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Nonlinear Optic Properties of *p*-Tricyanovinyl-, *p*-Dicyanovinyl, and *p*-Dicyano-methyleneamino-anilines and Poly(methylmethacrylate)s Covalently Functionalized with them. Syntheses with Nitriles C*

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ABSTRACT

Copolymers of methyl methacrylate and chromophores with methacrylate end groups were obtained by radical polymerization. Their nonlinear optical properties ware examined by electric field induced second-harmonic generation (EFISH) measurements and compared with corresponding monomeric dyes. All of them had maximum absorption wavelengths between 480 and 510 nm. Values for $\mu\beta$ *(dipole moment* μ*, molecular hyperpolarizability* β*) were remarkably high and reached* 530×10^{-68} Cm^5 V^{-1}*. According to quantum chemical calculations (*ab initio *and semi-empirical) increasing the acceptor strength in going from the dicyanovinyl to the dicyanomethyleneamino moiety also leads to an increase in the molecular hyperpolarizability. In contrast, further increasing the acceptor strength to the tricyanovinyl group is accompanied by a levelling off or, even, a decrease in the calculated* β*-value. © 1997 Elsevier Science Ltd*

INTRODUCTION

Intense materials research and development thereof for nonlinear optical applications started in the mid-1980s. Anorganic as well as organic systems

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have been investigated. Donor–acceptor substituted conjugated organic compounds offer great promise as materials for nonlinear optic (NLO) devices [1, 2]. For practical applications, thermoplastic polymeric materials containing NLO molecules can be used as films or coatings with NLO properties [3, 4]. NLO polymer films, typically, are glassy polymers containing asymmetric chromophores (or dyes), which point generally in the same direction, making the film asymmetrically polarizable [5]. For this 'poled polymer approach' the polymer is either heated above its glass transition temperature and then cooled to ambient temperature in a strong dc electric field, or spin coating techniques are used and the dc field is applied during evaporation of the solvent.

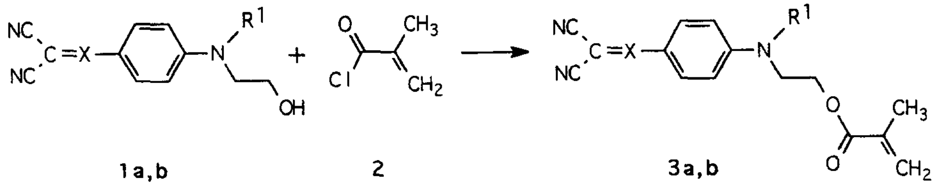
Compounds with cyano acceptor groups have been used in dye chemistry for years. Since their enhanced nonlinearity was reported some 10 years ago [6], only limited work has been reported [7–9]. In latter years some attempts were made to incorporate thiophene chromophores with tricyanovinyl acceptors into polymers [10–13]. Some *p*-tricyanovinyl-*N*,*N*-dialkylanilines are well known compounds in dye chemistry [6, 14–16], but no polymerizable compounds have been reported.

The formation of polymers with NLO chromophores by polymer analogous reactions often brings the problem that one practically never gets 100% conversions [17]. This is especially annoying if more than one reaction is necessary to obtain NLO side chains on the polymer. We decided to create polimerizable chromophores [**3(a,b)** and **5(a,b)**] first and then copolymerize them with methyl methacrylate (MMA). This should yield thermoplastic materials with glass transition temperatures above 120°C (atactic poly(methyl methacrylate)s typically have T_gs of approx. 380K) [18] and good solubility in standard solvents.

RESULTS AND DISCUSSION

Compounds **1(a,b)** and **4(a,b)** can be prepared easily from cheap starting materials in good quality and excellent yields. The methacrylates **3(a,b)** (Scheme 1) and **5(a,b)** (Scheme 2) were obtained by reacting the monohydroxy compounds **1(a,b)** and the dihydroxy compounds **4(a,b)**, respectively, with excess methacroyl chloride **(2)**. For good yields of monomeric products the use of mol sieves to trap the hydrochloric acid evolving during the reaction [19], and reaction times of 1–3 days, were necessary. Addition of triethylamine or alkali hydroxides to remove the hydrochloric acid resulted in MMA oligomers and poor yields of **3(a,b)** and **5(a,b)**. Dyes **3(a,b)** and **5(a,b)** showed λ_{max} from 480 **(5b)** to 512 **(3b)** nm and $\log\varepsilon > 4.6$.

