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Azomethines with Nonlinear Optical Properties and Polyesters Covalently Functionalized with them. Syntheses with Nitriles IC[1]

Renate Dworczak,[a]* Walter M. F. Fabian,[a] Dietmar Kieslinger[b] & Hans Junek[a]

[a]Karl-Franzens University of Graz, Institute of Organic Chemistry, Heinrichstrasse 28, A-8010, Graz, Austria
[b]Karl-Franzens University of Graz, Institute of Experimental Physics, Universitaets-Platz 5, A-8010, Graz, Austria

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ABSTRACT

Polyesters with covalently bound azomethine and carbonanalogous dye moieties were obtained by polymer analogous reactions. Their nonlinear optical properties were examined by electric field induced second harmonic generation measurements and compared with corresponding monomeric dyes. All of them had maximum absorption wavelengths between 400 and 546 nm. Values for $\mu\beta$ *(dipole moment* μ*, molecular hyperpolarizability* β*) reached* 290×10^{-68} Cm^5/V*. Quantum chemical calculations indicate the existence of various conformers of the dyes with large differences in their nonlinear optical properties. Furthermore, the calculations also point to a profound sensitivity of the molecular hyperpolarizability to environmental (solvent) effects amounting to an order of magnitude. © 1997 Elsevier Science Ltd*

Keywords: AM1 calculations, EFISH measurements, polyester dyes, SCRF calculations, second harmonic generation, ZINDO calculations.

INTRODUCTION

Donor–acceptor substituted conjugated organic compounds offer great promise as materials for nonlinear optic (NLO) devices.[1,2] For practical

[1] For no. 98 see Boila-Goeckel, A., Fabian, W. M. F. & Junek, H., *Liebigs Ann.* (1996) 397–402.

*Corresponding author.

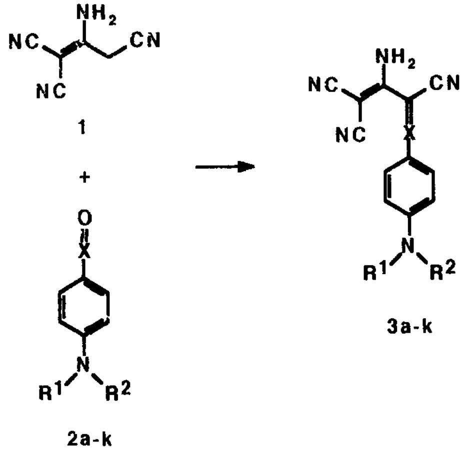
applications NLO materials have to be used as films or coatings on suitable carriers. Thus thermoplastic polymeric materials with glass transition temperatures above 130 °C and containing NLO molecules might be the materials of choice.[3,4] In general the "poled polymer approach" is a very promising strategy: a polymer, which contains another species with NLO activities, is heated above its glass transition temperature and then cooled to ambient temperature in a strong dc electric field. The NLO molecules can either be doped into the host polymer or chemically bonded to the polymer mainchain. Because of different polarities a solution of the NLO material in a polymer matrix may bring along problems with demixing phenomena and crystallization of the NLO moieties. Hence the concentration of the NLO compound in the polymer must be kept rather low. If the NLO material can be bound covalently to the polymer chain, higher concentrations can be obtained and demixing is avoided. The reaction of the polymer with the NLO material sometimes may be difficult. This is why we decided to start with an aromatic polyester, which contained anilino groups. Azomethine dyes were synthesized directly on the polymer chain by subsequent polymer analogous reactions. Second harmonic generation (SHG, i.e. conversion of an input optical wave into an output wave of twice the input frequency) was determined for the isolated dyes as well as for the functionalized polyesters.

RESULTS AND DISCUSSION

Dyes **3a–k** (Scheme 1) were obtained by reacting equimolar amounts of **1** and aldehydes **2a–e** or nitroso compounds **2f–k** in ethanol at room temperature for 2 h (nitroso compounds **2f–k**) or at boiling temperature for 4 h (aldehydes **2a–e**). Products precipitated either during the reaction or on cooling the reaction mixtures to room temperature. They were obtained in analytical purity.

