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Synthesis of new kinds of reactive azo dyes and their application for fibre-optical pH-measurements

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Abstract

The aim of these investigations was the synthesis of a new kind of reactive azo dyes and their application as reversible pH-sensors. For binding of the dyes to a polymer matrix acetal bonding was introduced as a new method. The required azo dyes containing a formyl group were synthesised by two different routes: by introducing this functional group to a suitable substituent within pre-formed azo dyes, or to the dye precursors. Using polyvinyl alcohol and its co-polymers as matrix materials, acetalisation of the formyl groups of the dye by the 1,3-alternating hydroxy groups of the polymer can take place—forming a stable six-membered 1,3-dioxane ring. These dye-polymer composites can be used directly for thin film preparation. The obtained sensor membranes exhibit very good response behaviour and excellent long term stability, even under strongly basic conditions. These membranes turned out to be promising materials for an in-situ monitoring of aggressive environments, e.g. in concrete.

Keywords: Optodes; pH-indicator azo dyes; Aldehydes as reactive group; Acetal bonding with polyvinyl alcohol; Fibre-optical sensors; Basic environment

1. Introduction

The pH is a very important property of solutions of many substances. Different methods can be used for its determination, e.g. pH-dependent electrical potential differences within glass electrodes or photometrically determined changes of the UV/vis-absorption and-fluorescence of appropriate indicator molecules. Devices based upon the latter method are so-called pH-optodes. Their advantages are (i) independence of the ionic strength of the solved ions, (ii) their stability at very high (i.e. basic) pH and (iii) the ability to transmit the optical signal by fibres over long distances. Usually, these optodes are made from composites of dyes with pH-dependent optical properties and a transparent polymer. The dyes

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are usually incorporated by two methods: as host–guest system or by covalent bonding. The first method is quite simple, but its limitations are dye aggregation and leaching. These can be overcome using the second method. There are different methods for the preparation of dyes, covalently bonded to the polymer backbone: either by co-polymerisation of dye-precursors and subsequent complete formation of the dye molecules within the polymer or by bonding of preformed dyes to the polymer using suitable functional groups.

Commonly used indicator azo dyes for alkyline pH-determination contain arylhydroxy group, which can be deprotonated in it, (e.g. reactive dyes, containing a vinylsulphone reactive group [1]). Their advantages are (i) stability both in acidic and basic environment, (ii) ease of attachment of different functional groups and (iii) they can be synthesised by simple chemical reactions.

Different polymers are used as dye carriers for such sensors. They have to fulfill several requirements like transparency within the UV/vis-range and a sufficient hydrophilicy to allow an interaction of the indicator dye and the sample. Mohr et al. [2] used polyester coated with cellulose acetate and have bonded vinylsulphone azo dyes by ether linkages to the hydroxy groups of cellulose [2,3]. This method led to sensors exhibiting fast response times and sufficient stability at pH 12.0–12.5, but they are restricted to short term measurements. pH-sensitive membranes based upon highly lipophilized dyes adsorbed on the surface of plasticised PVC have been reported [4]. Other authors have proposed immobilisation of the pH-sensitive dye using ion-exchangers [5]. In the first case leaching of the dye is the main problem and makes these systems useless for long term measurements. The second method is attractive, because the dye is tethered by means of strong electrostatic interactions. Hence, the sensors show fast response and leaching is not observed. On the other hand the dyes are charged—resulting in a number of other shortcomings.

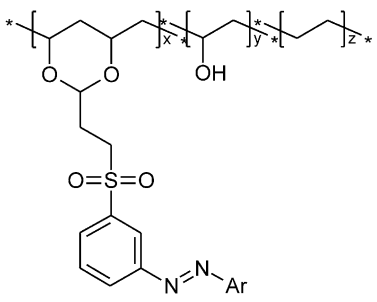
Acetal formation using the hydroxy groups of the polymer (e.g. polyvinyl alcohol) and formyl groups of different aliphatic aldehydes are known since 1924: the poly(vinyl acetal) resins [6,7]. This linkages posseses extreme stability under basic conditions. But to our knowledge, this procedure has not been used with dyes yet.

The following methods are commonly used for producing polyvinyl acetals:

1. conversion of polyvinyl acetate into polyvinyl alcohol in acidic solution followed by acetalisation [8,9];
2. reaction of an aqueous solution of polyvinyl alcohol with an aldehyde and subsequent precipitation of the acetals [10];
3. heterogenous reaction of a film, a fiber or a suspension of polyvinyl alcohol and an aldehyde.

The aim of present paper is the preparation of pH-sensors with long term stability within a wide range of alkaline pH-values—based upon azo dyes, which are covalently bonded to a polymer matrix (see Scheme 1).

We preferred the commercially available polyvinyl alcohol and its ethylene copolymers (see Scheme 1) as matrix material because of its good stability, flexibility and transparency within the visible range as well as of its content of reactive hydroxy groups in 1,3-alternating positions. Its application in sensors with dyes, bonded by ether linkages, has been already reported [11]. Some authors claim that polyvinyl acetals based upon polyvinyl formal should be stable even in an acidic environment [12].



Ar = Aryl

Scheme 1. General formula of the dye–polymer composites synthesized in this work.

2. Experimental

2.1. General remarks

All commercial reagents (Aldrich Chemical Company) were of analytical grade and were used as recieved. All solvents were purified by distillation before use. Photochemical reactions were carried out in a water cooled 400 ml reactor with mercury low-pressure (10 W) and medium-pressure (150 W) lamps (Heraeus) inside. 1,3-dioxolane, that plays the role of solvent and as well as reagent was freshly distilled and degased by means of passing argon for 15 min. Flash column chromatography (FC) was performed using silica gel "Kieselgel 60" (0.040–0.063 mm, Merck). Melting points were determined on Eleitz hot stage microscope apparatus and were uncorrected. Spectra (400 MHz ^{1}H and 100 MHz ^{13}C NMR) were recorded on a Bruker Avance GRX-400 spectrometer in $CDCl_3$ (tetramethylsilane (^{1}H) or the solvent (^{13}C) as internal standards) or DMSO-d_6 [solvent (^{1}H and ^{13}C) as standard]. Mass spectra were obtained on a Finnigan MAT 8400-MSSI spectrometer. UV–vis absorption spectra were recorded on a Hewlett Packard 8452 A diode array spectrophotometer. FT-IR spectra were run on a Nicolet 320 FT-IR spectrometer. Elemental analyses were carried out by the analytical laboratory of the Institute of Pharmaceutical Chemistry, Technical University of Braunschweig.