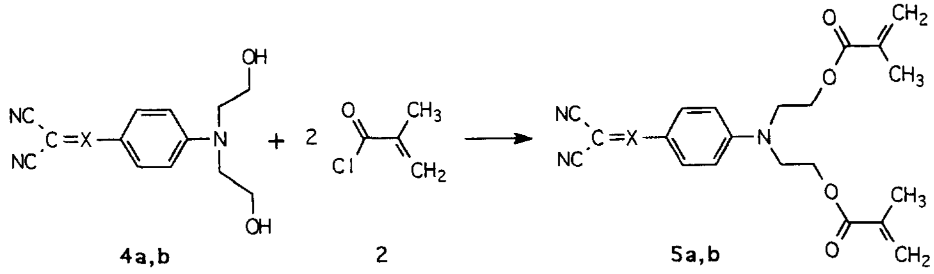
Azo-bis(isobutyronitrile) (AIBN) was used as initiator for the radical copolymerization of the methacrylate dyes **3(b)** and **5(a)** with MMA to give



1,3	X	R^1
a	N	Et
b	C(CN)	Et

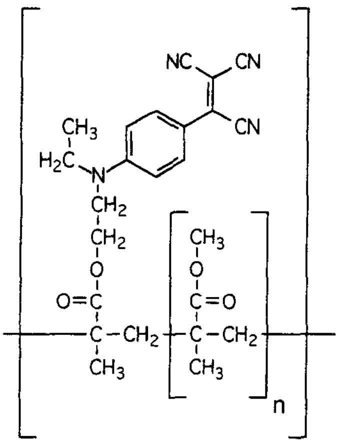
Scheme 1.

the polymers **6(a–c)** (Scheme 3) and **7(a,b)** (Scheme 4), respectively, which contained 5–25 mol% (15–53 wt%) of dye monomers (we have also produced copolymers which contained more than 25 mol% of dye monomers, but they were brittle, glassy products of poor solubility). Compounds **6(a–c)** had molar masses of 5800 (**6c**) to 41 300 (**6a**) depending on the percentage of **3(b)** and compounds **7(a,b)** had molar masses of 6400 and 4400, respectively. This interesting correlation between dye content and molar mass of the copolymers is the subject of current studies. Glass transition temperatures of all copolymers varied from approx. 180 to 210°C. There was no pronounced difference in T_g between **6(a–c)** [chain type copolymers from **3(b)** with one polymerizable methacrylate group] and **7(a,b)** [network type copolymers from **5(b)** with two polymerizable methacrylate groups]. The copolymers had maximum absorption wavelengths of 480 nm [**7(a,b)** with a dicyanomethyleneamino group as acceptor] and approx. 510 nm [**6(a–c)**, with a tricyanovinyl group as acceptors]. Logε values did not change compared to the monomeric



4,5	X
a	N
b	C(CN)

Scheme 2.

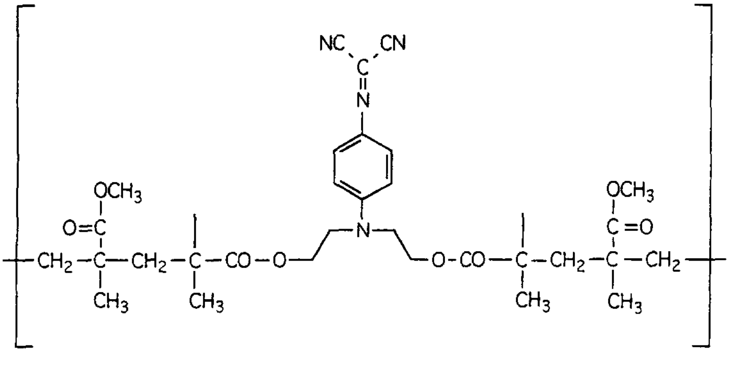


6	mol% 3b	weight% 3b	n
a	5	15	19
b	10	27	9
c	25	53	3

Scheme 3.

dyes, but corresponded with the amount of dye molecules in the copolymerization mixture. This indicates that **3(b)**, **5(a)** and MMA are incorporated into the copolymers statistically.

Polymers like these are likely candidates to be used for poled polymer films and thus the product $\mu\beta$ is a relevant figure of merit combining both the nonlinearity of the molecule and the ability of the molecule to couple with a macroscopic poling field. Therefore, $\mu\beta$, the product of first-order hyperpolarizability and ground state dipole moment, was used to compare the relative efficiencies of donor–acceptor compounds. The $\mu\beta$ values were measured in 1,4-dioxane by the electric-field-induced second harmonic generation



7	mol% 5a	weight% 5a
a	10	30
b	15	41

Scheme 4.