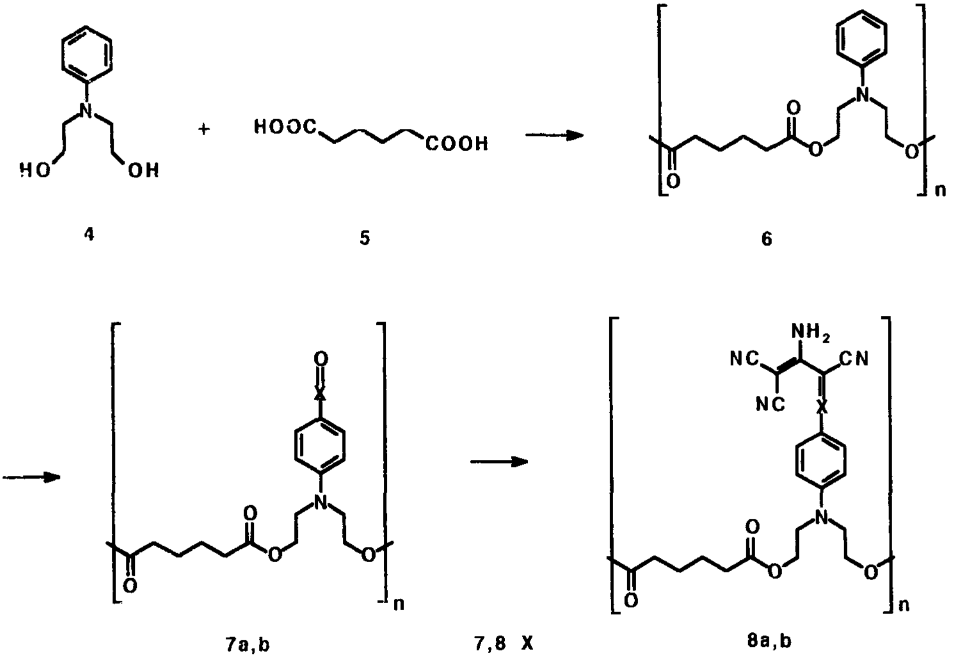
For the preparation of the polymeric materials (Scheme 2) we started with a polyester (**6**) from *N*-phenyldiethanolamine (**4**) and adipic acid (**5**) and reacted the anilino residues to obtain polyester dyes **8a** and **8b** by subsequent polymer analogous reactions. Compound **6** was either nitrosated with $NaNO_2$ in dioxane/HCl (to yield **7a**) or formylated with $POCl_3$ in dimethylformamide (DMF) (to yield **7b**). Dyes **8a,b** were obtained by combining **1** with **7a,b**, respectively in ethanol.[5–7] Transformation of **6** into nitrosated **7a** or formylated **7b** always produced significantly shorter chain lengths (probably caused by hydrolysis). While the M_W of **6** was approx. 13 000, **7a** and **7b** had M_Ws of approx. 2500 and 2800, respectively. When **7a,b** were reacted with **1** to afford **8a,b** no change of the chain lengths were observed.

^{1}H NMR measurements proved that nitrosation as well as formylation of **6** proceeded smoothly and **7a,b** were formed quantitatively: the signals of



2,3	X	R1	R2
a	CH	Me	n-Bu
b	CH	Me	1-Me-Pr
c	CH	Me	Allyl
d	CH	Me	n-Hex
e	CH	Me	n-Oct
f	N	Et	Hydroxy-Et
g	N	Hydroxy-Et	Hydroxy-Et
h	N	Me	1-Me-Pr
i	N	Me	Allyl
j	N	Me	n-Hex
k	N	Me	n-Oct

Scheme 1. Synthesis of monomeric dyes **3a–k** from dimeric malononitrile (**1**) and aldehydes **2a–e** or nitroso compounds **2f–k**.



7,8	X
a	N
b	CH

Scheme 2. Synthesis of polyester **6** and polymer analogous reactions yielding polymeric NLO materials **8a,b**.

the unsubstituted phenyl group—a triplet at 6.7 and a multiplet from 7.0 to 7.4 ppm—disappeared and two doublets at 6.9 ppm and 7.7 ppm (**7a**) or 6.8 ppm and 7.7 ppm (**7b**) occurred. The reaction of **7a** with **1** was monitored by visible (Vis) spectra: In **8a** only approx. 75% of the nitroso groups ($\lambda_{max} = 420$ nm) of **7a** had reacted with **1** to give dye **8a** ($\lambda_{max} = 503$ nm). In the case of the reaction of **7b** with **1** the degree of conversion was examined by ^{1}H NMR spectroscopy (the integral for the remaining formyl CH at 9.7 ppm was compared with the integrals obtained for the aromatic protons) and it was even lower. Only approx. 10% of the formyl groups in **7b** reacted with **1**. Neither longer reaction times nor an excess of **1** gave higher transformation rates. Moreover the longer the reaction times the lower were the M_Ws of **7a,b**.