2.2. General procedures

2.2.1. Synthesis of azo dyes

2.2.1.1. Diazotation. The amine (10 mmol) was dissolved in 6 N HCl (25–30 mmol). The mixture was cooled by means of an ice-water bath and an aqueous solution of $NaNO_2$ (15%, 7 ml) was added dropwise within 15 min. The resulting yellow to orange solution was stirred at that temperature for 1 h. Finally the excess of HNO_2 was destroyed by adding solid urea (0.5 g).

2.2.1.2. Coupling. The thus prepared solution was added to a solution of the appropriate hydroxyaryl compound (10 mmol) in aqueous NaOH solution (10%, 15 ml) at 3–5 °C with vigorous stirring. After stirring for 40 min, the mixture was neutralized by adding 2 N HCl (20 ml). The precipitated dye was isolated by filtration and washed with water (3×50 ml). Purification was achieved by flash column chromatography and recrystallisation using the solvents given below.

2.2.2. Introduction of the vinylsulphonyl group

The following procedure is an improvement of the method described in [13].

Concentrated sulphuric acid (20 ml) was added in small portions and under vigorous stirring to a solution of 2-(3-aminophenylsulphonyl)ethanol hydrochloride **1** (5 mmol) at 25 °C under nitrogen atmosphere. After stirring for 2 h under these conditions the mixture was poured into ice water (100 ml) and neutralised by careful addition of solid Na_2CO_3. The temperature was kept at 15–20 °C by adding the appropriate amount of ice. After addition of diethyl ether (100 ml) aqueous NaOH (30%, 20 ml) was added carefully. The organic phase was separated and the aqueous phase was extracted with diethyl ether (3×50 ml). The combined ethereal solutions were dried (Na_2SO_4) and the solvent was removed. The crude product was purified by flash column chromatography.

2.2.3. Photochemical addition

We have used procedure [13] for photochemical synthesis of acetals. Benzophenone was used as a photochemical initiator in molar ratio 1:1 with respect to the vinylsuphonyl compound. The reaction was also carried out under argon and cooled with water and was completed in 5–60 min. Purification was done by flash column chromatography.

2.2.4. Deprotection of the formyl group

To a solution of the protected dyes **6a**–**c** (2 mmol) in a mixture of acetone (30%) in water (total volume: 30 ml) H_2SO_4 (15%, 10 ml) was added and the resulting mixture was refluxed for 3 h. After that, water (200 ml) was added and the resulting precipitate was isolated by filtration and washed with water (2×50 ml). The filtrate was extracted with diethyl ether (3×30 ml) and the combined ethereal solutions were washed with aqueous $NaHCO_3$ (1%, 50 ml). After drying (Na_2SO_4)

the solvent was removed. The aldehydes **7a**–**c** were purified by flash column chromatography.

2.2.5. Covalent bonding of the dyes

Poly-(vinylalcohol-*co*-ethylene) (500 mg, ethylene content: 27%) was dissolved in DMF (30 ml) at 100 °C and the reactive dyes **7a**–**c** (40 mg, 0.11–0.12 mmol) were added. After addition of conc. HCl (2 ml) the mixture was stirred for 3 h at 70 °C. Water was added and the precipitated polymer was filtrated. After washing with water (100 ml), acetone (50 ml), 2 N NaOH (50 ml) and water (100 ml) the polymer was purified twice by redissolving in 30 ml DMF and subsequent precipitation in 2 N NaOH (100 ml), washed with copious amounts of water and dried in vacuo at 50 °C for 3 h.

2.3. Azo-dyes

2.3.1. 2-[3-(2-Hydroxy-ethanesulphonyl)phenylazo]-4-methylphenol (2)

2-(3-Amino-benzenesulphonyl)-ethanol (3.00 g) was diazotised and the salt was coupled with 1.36 g of paracresole according to Section 2.2.1. Dye **2** was purified by FC (*t*-butyl methyl ether), followed by recrystallisation from ethanol which gave the product as yellow-orange needles (yield 3.00 g, 75%), m.p. 145 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 12.27 (s, 1H, Ar–OH), 8.41 (t, J = 1.8 Hz, 1H, ArH), 8.14 (ddd, J = 7.9 Hz, 1.8 Hz, 1.1 Hz, H, ArH), 8.02 (ddd, J = 7.9 Hz, 1.8 Hz, 1.1 Hz, 1H, ArH), 7.77 (d, J = 2.4 Hz, 1H, ArH), 7.74 (t, J = 7.9 Hz, 1H, ArH), 7.22 (dd, J = 8.4 Hz, 2.2 Hz, 1H, ArH), 6.95 (d, J = 8.4 Hz, 1H, ArH), 4.77 (s, 1H, $CH_2CH_2O\underline{H}$), 4.06 (t, J = 5.3 Hz, 2H, $CH_2C\underline{H}_2OH$), 3.45 (t, J = 5.3 Hz, 2H, $C\underline{H}_2CH_2OH$), 2.40 (s, 3H, CH_3).

^{13}C NMR ($CDCl_3$): δ (ppm) = 151.2 (ArC), 150.6 (ArC), 140.7 (ArC), 137.1 (ArC), 135.7 (ArCH), 133.4 (ArCH), 130.6 (ArCH), 129.7 (ArCH), 129.4 (ArCH), 128.0 (ArCH), 120.7 (ArCH), 118.0 (ArCH), 58.3 (CH_2), 56.3 (CH_2), 20.2 (CH_3). MS: m/z (%): 320 (80%, M^+), 107 (base peak). Calculated for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.03; N, 8.74; S, 10.01. Found: C, 56.27; H, 4.98; N, 8.51; S, 10.06.