(EFISH) technique [20, 21]. A Nd-YAG laser ($\lambda = 1064$ nm) was used. For **3(b)** and **5(a,b)** remarkably high values for $\mu\beta$ were obtained. **5(b)** showed the highest value ($\mu\beta = 530 \times 10^{-68} Cm^5 V^{-1}$), but copolymerization of **5(b)** with MMA gave products of inadequate solubility. **3(b)** and **5(a)** were copolymerized with different amounts of MMA to yield products **6(a–c)** and **7(a,b)**, respectively. From the results given in Table 1 it may be concluded that rather low contents of chromophores in the copolymerization mixture gave products with high $\mu\beta$ values. This coincides with earlier observations; Sheeren *et al.* found optimum NLO properties for MMA copolymers with low dye content [22, 23]. Higher dye contents possibly disturb the ideal parallel orientation of the side chains.

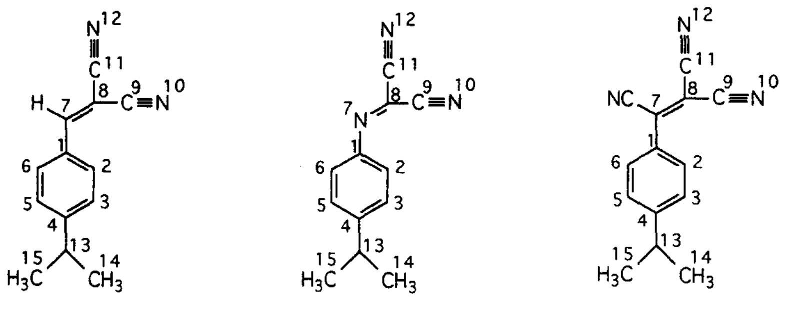
As can be seen by a comparison of the $\mu\beta$ values of **5(a)** vs. **5(b)**, replacement of the dicyanomethyleneamino group by the tricyanovinyl moiety leads to a substantial increase of the molecular hyperpolarizability. Obviously, as is also evidenced by the Uv-vis data of these two compounds, the tricyanovinyl group is a stronger acceptor. However, there also seems to be an at least comparable effect of the *p*-amino substituent (comparing **3(b)** and **5(b)**: **3(b)** absorbs at longer wavelength and yet has a lower $\mu\beta$ value. Moreover, it is well known that simply increasing the donor and/or acceptor strength does not necessarily lead to increased hyperpolarizabilities but, instead, there exists an optimal donor–acceptor combination for a given parent chromophor [24–29]. We, therefore, found it worthwhile to study the effect of the acceptor strength (dicyanovinyl vs dicyanomethyleneamino vs tricyanovinyl) in the dimethylamino-derivatives **8–10** (Scheme 5). According to the Uv–vis spectra (Table 2) the acceptor strength increases in the series **8–9–10** with a concomitant bathochromic shift of the first absorption band. In line with this finding compound **10** is also known[6,30], to have a higher β-value than **8**. If the hyperpolarizability were simply determined by the acceptor strength, one would expect for **9**, a β-value intermediate between **8** and **10**. EFISH measurements, however, gave a $\mu\beta$-value for **9** higher than that of **10**. This unexpected behavior is further corroborated by quantum chemical (*ab initio*

TABLE 1

Composition and β Values For MMA Copolymers **6(a–c)** and **7(a, b)**

Copolymer	*Contains*	*Mol%*	*Wt%*	μβ *($10^{-68} Cm^{-5} V^{-1}$)*
6(a)	**3(b)**[a]	5	15	520
6(b)	**3(b)**[a]	10	27	400
6(c)	**3(b)**[a]	25	53	330
7(a)	**5(a)**[b]	10	30	520
7(b)	**5(a)**[b]	15	41	380

[a] $\mu\beta = 400 \times 10^{-68} Cm^{-5} V^{-1}$.
[b] $\mu\beta = 390 \times 10^{-68} Cm^{-5} V^{-1}$.