For a first screening of NLO properties, SHG of monomeric azomethines as well as of polyester dyes, was determined by electric field induced second harmonic generation (EFISH) measurements in 1,4-dioxane according to procedures described previously.[8] Despite the difference in absorption spectra (see Table 1) of azomethines dyes, e.g. **3j** compared with the CH analogues, e.g. **3d** (approx. 3900 cm^{-1}), $\mu\beta$ values are surprisingly similar [270×10^{-68} Cm^5/V (**3j**) and 290×10^{-68} Cm^5/V (**3d**)]. Functionalization of the benzaldehydes **2a–e** or nitroso anilines **2f–k** thus increases the SHG efficiencies by at least an order of magnitude ($\mu\beta$ values for 4-dimethylaminobenzaldehyde and 4-dimethylaminonitrosobenzene are, respectively, 4 and 10×10^{-68} Cm^5/V).[9] Given the moderate conversion of polyesters **7a,b** to the polymeric dyes **8a,b** discussed above, their nonlinear optical properties (see Table 1) are, although lower than for the monomeric dyes, rather high. In fact the differences between the monomers and the polymers are far too small to be explained only by the small number of chromophoric groups along the polyester chains of **8a,b**. Apparently the polyester chain exerts some kind of preorganization or conformational effect on the dye moieties leading to enhanced SHG efficiency. In line with this assertion is the result for **7b**, which also shows a significantly higher $\mu\beta$ value (see Table 1) than the monomeric chromophore 4-dimethylaminobenzaldehyde. Furthermore,

TABLE 1
NLO and Dye Properties of Selected Monomeric Dyes and Functionalized Polyesters

	$\mu\beta(10^{-68}\ Cm^5/V)$	$\lambda_{max}(nm)$	$\log \varepsilon$
3d	290	434[a]	4.35[a]
3j	270	524[a]	4.67[a]
7b	65	—	—
8a	160	503[b]	4.07[b]
8b	190	416[b]	3.65[b]

[a] In acetone.
[b] In 1,4-dioxane.

TABLE 2
Calculated λ_{max} (nm), Dipole Moments μ (debye) and $\mu\beta$ (10^{-68} Cm^5/V) for Model Compounds **3l,m**

		Gas			*Dioxane*			*Acetone*		
		λ_{max}	μ	$\mu\beta$	λ_{max}	μ	$\mu\beta$	λ_{max}	μ	$\mu\beta$
3l	*s-trans*	353	8.0	14	379	9.0	30	405	11.0	101
	s-cis	348	6.6	14	374	7.7	27	400	9.6	82
3m	*s-trans*	397	9.3	32	435	10.9	72	467	14.0	475
	s-cis	403	8.3	23	431	9.4	44	448	11.2	132

semi-empirical quantum chemical calculations [Austin Method 1 (AM1)][10] on model compounds ($R^1 = R^2 = H$) for dyes **3d** and **3j** indicate the existence of at least two conformers (*s-cis* and *s-trans*) with very similar energies ($\Delta\Delta H_f \leq 0.5$ kcal mol^{-1}). In contrast, hyperpolarizabilities calculated by the ZINDO (Zernev's Intermediate Neglect of Differential Overlap) method[11,12] are quite sensitive to the conformation used in the calculation (see Table 2 and Scheme 3). Even more pronounced is the effect of solvents as obtained by the SCRF (self consistent reaction field) approximation.[13–16] Obviously, even subtle conformational changes or intermolecular interactions with the environment can cause quite substantial effects on the results of EFISH measurements. Therefore, the above mentioned conformational or preorganizational effects of the polyester chain on molecular hyperpolarizabilities seem reasonable in the light of the computational results. Finally, although the calculated λ_{max} values are somewhat too low, the bathochromic shift resulting from replacement of a CH group in **3d** by a N atom leading to **3j** is satisfactorily reproduced by the calculations.