2.3.2. 2-(3-Ethenesulphonyl-phenylazo)-4-methylphenol (3)

The dye **3** was obtained from 1.72 g of **2** according to Section 2.2.2. without extraction with diethyl ether, 5 min after adding NaOH the solution was neutralised with 2 N HCl and the precipitated dye was filtered. Purification by FC (CH_2Cl_2) and recrystallisation from ethanol–water gave dye **3** as orange needles (1.30 g, 80%), m.p. 122 °C.

^{1}H NMR (DMSO-d_6): δ (ppm) = 10.72 (s, 1H, Ar–OH), 8.42 (t, J = 1.8 Hz, 1H, ArH), 8.34 (ddd, J = 7.9 Hz, 1.8 Hz, 1.1 Hz, H, ArH), 8.02 (ddd, J = 7.9 Hz, 1.8 Hz, 1.1 Hz, 1H, ArH), 7.88 (t, J = 7.9 Hz, 1H, ArH), 7.57 (d, J = 1.3 Hz, 1H, ArH), 7.30 (dd, J = 8.4 Hz, 2.2 Hz, 1H, ArH), 7.25 (q, J = 9.8 Hz, 16.4 Hz, 1H, CH), 7.00 (d, J = 8.4 Hz, 1H, ArH), 6.45 (d, J = 16.4 Hz, 1H, CH_2), 6.30 (d, J = 9.8 Hz, 1H, ArH), 2.30 (s, 3H, CH_3).

^{13}C NMR (DMSO-d_6): δ (ppm) = 153.5 (ArC), 152.0 (ArC), 141.0 (ArC), 138.2 (ArCH), 135.5 (CH), 131.0 (ArCH), 130.1 (ArCH), 129.1 (ArC), 128.7 (CH_2), 128.6 (ArCH), 120.1 (ArCH), 118.3 (ArCH), 19.9 (CH_3). MS: m/z (%): 302 (28%, M^+), 107 (base peak). Calculated for $C_{15}H_{14}N_2O_3S$: C, 59.59; H, 4.67; N, 9.26. Found: C, 59.96; H, 4.65; N, 8.95.

2.3.3. 2-{3-[2-([1,3]-Dioxolan-2-yl)ethanesulphonyl]phenylazo}-4-methylphenol (6a)

- Route A: 1.55 g of **3** was irradiated for 1 h as is described in Section 2.2.3.. Purification was achieved by FC ($CHCl_3$:*c*-C_6H_{12}:EtAc-5:3:2) and recrystallisation from ethanol. **6a** was obtained as solvent free orange needles after redissolving in chloroform and evaporation to dryness (0.48 g, 25%).
- Route B: 2.90 g (11.3 mmol) of **5** was diazotised and coupled with 1.22 g (11.3 mmol) paracresole as described in Section 2.2.1. The dye **6a** was purified by FC (*t*-butyl methyl ether), followed by recrystallisation from ethanol which gave the product as dark orange needles (yield 3.40 g, 80%), m.p. 160 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 12.30 (s, 1H, Ar–OH), 8.40 (t, J = 1.8 Hz, 1H, ArH), 8.13 (ddd, J = 7.9 Hz, 1.8 Hz, 1.1 Hz, 1H, ArH), 7.99 (ddd, J = 7.9 Hz, 1.8 Hz, 1.1 Hz, 1H, ArH), 7.78 (d, J = 1.5 Hz, 1H, ArH), 7.73 (t, J = 7.9 Hz, 1H, ArH), 7.21 (dd, J = 8.4 Hz, 2.1 Hz, 1H, ArH), 6.96 (d, J = 8.4 Hz, 1H, ArH), 4.98 (t, J = 3.9 Hz, 1H, –O–

CH–O–), 3.90 (m, 4H, O–CH_2–CH_2–O), 3.31 (m, 2H, CH_2), 2.17 (s, 3H, CH_3), 2.15 (m, 2H, CH_2).

^{13}C NMR($CDCl_3$): δ (ppm) = 151.1 (ArC), 150.6 (ArC), 140.6 (ArC), 137.1 (ArCH), 133.4 (ArCH), 130.4 (ArCH), 129.7 (ArC), 129.6 (ArC), 127.7 (ArCH), 121.0 (ArCH), 118.0 (ArCH), 101.6 (ArCH), 65.1 (CH_2), 50.6 (CH_2), 30.9 (CH), 26.9 (CH_2), 20.2 (CH_3). MS: *m*/*z* (%): 376 (90%, M^+), 107 (base peak). Calculated for $C_{18}H_{20}N_2O_5S$: C, 57.43; H, 5.36; N, 7.44; S, 8.52. Found: C, 57.48; H, 5.55; N, 7.43; S, 8.47.

2.3.4. 3-[3-(2Hydroxy-5-methylphenylazo)benzenesulphonyl]propanal (7a)

Cleavage of 1.23 g of **6a** according to Section 2.2.4 and purification by FC ($CHCl_3$:*c*-C_6H_{12}:EtAc 5:3:2), followed of recrystallisation from ethanol gave **7a** as orange needles (0.65 g, 60%), m.p. 130 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 12.18 (s, 1H, Ar–OH), 9.70 (s, 1H, CHO), 8.31 (t, *J* = 1.8 Hz, 1H, ArH), 8.08 (ddd, *J* = 7.9 Hz, 1.8 Hz, 1.0 Hz, 1H, ArH), 7.93 (ddd, *J* = 7.9 Hz, 1.8 Hz, 1.0 Hz, 1H, ArH), 7.70 (d, *J* = 1.6 Hz, 1H, ArH), 7.65 (t, *J* = 7.9 Hz, 1H, ArH), 7.15 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H, ArH), 6.89 (d, *J* = 8.4 Hz, 1H, ArH), 3.44 (t, *J* = 5.0 Hz, 2H, CH_2), 2.97 (t, *J* = 7.5 Hz, 2H, CH_2), 2.32 (s, 3H, CH_3).