8 **9** **10**

Scheme 5.

and semi-empirical) calculations. Geometries of compounds **8–10** were completely optimized by HF/3-21G *ab initio* [31] and semi-empirical AM1 [32, 33], methods. Static hyperpolarizabilities were calculated at the *ab initio* HF/3-21G level using the finite field approach [34] whereas frequency dependent βs were obtained by the sum-over-states approximation[35–71] using the semi-empirical ZINDO method [72, 73]. The effect of the solvent was treated

TABLE 2
Experimental and Calculated Dipole Moments (Debye) and Excitation Energies (cm^{-1}) for Compounds **8–10**

	μ					ν			
	exp.	*ab initio*[a]	*ZINDO (I)*[b]	*ZINDO (II)*[c]	*ZINDO (III)*[d]	*exp.*	*ZINDO (I)*[b]	*ZINDO (II)*[c]	*ZINDO (III)*[d]
8	8.7[e]	10.10	8.71	7.77	8.34	22 746[e]	29 327	29 562	29 495
	7.8[f]		11.08	9.65	10.26	23 810[f]	25 975	26 026	25 938
			19.12	14.33	15.12	23 310[g]	24 066	23 846	23 752
9	—	9.53	7.44	6.79	6.58	20 450[g]	27 805	23 962	23 942
			9.56	8.64	8.36	21 600[h]	23 794	21 348	21 326
			18.92	15.08	14.29		22 721	20 178	20 117
10	10.9[e]	9.88	8.64	7.92	8.12	18 955[e]	27 567	27 022	26 995
	8.2[f]		10.6	9.63	9.90	19 380[f]	23 108	22 557	22 518
			15.88	13.67	14.18	19 418[g]	21 474	20 717	20 692

[a] Gas phase values.

[b] ZINDO calculations with *ab initio* geometries; values given refer to gas phase, dioxane and acetone as solvent, respectively.

[c] ZINDO calculations with AM1 geometries (amino group pyramidalization and acceptor torsion on the same side of the benzene ring); values given refer to gas phase, dioxane and acetone as solvent, respectively.

[d] ZINDO calculations with AM1 geometries (amino group pyramidalization and acceptor torsion on the opposite side of the benzene ring); values given refer to gas phase, dioxane and acetone as solvent, respectively.)

[e] Ref.[6].

[f] Ref.[30].

[g] This work.

[h] Ref.[81].

by the self-consistent reaction field approach [74–77]. The well known tendency of the AM1 method to overestimate torsional angles around formal single bonds in conjugated molecules [78] is also evident in **8–10**: at the *ab initio* level for all three compounds completely planar dimethylamino groups are obtained: (τ_1 (C3–C4–N13–C14)$\approx 0°$, τ_2(C5–C4–N13–C15)$\approx 0°$ (for numbering see Scheme 5.) In addition, for **8** and **9** the acceptor group also is coplanar (τ_3(C2–C1–X7–C8)$=0°$ (**8**: X = C, **9**: X = N) with the aromatic ring, only the tricyanovinyl group of **10** is calculated to be twisted out of the molecular plane ($\tau 3 = -31°$). In contrast, AM1 yields slightly pyramidal dimethylamino groups ($\tau_1 \approx 11$–$15°$, $\tau_2 \approx -11$ to $-15°$) as well as a twisted acceptor moiety ($\tau_3 = -32$, -29, and $-40°$ for **8, 9**, and **10**, respectively), of essentially equal energy turned out conformations with reversed signs of τ_3. To study the influence of the molecular geometry on calculated properties (dipole moments, excitation energies and hyperpolarizabilities) these three geometries (*ab initio* and the two possible AM1 structures) were used in the following. The results together with the corresponding experimental data, are summarized in Table 2 (dipole moments and excitation energies) and Table 3 (hyperpolarizabilities). With respect to excitation energies two points

TABLE 3
Experimental and Calculated Hyperpolarizabilities for Compounds **8–10**

	β_o[a]					β[b]			
	exp.	*ab initio*[a]	*ZINDO (I)*[b]	*ZINDO (II)*[c]	*ZINDO (III)*[d]	*exp.*	*ZINDO (I)*[b]	*ZINDO (II)*[b]	*ZINDO (III)*[d]
8	16^g	22	14	11	10	31^g	30	24	23
	25^h		23	18	17	32^h	58	45	44
			63	47	48	$(250)^{i,j}$	327	219	231
9	—	31	23	22	24	240^i	56	67	70
			36	35	38		105	143	140
			95	97	113		866	−4127	−5354
10	26^g	31	17	15	15	78^g	41	37	38
	33^h		28	24	25	50^h	88	80	82
			80	66	68	190^i	1179	1243	1506

[a] Static hyperpolarizabilities (in 10^{-30} cm^5 esu^{-1}).

[b] Frequency dependent hyperpolarizabilities (in 10^{-30} cm^5 esu^{-1}).

[c] Gas phase values.

[d] ZINDO calculations with *ab initio* geometries; values given refer to gas phase, dioxane and acetone as solvent, respectively.

[e] ZINDO calculations with AM1 geometries (amino group pyramidalization and acceptor torsion on the same side of the benzene ring); values given refer to gas phase, dioxane and acetone as solvent, respectively.