CONCLUSIONS AND OUTLOOK

Polyesters **8a,b** showed remarkably high NLO activities although the numbers of chromophores along the polymer chains were rather low. The measurements as well as quantum chemical calculations make these compounds interesting for further investigations. So, e.g. more chromophores along the chain should result in higher molecular hyperpolarizabilities. In addition materials with higher molar masses should have sufficiently high glass transition temperatures for producing films of adequate thermal stability.

EXPERIMENTAL

General

All melting points are uncorrected. Spectral data were recorded with the following instruments: IR spectra, Perkin–Elmer 298 Spectro-photometer (KBr); ^{1}H NMR spectra, Varian LX 200 and Bruker 360 (spectra referenced to tetramethylsilane and generally recorded in dimethyl sulfoxide-d_6, other solvents are indicated); UV–Vis spectra, Hitachi U-3501 Spectrophotometer (quartz cuvettes). HPLC system: HPLC Gynkotek High Precision Pump 300 C, columns PL Microgel M 10 μ, 600×7.8 mm (from Polymer Laboratories) and Phenogel 500 Å, 10 μ, 600×7.8 mm (from Phenomenex), ERC 7512 Refractive Index Detector and density detector DDS 70 with software Chroma (from Chromtech, Graz Austria), chloroform (Promochem) as solvent; M_W standards, poly(ethylene glycol)s from Fluka and Aldrich and poly(methyl methacrylate)s from Polymer Laboratories.

Dimeric malononitrile **1**,[17] benzaldehydes **2a–e**[18] and nitroso compounds **2f–k**[18] were prepared according to standard procedures.

Preparation of dyes 3a–k, general procedure

Equimolar amounts of **1** and of aldehydes **2a–e** or nitroso compounds **2f–k** were stirred in ethanol (10 ml/g of starting materials) at room temperature for 2 h (nitroso compounds **2f–k**) or refluxed for 4 h (aldehydes **2a–e**). Dyes **3a–e** precipitated on cooling the reaction mixtures to room temperature. Dyes **3f–k** crystallized during the reaction. They were collected by suction. Most of the products were analytically pure.

*2-Amino-4-(4-*N*-butyl-*N*-methylaminophenyl)-1,3-butadiene-1,1,3-tricarbonitrile (**3a**)*

Yield 39%, orange crystals, m.p. 122 °C (toluene). IR: $\nu = 3320, 3220, 2920, 2210, 2190, 1645, 1610, 1560, 1510$ cm^{-1}. ^{1}H NMR: $\delta = 0.92$ (t, 3H, CH$_3$), 1.32 (m, 2H, CH$_2$), 1.54 (m, 2H, CH$_2$), 3.05 (s, 3H, CH$_3$), 6.86 (d, 2H, arom. protons), 7.75 (s, 1H, olefinic CH), 7.89 (d, 2H, arom. protons), 8.80 (br. s, 2H, NH$_2$) ppm. UV–Vis (acetone) λ_{max} (log ε): 433 (4.50) nm. Calculated for $C_{18}H_{19}N_5$: C, 70.80; H, 6.27; N, 22.93; found: C, 70.41; H, 6.25; N, 22.80.

*2-Amino-4-[4-*N*-(1-methylpropyl)-*N*-methylaminophenyl]-1,3-butadiene-1,1,3-tricarbonitrile (**3b**)*

Yield 25%, red crystals, m.p. 195 °C (toluene). IR: $\nu = 3420, 3330, 3230, 2960, 2215, 2200, 1645, 1610, 1560, 1515$ cm^{-1}. ^{1}H NMR: $\delta = 0.80$ (t, 3H,

CH_3), 1.15 (d, 3H, CH_3), 1.57 (m, 2H, CH_2), 2.84 (s, 3H, CH_3), 4.14 (m, 1H, CH), 6.96 (d, 2H, arom. protons), 7.74 (s, 1H, olefinic CH), 7.87 (d, 2H, arom. protons), 8.77 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 400 (4.56) nm. Calculated for $C_{18}H_{19}N_5$: C, 70.80; H, 6.27; N, 22.93; found: C, 71.00; H, 6.15; N, 22.72.