^{13}C NMR($CDCl_3$): δ (ppm) = 196.5 (CHO), 151.3 (ArC), 150.6 (ArC), 140.4 (ArC), 137.2 (ArC), 135.8 (ArCH), 133.3 (ArCH), 130.6 (ArCH), 129.7 (ArCH), 129.4 (ArC), 128.0 (ArCH), 120.8 (ArCH), 118.0 (ArCH), 49.0 (CH_2), 36.4 (CH_2), 20.2 (CH_3). MS: *m*/*z* (%): 332 (65%, M^+), 107 (base peak). Calculated for $C_{16}H_{16}N_2O_4S$: C, 57.82; H, 4.85; N, 8.43; S, 9.65. Found: C, 57.80; H, 4.98; N, 8.07; S, 9.48.

2.3.5. 3-Ethenesulphonylaniline (4)

The aniline **4** was prepared from 3.00 g of 2-(3-aminobenzenesulphonyl)ethanol according to Section 2.2.2 and purified by FC (diethyl ether). All spectroscopic data of the crude product (2.00 g, 86%) corresponds to those found in the literature [12].

2.3.6. 3-[2-([1,3]-Dixolan-2-yl)ethanesulphonyl]-aniline (5), as hydrochloride (5XX)

Aniline **5** was prepared according to Section 2.2.3 and purified by FC (diethyl ether) and was converted into its hydrochloride. **5** appeared as an oil, which decomposed during attempted distillation (150 °C/0.5 mm Hg). The compound **5XX** gave white crystals (0.50 g, 94%) after recrystallisation from methanol, m.p. 135 °C.

^{1}H NMR (**5XX**/DMSO-d_6): δ (ppm) = 7.58 (m, 3H, Ar–H), 7.44 (d, *J* = 7.5 Hz, 1H, Ar–H), 7.20 (br. s., 3H, NH_3^+), 4.90 (t, *J* = 4.2 Hz, 1H, –O–CH–O–), 3.85 (m, 4H, O–CH_2–CH_2–O), 3.30 (m, 2H, CH_2), 1.85 (m, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 139.9 (ArC), 139.5 (ArC), 130.7 (ArCH), 124.8 (ArCH), 121.7 (ArCH), 118.2 (ArCH), 101.0 (CH), 64.5 (2×CH_2), 50.0 (CH_2), 27.0 (CH_2). MS: *m*/*z* (%): 257 (8%, M^+), 73 (base peak). High-resolution MS: Calculated for $C_{11}H_{15}NO_4S$: 257.07218. Found: 257.07265.

2.3.7. 1-{3-[2-([1,3]-Dioxolan-2-yl)ethanesulphonyl]phenylazo}naphthalene-2-ol (6b)

5XX (0.90 g) was diazotised and coupled with 2-naphthol according to Section 2.2.1. Purification by FC ($CHCl_3$:*c*-C_6H_{12}:EtAc 5:3:2), followed by recrystallisation from acetone–water, gave orange needles from **6b** (1.00 g, 80%), m.p. 190 °C.

^{1}H NMR (DMSO-d_6): δ (ppm) = 15.49 (br. s., 1H, Ar–OH), 8.50 (d, *J* = 8.1 Hz, 1H, ArH), 8.30 (d, *J* = 1.7 Hz, 1H, ArH), 8.2 (dt, *J* = 7.5 Hz, 1.7 Hz, ArH), 7.95 (d, *J* = 9.5 Hz, 1H, ArH), 7.82 (m, 1H, ArH), 7.78 (t, *J* = 9.5 Hz, 1H, ArH), 7.61 (td, *J* = 7.1 Hz, 1.1 Hz, 1H, ArH), 7.49 (td, *J* = 7.1 Hz, 1.1 Hz, 1H, ArH), 6.86 (d, *J* = 9.5 Hz, 1H, ArH), 4.94 (t, *J* = 4.3 Hz, 1H, O–CH–O), 3.86 (m, 4H, O–CH_2–CH_2–O), 3.44 (m, 2H, CH_2), 1.95 (m, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 145.4 (ArC), 141.3 (ArCH), 140.2 (ArC), 134.5 (ArC), 132.6 (ArC), 131.0 (ArCH), 129.4 (ArCH), 130.0 (ArCH), 129.0 (ArCH), 128.0 (ArCH), 125.6 (ArCH), 124.7 (ArCH), 123.1 (ArCH), 121.6 (ArCH), 117.4 (ArCH), 101.1 (CH), 64.5 (2×CH_2), 49.8 (CH_2), 26.9 (CH_2). MS: *m*/*z* (%): 412 (85%, M^+), 143 (base peak). Calculated for $C_{21}H_{20}N_2O_5S$: C, 61.15; H, 4.89; N, 6.79. Found: C, 61.01; H, 4.89; N, 6.57.

2.3.8. 4-{3-[2-([1,3]-Dioxolan-2-yl)ethanesulphonyl]phenylazo}naphthalene-1-ol (6c)

According to Section 2.2.1, 0.56 g of **5XX** was diazotised and coupled with 1-naphthol. After FC

($CHCl_3$:c-C_6H_{12}:EtAc 5:3:2) and recrystallisation from acetone-water **6c** appeared as orange needles (0.55 g, 65%), m.p. 195 °C.

^{1}H NMR (DMSO-d_6): δ (ppm) = 11.60 (br. s., 1H, Ar–OH), 8.75 (br. s., 1H, ArH), 8.20 (br. d., J = 7.7 Hz, 3H, ArH), 8.08 (br. d., J = 7.9 Hz, 1H, ArH), 7.83 (br. d., J = 6.9 Hz, 1H, ArH), 7.75 (t, J = 7.7 Hz, 2H, ArH), 7.60 (t, J = 7.9 Hz, 1H, ArH), 6.96 (d, J = 6.9 Hz, 1H, ArH), 4.93 (t, J = 4.3 Hz, 1H, O–CH–O), 3.80 (m, 4H, O–CH_2–CH_2–O), 3.43 (m, 2H, CH_2), 1.92 (m, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 139.9 (ArC), 130.9 (ArCH), 126.4 (ArCH), 122.6 (ArCH), 120.6 (ArCH), 101.1 (CH), 64.5 (2×CH_2), 50.0 (CH_2), 27.0 (CH_2). MS: m/z (%): 412(45%, M^+), 143 (base peak). Calculated for $C_{21}H_{20}N_2O_5S$: C, 61.15; H, 4.89; N, 6.79; S, 7.77. Found: C, 61.30; H, 5.05; N, 6.93; S, 7.72.

