other hand, SQS layers are very stable. On a pregrooved PMMA substrate SQS layers still had a CNR-value of more than 60 dB after keeping them in an ordinary office for a year.

In the Z/AD tests both SQS and TPMP films are found to be very stable. In fig. 11 the transmittance of an SQS film on a PMMA substrate and a TPMP film on a lacquer-coated glass substrate are shown as a function of the time spent in the environmental chamber. In both films the transmittance increases only slightly during ageing.

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**Fig. 11. Transmittance T for an SQS film on a PMMA substrate and for a TPMP film on a lacquer-coated glass substrate during ageing in a Z/AD test \[11\], as a function of time t (in days) in the environmental test chamber. In both films the transmittance increases only slightly during ageing.**

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**Fig. 12. Effect of the ambient atmosphere on the fading rate of SQS films on irradiation with white light of intensity 1000 W/m² at 40 °C. As a measure of fading the transmittance T is plotted as a function of the irradiation time t (in days). The transmittance increases more slowly in dry oxygen (O₂) than in wet oxygen (O₂/H₂O). The light-fastness is even better in wet nitrogen (N₂/H₂O) and in dry nitrogen (N₂).**

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The light-fastness of the dye films was studied in a 'Xenotest', in which the films were irradiated with white light of 1000 W/m² intensity — about 500 times the illuminance in an ordinary office. During the irradiation the temperature was maintained at about 40 °C and the relative humidity at about 65%. The transmittance and reflectance were measured at different times. The fading caused by the irradiation was much slower with TPMP films than with SQS films. An increase in the transmittance by a factor of about 2 was found with SQS films after 100 hours of irradiation, and not until after 400 hours of irradiation for TPMP films. The fading rate of SQS films is strongly affected by the ambient atmosphere; see fig. 12. In dry oxygen the fading is much slower than in wet oxygen.

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