*2-Amino-4-(4-*N*-allyl-*N*-methylaminophenyl)-1,3-butadiene-1,1,3-tricarbonitrile (**3c**)*

Yield 35%, red crystals, m.p. 153 °C (toluene). IR: ν = 3330, 3220, 2220, 2200, 1645, 1610, 1545, 1520 cm^{-1}. ^1H NMR: δ = 3.08 (s, 3H, CH_3), 4.13 (d, 2H, olefinic CH_2), 5.14 (t, 2H, CH_2), 5.85 (m, 1H, olefinic CH), 6.87 (d, 2H, arom. protons), 7.75 (s, 1H, olefinic CH), 7.87 (d, 2H, arom. protons), 8.80 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 430 (4.58) nm. Calculated for $C_{17}H_{15}N_5$: C, 70.57; H, 5.23; N, 24.20; found: C, 70.31; H, 5.09; N, 23.99.

*2-Amino-4-(4-*N*-hexyl-*N*-methylaminophenyl)-1,3-butadiene-1,1,3-tricarbonitrile (**3d**)*

Yield 87%, red crystals, m.p. 122 °C (toluene). IR: ν = 3350, 3240, 2950, 2920, 2850, 2210, 2190, 1650, 1610, 1600, 1570, 1525 cm^{-1}. ^1H NMR (deuterio chloroform): δ = 0.90 (t, 3H, CH_3), 1.32 (m, 6H, 3 CH_2 groups), 1.62 (m, 2H, CH_2), 3.10 (s, 3H, CH_3), 3.44 (m, 2H, CH_2), 6.00 (br. s, 2H, NH_2) [the signals of the olefinic CH-group (doublets at 6.78 and 7.90 ppm) and of two aromatic protons (at 6.79 and 7.72 ppm) indicated that *E*- and *Z*-isomers were present (ratio approx. 2:1)]; 9.70 (d, 2H, arom. protons) ppm. UV–Vis (acetone) λ_{max} (log ε): 434 (4.35) nm. Calculated for $C_{20}H_{23}N_5$: C, 72.04; H, 6.95; N, 21.00; found: C, 71.59; H, 7.09; N, 20.65.

*2-Amino-4-(4-*N*-methyl-*N*-octylaminophenyl)-1,3-butadiene-1,1,3-tricarbonitrile (**3e**)*

Yield 38%, orange crystals, m.p. 128 °C (toluene). IR: ν = 3400, 3320, 3220, 2920, 2850, 2210, 2200, 1650, 1610, 1560, 1530, 1510 cm^{-1}. ^1H NMR: δ = 0.87 (t, 3H, CH_3), 1.30 (m, 10H, 5 CH_2 groups), 1.54 (m, 2H, CH_2), 3.07 (s, 3H CH_3), 3.48 (t, 2H, CH_2), 6.85 (d, 2H, arom. protons), 7.74 (s, 1H, olefinic CH), 7.87 (d, 2H, arom. protons), 8.77 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 437 (4.49) nm. Calculated for $C_{22}H_{27}N_5$: C, 73.10; H, 7.53; N, 19.37; found: C, 72.80; H, 7.50; N, 19.04.

*2-Amino-3-[4-*N*-ethyl-*N*-(2-hydroxyethyl)-aminophenylimino]-1-propene-1,1,3-tricarbonitrile (**3f**)*

Yield 65%, violet crystals, m.p. 205 °C (butanone/ethanol, decomp.). IR: ν = 3500, 3490, 3290, 3200, 2870, 2840, 2220, 2200, 1610, 1530 cm^{-1}. ^1H

NMR: $\delta = 1.17$ (t, 3H, CH_3), 3.58 (m, 6H, CH_2), 4.88 (br. s, 1H, OH), 6.95 (d, 2H, arom. protons), 7.77 (d, 2H, arom. protons), 8.78 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 526 (4.66) nm. Calculated for $C_{16}H_{16}N_6O$: C, 62.32; H, 5.23; N, 27.26; found: C, 62.01; H, 5.40; N, 27.05.