*2.3.9. 2-{3-[2-([1,3]-Dioxolan-2-yl)ethanesulphonyl] phenylazo}naphthalene-1-ol (**6d**)*

The dye **6d** was formed as byproduct in 2.3.8. Purification as described there afforded orange needles (0.15 g, 9.5%), m.p. 211 °C.

^{1}H NMR (DMSO-d_6): δ (ppm) = 14.40 (br. s., 1H, Ar–OH), 8.36 (d, J = 8.1 Hz, 1H, ArH), 8.18 (d, J = 7.7 Hz, 1H, ArH), 7.83 (m, 2H, ArH), 7.80 (t, J = 7.7 Hz, 1H, ArH), 7.58 (t, J = 7.7 Hz, 1H, ArH), 7.43 (d, J = 9.3 Hz, 1H, ArH), 7.24 (d, J = 9.3 Hz, 1H, ArH), 4.93 (t, J = 4.2 Hz, 1H, O–CH–O), 3.80 (m, 4H, O–CH_2–CH_2–O), 3.44 (m, 2H, CH_2), 1.92 (m, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 140.1 (ArC), 136.7 (ArC), 133.3 (ArC), 132.1 (ArCH), 130.8 (ArCH), 128.0 (ArCH), 126.8 (ArCH), 125.9 (ArCH), 125.7 (ArCH), 124.6 (ArCH), 121.6 (ArCH), 117.3 (ArCH), 103.0 (ArC), 101.1 (CH), 64.5 (2×CH_2), 49.8 (CH_2), 26.9 (CH_2). MS: m/z (%): 412 (100%, M^+). Calculated for $C_{21}H_{20}N_2O_5S$: C, 61.15; H, 4.89; N, 6.79. Found: C, 61.21; H, 4.95; N, 6.71.

*2.3.10. 3-[3-(2-Hydroxynaphthalene-1-ylazo)-benzelnesulphonyl]propionaldehyde (**7b**)*

Acetal **6b** (1.12 g) was deprotected according to Section 2.2.4. After FC ($CHCl_3$:MeOH:c-C_6H_{12}-9:1:4) and recrystallisation from EtOH **7b** was obtained as orange needles (0.80 g, 80%), m.p. 186 °C.

^{1}H NMR (DMSO-d_6): δ (ppm) = 15.56 (s, 1H, Ar–OH), 9.61 (s, 1H, CHO), 8.48 (d, J = 7.8 Hz, 1H, ArH), 8.29 (s, 1H, ArH), 8.20 (d, J = 6.0 Hz, 1H, ArH), 7.96 (d, J = 9.5 Hz, 1H, ArH), 7.80 (m, 2H, ArH), 7.76 (d, J = 7.8 Hz, 1H, ArH), 7.63 (t, J = 7.2 Hz, 1H, ArH), 7.48 (t, J = 7.2 Hz, 1H, ArH), 6.86 (d, J = 9.5 Hz, 1H, ArH), 3.73 (t, J = 7.0 Hz, 2H, CH_2), 2.86 (t, J = 7.1 Hz, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 199.3 (CHO), 172.3 (ArC), 145.2 (ArC), 141.5 (ArCH), 140.0 (ArC), 132.6 (ArC), 131.0 (ArCH), 130.0 (ArCH), 129.4 (ArCH), 129.1 (ArCH), 128.0 (ArC), 126.5 (ArCH), 125.6 (ArCH), 124.6 (ArCH), 123.2 (ArCH), 121.6 (ArCH), 117.4 (ArCH), 48.3 (CH_2), 36.0 (CH_2). MS: m/z (%): 368 (97%, M^+), 143 (base peak). Calculated for $C_{19}H_{16}N_2O_4S$: C, 61.94; H, 4.38; N, 7.60. Found: C, 61.75; H, 4.48; N, 7.27.

*2.3.11. 3-[3-(4-Hydroxynaphthalene-1-ylazo)-benzenesulphonyl]propionaldehyde (**7c**)*

Deprotection of 0.74 g of acetal **6c** by Section 2.2.4 and purification of the product by FC ($CHCl_3$:MeOH:c-C_6H_{12} 9:1:4), followed by recrystallisation from EtOH yielded **7c** as orange needles (0.45 g, 68%), m.p. 172 °C.