*2-Amino-3-[4-*N,N*-bis(2-hydroxyethyl)-aminophenylimino]-1-propene-1,1,3-tricarbonitrile (**3g**)*

Yield 64%, violet crystals, m.p. 207 °C. IR: $\nu = 3420$, 3280, 3200, 2220, 2200, 1675, 1610, 1530 cm^{-1}. ^1H NMR: $\delta = 3.64$ (m, 8H, CH_2), 4.91 (br. s, 2H, OH), 6.98 (d, 2H, arom. protons), 7.75 (d, 2H, arom. protons), 8.77 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 525 (4.62) nm. Calculated for $C_{16}H_{16}N_6O_2$: C, 59.25; H, 4.97; N, 25.91; found: C, 59.02; H, 5.07; N, 25.60.

*2-Amino-3-[4-*N*-methyl-*N*-(1-methylpropyl)-aminophenylimino]-1-propene-1,1,3-tricarbonitrile (**3h**)*

Yield 82%, violet crystals, m.p. 221 °C. IR: $\nu = 3400$, 3280, 3180, 2970, 2920, 2870, 2210, 2190, 1610, 1600, 1530 cm^{-1}. ^1H NMR: $\delta = 0.80$ (t, 3H, CH_3), 1.16 (d, 3H, CH_3), 1.60 (m, 2H, CH_2), 2.89 (s, 3H, CH_3), 4.18 (m, 1H, CH), 7.03 (d, 2H, arom. protons), 7.65 (d, 2H, arom. protons), 8.77 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 525 (4.66) nm. Calculated for $C_{17}H_{18}N_6$: C, 66.65; H, 5.92; N, 27.43; found: C, 66.45; H, 5.89; N, 28.07.

*2-Amino-3-(4-*N*-allyl-*N*-methylaminophenylimino)-1-propene-1,1,3-tricarbonitrile (**3i**)*

Yield 76%, violet crystals, m.p. 212 °C. IR: $\nu = 3390$, 3280, 2210, 2190, 1640, 1600, 1520 cm^{-1}. ^1H NMR: $\delta = 3.19$ (s, 3H, CH_3), 4.17 (d, 2H, CH_2), 5.16 (t, 2H, $=CH_2$), 5.87 (m, 1H, CH), 6.93 (d, 2H, arom. protons), 7.75 (d, 2H, arom. protons), 8.83 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 516 (4.60) nm. Calculated for $C_{16}H_{14}N_6$: C, 66.19; H, 4.86; N, 28.95; found: C, 66.03; H, 4.87; N, 29.13.

*2-Amino-3-(4-*N*-hexyl-*N*-methylaminophenylimino)-1-propene-1,1,3-tricarbonitrile (**3j**)*

Yield 65%, dark violet crystals, m.p. 214 °C. IR: $\nu = 3400$, 3280, 2950, 2920, 2210, 2190, 1615, 1600, 1530 cm^{-1}. ^1H NMR: $\delta = 0.87$ (t, 3H, CH_3), 1.30 (m, 6H, 3 CH_2 groups), 1.57 (m, 2H, CH_2), 3.11 (s, 3H, CH_3), 3.52 (t, 2H, CH_2), 6.80 (d, 2H, arom. protons), 7.77 (d, 2H, arom. protons), 8.76 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 524 (4.67) nm. Calculated for $C_{19}H_{22}N_6$: C, 68.24; H, 6.63; N, 25.13; found: C, 68.29; H, 6.76; N, 25.22.

*2-Amino-3-(4-*N*-methyl-*N*-octylaminophenylimino)-1-propene-1,1,3-tricarbonitrile (3k)*

Yield 60%, dark blue crystals, m.p. 228 °C (decomp.). IR: $\nu = 3400$, 3290, 2960, 2910, 2210, 2190, 1620, 1600, 1525 cm^{-1}. ^{1}H NMR: $\delta = 0.87$ (t, 3H, CH_3), 1.30 (m, 10H, 5 CH_2 groups), 1.53 (m, 2H, CH_2), 3.05 (s, 3H, CH_3), 3.50 (t, 2H, CH_2), 6.82 (d, 2H, arom. protons), 7.76 (d, 2H, arom. protons), 8.75 (br. s, 2H, NH_2) ppm. UV–Vis (acetone) λ_{max} (log ε): 546 (3.72) nm. Calculated for $C_{21}H_{26}N_6$: C, 69.59; H, 7.23; N, 23.18; found: C, 69.40; H, 7.17; N, 22.99.

Polyester from adipic acid and *N,N-bis*(*β*-hydroxyethyl)aniline (6)

A mixture of *N,N*-bis(*β*-hydroxyethyl)aniline (**4**, 18.1 g, 0.1 mol), adipic acid (**5**, 14.6 g, 0.1 mol) and *p*-toluene sulfonic acid (0.3 g) were stirred under vacuum (13–18 mbar) first at 140 °C for 4 h and then at 160 °C for an additional 2 h. After cooling to room temperature the product was dissolved in chloroform, washed repeatedly with aqueous sodium bicarbonate and then with water and the organic phase dried over sodium sulfate. After evaporation of the solvent 22.3 g (77%) of brownish, honey-like polyester **6** were obtained. $M_W = 13\,000$ (approx.[2]). ^{1}H NMR (deuteriochloroform): $\delta = 1.60$ (m, 4H, CH_2), 2.30 (m, 4H, CH_2), 3.60 (m, 4H, CH_2), 4.20 (m, 4H, CH_2), 6.70 (t, 2H, arom. protons), 7.00–7.40 (m, 3H, arom. protons) ppm.

Nitrosated polyester (7a)

To a solution of **6** (15.O g, 51 mmol) in 1,4-dioxane (120 ml) concentrated hydrochloric acid (23 ml) was added. The mixture was cooled to 0 °C and $NaNO_2$ (4.00 g, 58 mmol) in water (15 ml) was added dropwise under stirring and at temperatures below 5 °C. Stirring was continued for one additional hour. The nitroso compound was set free by addition of sodium hydrogen carbonate and dissolved in chloroform. The organic phase was washed with water, dried over sodium sulfate and the solvent evaporated to yield 9.1 g (55%) of dark green, honey-like **7a**. It was purified by reprecipitation from chloroform/methanol. $M_W = 2500$ (approx.[2]). ^{1}H NMR (deuteriochloroform): $\delta = 1.70$ (m, 4H, CH_2), 2.30 (m, 4H, CH_2), 3.70 (m, 4H, CH_2), 4.20 (m, 4H, CH_2), 6.90 (d, 2H, arom. protons), 7.70 (d, 2H, arom. protons) ppm. UV–Vis (1,4-dioxane) λ_{max} (log ε): 412 (4.52) nm.

[2] As appropriate poly(ester) standards were not available, we have used poly(ethylene glycol)s and poly(methyl methacrylate)s as standards for the determinations of M_Ws. This is why M_Ws cannot be given more precisely.

Formylated polyester (7b)

Compound **6** (2.91 g, 10 mmol) was dissolved in dry DMF (10 ml, freshly distilled). $POCl_3$ (1.53 g, 10 mmol) was added dropwise under stirring and at temperatures below 5 °C. The mixture was stirred for one additional hour at room temperature and then 3 h at 100 °C. After cooling to room temperature ice/water (50 ml) and NaOH (25% in water) were added to obtain $pH = 6$. The aqueous phase was decanted and discharged, the residue dissolved in chloroform, washed with aqueous sodium bicarbonate and twice with water, then the organic phase was dried over sodium sulfate. After evaporation of the solvent 1.30 g (41%) of formylated polyester **7b** were obtained. It was purified by reprecipitation from dichloromethane/methanol. $M_W = 2800$ (approx.[2]). ^1H NMR (deuteriochloroform): $\delta = 1.65$ (m, 4H, CH_2), 2.25 (m, 4H, CH_2), 3.60 (m, 4H, CH_2), 4.30 (m, 4H, CH_2), 6.80 (d, 2H, arom. protons), 7.70 (d, 2H, arom. protons), 9.70 (s, 1H, formyl CH) ppm.

Formation of polymeric dye (8a)

Compound **7a** (3.2 g, 10 mmol) and **1** (1.45 g, 11 mmol) were dissolved in chloroform (50 ml) and stirred for 2 h at room temperature. The solution was washed with water and subsequently poured into methanol (300 ml). The product was isolated by centrifugation, purified by reprecipitation from chloroform/methanol and dried under vacuum at 40 °C. Yield: 2.3 g (72%). $M_W = 2600$ (approx.[2]). ^1H NMR (deuteriochloroform): $\delta = 1.75$ (m, 4H, CH_2), 2.20 (m, 4H, CH_2), 3.70 (m, 4H, CH_2), 4.30 (m, 4H, CH_2), 6.80 (d, 2H, arom. protons), 7.70 (d, 2H, arom. protons) ppm. UV–Vis (1,4-dioxane) λ_{max} (log ε): 393 (3.59) and 503 (4.07) nm.