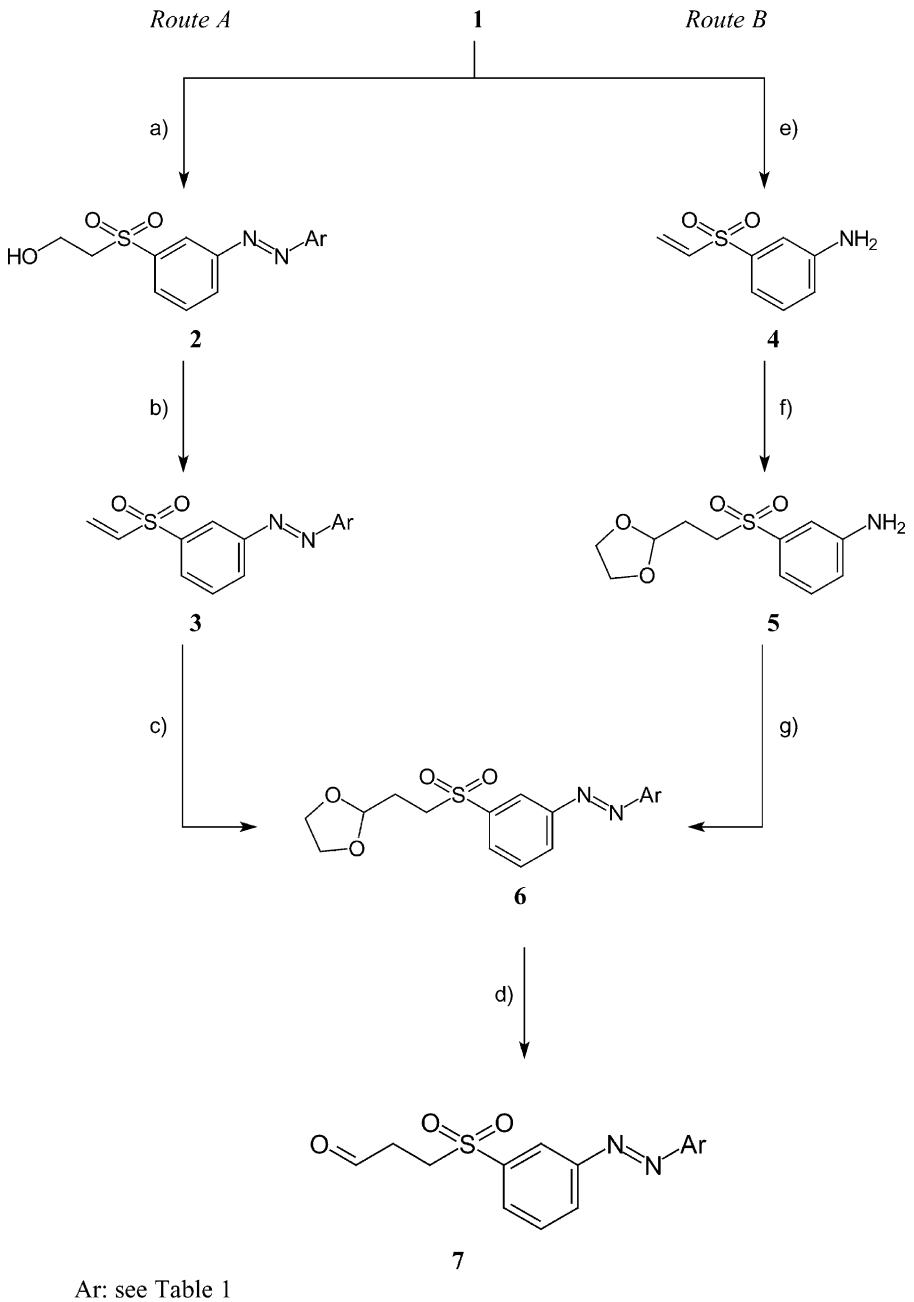
^{1}H NMR (DMSO-d_6): δ (ppm) = 11.80 (br. s., 1H, Ar–OH), 9.61 (s, 1H, CHO), 8.90 (br. s., 1H, ArH), 8.32 (m, 2H, ArH), 8.15 (m, 2H, ArH), 7.78 (t, J = 5.8 Hz, 3H, ArH), 7.60 (s, 1H, ArH), 7.05 (s, 1H, ArH), 3.88 (s, 2H, CH_2), 2.86 (t, J = 7.0 Hz, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 199.3 (CHO), 139.8 (ArCH), 130.9 (ArCH), 122.6 (ArCH), 95.4 (ArCH), 48.4 (CH_2), 36.1 (CH_2). MS: m/z (%): 368 (78%, M^+), 143 (base peak). Calculated for $C_{19}H_{16}N_2O_4S$: C, 61.94; H, 4.38; N, 7.60. Found: C, 61.62; H, 4.52; N, 7.68.

*2.3.12. 3-[3-(1-Hydroxynaphthalene-2-ylazo)-benzelnesulphonyl]propionaldehyde (**7d**)*

Cleavage of the 0.15 g of acetal **6d** according to Section 2.2.4 and further purification by FC ($CHCl_3$:MeOH:c-C_6H_{12} 9:1:4) and recrystallisation from EtOH gave the aldehyde **7d** as orange needles (0.10 g, 73%), m.p. 201–202 °C.

^{1}H NMR (DMSO-d_6): δ (ppm) = 14.35 (br. s., 1H, Ar–OH), 9.60 (s, 1H, CHO), 8.35 (d, J = 7.2

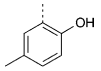
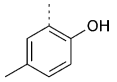
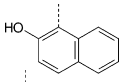
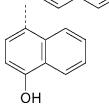
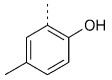
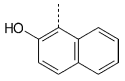
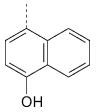
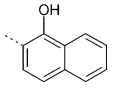


Scheme 2. Synthesis of the 2-formylethyl substituted azo dyes 7; (a, g) 1. 10% aqueous $NaNO_2$/6 N HCl, 0–5 °C, 1 h; 2. Ar–OH/NaOH 15% aqueous soln, 3–5 °C, 1 h; (b, e) conc. H_2SO_4 RT, 2 h; (c) [1,3]-dioxolan, UV-light, benzophenone, 1 h; (d) 15% H_2SO_4, acetone soln., refl, 3 h; (f) [1,3]-dioxolan, UV-light, benzophenone, RT, 5–10 min.

Hz, 1H, ArH), 8.18 (d, $J=7.2$ Hz, 2H, ÀrH), 7.80 (m, 3H, ArH), 7.78 (t, $J=6.8$ Hz, 1H, ArH), 7.58 (t, $J=7.2$ Hz 1H, ArH), 7.42 (d, $J=9.2$ Hz, 1H, ArH), 7.25 (d, $J=9.2$ Hz, 1H, ArH), 3.70 (t, $J=7.2$ Hz, 2H, CH_2), 2.85 (t, $J=7.2$ Hz, 2H, CH_2).

^{13}C NMR (DMSO-d_6): δ (ppm) = 199.3 (CHO), 146.3 (ArC), 140.0 (ArC), 136.7 (ArC), 133.2 (ArC), 132.2 (ArCH), 130.8 (ArC), 128.0 (ArCH), 126.8 (ArCH), 126.0 (ArCH), 125.7 (ArCH), 124.5 (ArCH), 121.8 (ArCH), 117.4 (ArCH), 103.0 (ArCH), 48.3 (CH_2), 36.0 (CH_2). MS: m/z (%): 368 (78%, M^+), 143 (base peak). Calculated for $C_{19}H_{16}N_2O_4S$: C, 61.94; H, 4.38; N, 7.60. Found: C, 61.77; H, 4.74; N, 7.74.