Formation of polymeric dye (8b)

Compound **7b** (3.2 g, 10 mmol) and **1** (1.45 g, 11 mmol) were dissolved in chloroform (50 ml) and refluxed for 60 h. The solution was washed with water and subsequently poured into methanol (300 ml). The product was isolated by centrifugation, purified by reprecipitation from chloroform/methanol and dried under vacuum at 40 °C. Yield: 2.0 g (62%). $M_W = 2900$ (approx.[2]). ^1H NMR (deuteriochloroform): $\delta = 1.70$ (m, 4H, CH_2), 2.30 (m, 4H, CH_2), 3.70 (m, 4H, CH_2), 4.20 (m, 4H, CH_2), 6.90 (d, 2H, arom. protons), 7.70 (d, 2H, arom. protons) 9.75 (s, formyl CH, the integral equals approx. 0.9 H) ppm. UV–Vis (1,4-dioxane) λ_{max} (log ε): 416 (3.65) nm.

REFERENCES

1. Marder, S. R., Tiemann, B. G., Perry, J. W., Cheng, L. T., Tam, W., Schaefer, W. P. & Marsh, R. E., in *Materials for Nonlinear Optics, Chemical Perspectives*, eds S. R. Marder, E. J. Sohn & G. D. Stucky, American Chemical Society, Washington, DC, 1991, Vol. 455, pp. 187–199.
2. Tam, W., Cheng, L.-T., Bierlein, J. D., Cheng, L. K., Wang, Y., Feiring, A. E., Meredith, G. R., Eaton, D. F., Calabrese, J. C. & Rikken, J. A., in *Materials for Nonlinear Optics, Chemical Perspectives*, eds S. R. Marder, E. J. Sohn & G. D. Stucky, American Chemical Society, Washington, DC, 1991, Vol. 455, pp. 158–169.
3. Eaton, D. F., in *Materials for Nonlinear Optics, Chemical Perspectives*, eds S. R. Marder, E. J. Sohn & G. D. Stucky, American Chemical Society, Washington, DC, 1991, Vol. 455, pp. 128–156.
4. Eaton, D. F. *Science*, **253** (1991) 281–287.
5. Vanmaele, J. L., Junek, H. & Dworczak, R., Agfa-Gevaert, N.V., Mortsel, Belgium, *US Patent* 5,324,601 (1994).
6. Vanmaele, J. L., Agfa-Gevaert, N. V., Mortsel, Belgium, *US Patent* 5,026,677 (1991).
7. Vanmaele, J. L. *Tetrahedron Lett.*, **33** (1992) 961–964.
8. Kieslinger, D. W., Masters thesis, Institute of Experimental Physics, University of Graz, 1995.
9. Matsuzawa, N. & Dixon, D. A. *J. Phys. Chem.*, **96** (1992) 6232–6241.
10. Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. & Stewart, J. J. P. *J. Am. Chem. Soc.*, **107** (1985) 3902–3909.
11. Ridley, J. E. & Zerner, M. C. *Theor. Chim. Acta*, **32** (1973) 111–134.
12. Zerner, M. C., *ZINDO, A Comprehensive Semiempirical Quantum Chemistry Package*, Quantum Theory Project, Gainesville, Florida, U.S.A., 1993.
13. Tapia, O. & Goscinski, O. *Mol. Phys.*, **29** (1975) 1653–1661.
14. Karelson, M. M. & Zerner, M. C. *J. Phys. Chem.*, **96** (1992) 6949–6957.
15. Szafran, M., Karelson, M. M., Katritzky, A. R., Koput, J. & Zerner, M. C. *J. Comput. Chem.*, **14** (1994) 371–377.
16. Yu, J. & Zerner, M. C. *J. Chem. Phys.*, **100** (1994) 7487–7494.
17. Mittelbach, M. *Monatsh. Chem.*, **116** (1985) 689–691.
18. Schwetlick, K. (ed.), *Organikum*, VEB Deutscher Verlag der Wissenschaften, Berlin, 1976, pp. 409 and 420.