Table 1
Structural details and yields of the 2-formylethylsulphonyl substituted azo dyes **7a–c** and their precursors **2–6**

	Ar	Yield (%)	
		Route A	Route B
2		75	–
3		80	–
4	–	–	86
5	–	–	94
6a		25	80
6b		–	80
6c		–	65
6d		–	9.5
7a		60	60
7b		–	80
7c		–	68
7d		–	67

3. Results and discussion

3.1. Synthesis

The reactive formyl group within the azo dyes **7** (see Scheme 2) is part of a (2-formylethyl)sulphonyl group. The dyes were obtained by two different synthetic routes, which are outlined in Scheme 2. The synthesis of indicator dyes for basic pH-range necessitates a broad variation within the structure of the dyes and investigation of their properties. The electron-withdrawing effect of the substituent to the azo chromophore and its behaviour within the observed pH-range is rather small.

- *Route A*: We planned to prepare the hydroxyethylsulphonyl substituted azo dyes **2** by coupling 2-(3-aminophenylsulphonyl)ethanol (**1**) with various phenols and naphthols. These were converted to the vinylsulphonyl derivatives **3** by elimination reaction. The protected aldehyde group was introduced by photochemical addition [13–15] of 1,3-dioxolane to give the acetals **6**. Unfortunately, this procedure was only successful for dye **6a**—derived of *p*-cresole (25%). Deprotection yielded the aldehyde **7a**. All attempts to obtain naphthol azo dyes failed, probably due to a photochemical cleavage of the N=N-bond, indicated by colorless reaction solution.

- *Route B*: The amine **5** bearing the protected formyl group was prepared in two steps using similar methods as described for route A. Subsequent coupling with various phenols and naphthols gave the azo dyes **6a–c**, which were deprotected to **7a–c**. The photochemical reaction (**4–5**) worked very well with high yields and markedly reduced reaction times (5–10 min instead of 1 h for the analogous reactions **3–6** in route A). The crucial step was the diazotation of acetal **5** due to its instability under the acidic conditions used. Possible side reactions of the resulting

deprotected aldehyde were oxidation to the carboxylic acid by HNO_2 or polymerisation by formation of Schiff-bases with the amino groups. Structural details and yields can be found in Table 1.

Polymers with a sufficient content of 1,3-diole moieties to form the 1,3-dioxolane unit were those with an ethylene content corresponding to $z = 27$ (see Scheme 1). DMF was used as solvent for thin film preparation.

3.2. Evidence for covalent bonding between the azodyes and the polymer

All reactive azo dyes **7a**–**c** were successfully bounded this way, which was proved by thin layer chromtography and different spectroscopical methods (vide infra).

3.2.1. FT-IR spectra

The FT-IR spectra of the covalently linked dyes **7a**–**c** show absorption bands at ca. 1025 cm^{-1}, which are very similar to those observed for the protected derivatives **6**. In addition, no absorption in the range from 1700 to 1740 cm^{-1} could be observed, which indicates the absence of any formyl groups.

3.2.2. ^1H NMR

Fig. 1 shows the aromatic region of the ^1H NMR spectrum of the bounded dye **7a**. As can be seen, no significant absorption of aldehyde protons (range between 9.5 and 9.7 ppm) can be observed, which corroborates the results obtained from the FT-IR spectrum (vide supra). In addition, the signal corresponding to the phenolic hydroxy group of the dye within the polymer is

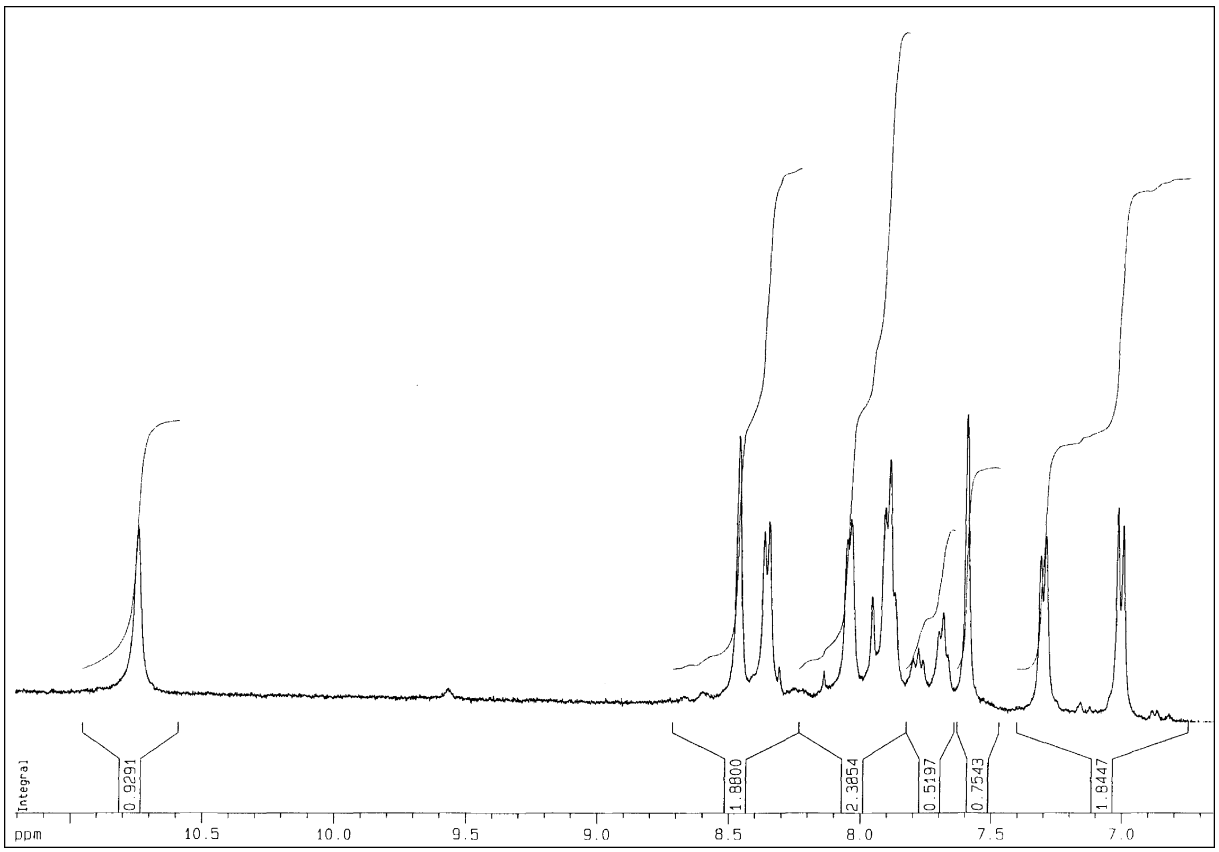


Fig. 1. ^1H NMR of composite-polymer bonded dye **7a** (DMSO-d_6).

shifted to higher fields with respect to the signal of its unbounded form (from 12.3 to 10.8 ppm). This can be explained by different media surrounding the bonded and free dye.

3.2.3. Optical properties

The UV/vis absorption spectra of dyes **6a**, **6c** and **6d** are shown in Figs. 2, 3 and 4.

As can be seen from Fig. 2, **6a** posseses excellent indicator properties within the alkaline pH-range. The distinct maximum of its absorption spectrum is shifted both bathochromically and—to a less extent—hyperchromically with any increase of the pH-value.

All the other dyes do not show as marked pH-dependence of their absorption spectra. This can be explained by azo-hydrazo tautomerism for **6c**—leading to a mixture of both forms in solution (Fig. 3). The absorption spectra of **6d** are characterised by hyperchromic shifts instead of bathochromic (Fig. 4). This is not a precise tool for pH-measurements.

The absorption spectra of the polymer bond dye **7a** (see Fig. 5) recorded for different pH-values show a considerable shift with respect to the ones observed for the free dye. We consider, that the polymeric environment renders deprotonation of the dye more difficult and therefore requirers

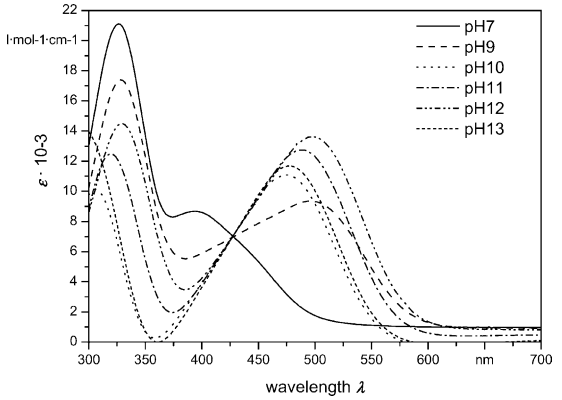


Fig. 2. UV/vis spectra of phenolic azo dye **6a** at different pH-values ($c = 4.5 \times 10^{-5}$ mol l^{-1}).

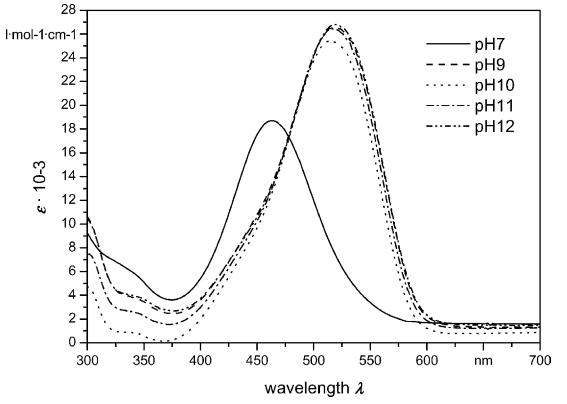


Fig. 4. UV/vis spectra of *p*-α-naphthol azo dye **6c** at different pH-values ($c = 6.7 \times 10^{-4}$ mol l^{-1}).

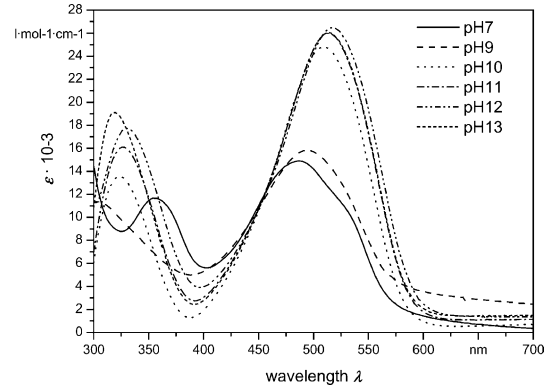


Fig. 3. UV/vis spectra of *o*-α-naphthol azo dye **6d** at different pH-values ($c = 5.0 \times 10^{-5}$ mol l^{-1}).

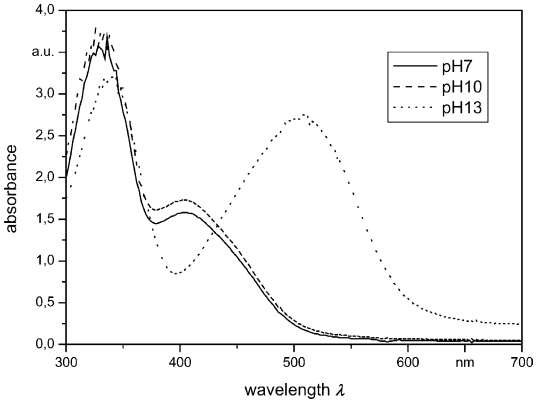


Fig. 5. UV/vis spectra of polymer bonded phenol azo dye at different pH-values.

higher pH-values. This is supported by the high-field shift of the hydroxy proton in the ^{1}H NMR spectrum within the covalently bound dye (Fig. 1) with respect to its non-tethered form.

These covalent connected dye–polymer composites are convenient for preparing films with excellent quality, flexibility and transparency, and they are suitable for fibreoptic measurements.

4. Conclusion

We describe the preparation of new pH-indicating sensors based on thin films prepared from azo dyes that are covalently bonded by an acetal linkage to a vinylalcohol–ethylene copolymer. The 1,3-dioxane (acetal) group was formed from an aldehyde group of the dye and 1,3-diole moieties of the polymer. This type of covalent bonding is assumed to be stable for long period of time under basic conditions and does not affect the optical determination of the absorption changes of the dyes. The sensor behaviour is completely reversible and allows precise determination of the pH-value. These sensors can be tethered to optical fibres and are promising candidates for the application in long term monitoring of a broad variety of systems, e.g. concrete structures.

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