[f] ZINDO calculations with AM1 geometries (amino group pyramidalization and acceptor torsion on the opposite side of the benzene ring); values given refer to gas phase, dioxane and acetone as solvent, respectively.

[g] DMSO as solvent, β obtained at 1.3μm, ref.[6].

[h] β obtained at 1.91μm, ref.[30].

[i] $\mu^*\beta$ (in 10^{-68}Cm^{5}V^{-1}) obtained at 1.06μm, this work.

[j] Not very reliable.

are worth mentioning; *viz*(i) inclusion of solvent effects in the calculations is necessary to obtain reasonable agreement with experimental values; (ii), for **8** all three geometries yield similar excitation energies; for **9**, however, with the planar *ab initio* geometry, absorption at shorter wavelengths is predicted than when twisted structures are used in the calculations. This is in contrast to what one would usually expect for compounds with decreased conjugation. This effect of a bathochromic shift with increasing torsional angles, originally described for indoaniline dyes, can be attributed to an increased interaction between the nitrogen lone pair and the π-system of the chromophore in the twisted geometry, thus leading to an accompanying raising of the HOMO energy level [79, 80]. As a consequence, the experimentally observed trend of a bathochromic shift in the series **8–9–10** can only be reproduced by the calculations if the *ab initio* geometries are used, thus stressing the importance of a good choice of structures [52]. The most noteworthy feature of the hyperpolarizabilities presented in Table 3 is the fact that irrespective of the geometry and method used, it is compound **9** for which the largest β-value is predicted, in striking contrast to the trend found for absorption spectra. The experimental data seem to corroborate this result; from the measured $\mu\beta$ values for **9** and **10** using the ZINDO–SCRF (dioxane, *ab initio* geometry) calculated dipole moments β-values of 181 and 129×10^{-30} cm^5 esu^{-1}, respectively, can be estimated (to be compared to values of 105 and 88×10^{-30} cm^5 esu^{-1}; see Table 3). The extremely high calculated β-values for **9** and **10** in acetone most probably are an artifact of the perturbational approach, since here the first electronic transition energy approaches close to twice the excitation frequency ($E = 1.17$ eV).

EXPERIMENTAL

General

All melting points are uncorrected. Spectral data were recorded with the following instruments: IR spectra: Perkin-Elmer 298 Spectrophotometer (KBr); ^{1}H NMR spectra: Varian LX 200 and Bruker 360 (spectra referenced to tetramethylsilane and generally recorded in DMSO-d_6, other solvents are indicated); Uv–vis spectra: Hitachi U-3501 Spectrophotometer (quartz cuvettes). HPLC system: HPLC Gynkotek High Precision Pump 300 C, column PL Microgel M 10μ, 600×7.8 mm (from Polymer Laboratories), 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(methyl-methacrylate)s from Polymer Laboratories. The equipment used for EFISH measurements was described earlier [21].

General methods

1(b) and **4(b)** were obtained according to ref [16] by combining *N*-ethyl-*N*-(β-hydroxyethyl)-aniline and *N*,*N*-bis(β-hydroxyethyl)aniline, respectively, with tetracyanoethylene in DMF. For copolymerizations methyl methacrylate was distilled and azo-bis(isobutyronitrile) was recrystallized from methanol. 1,4-Dioxane for EFISH measurements was purified and dried over Al_2O_3 immediately before use.

4-Dicyanmethyleneamino-*N*-ethyl-*N*-β-hydroxyethylaniline (1a)

N-ethyl-*N*-β-hydroxyethyl-*p*-nitrosoaniline (10 mmol) and malononitrile (10 mmol) were dissolved in absolute ethanol (20 ml) and heated under reflux for 1 h. The product was precipitated by addition of water. Yield 80%, dark violet needles, m.p. 104°C (glacial acetic acid/water) IR: $\nu = 3500–3300, 3000–2800, 2210, 1610, 1525\ cm^{-1}$. ^1H NMR: $\delta = 1.17$ (t, 3H, CH_3), 3.62 (m, 6H, CH_2), 4.94 (br. s, 1H, OH), 6.97 (d, 2H, arom. protons), 7.74 (d, 2H, arom. protons) ppm. Uv–vis (acetone) λ_{max} (logε): 495 (4.78) nm. Calculated for $C_{13}H_{14}N_4O$: C, 64.5; H, 5.8; N, 23.1; found: C, 64.2; H, 5.5; N, 22.8.

Preparation of monomethyl methacrylates 3(a,b) and dimethyl methacrylates 5(a,b); general procedure

The hydroxy compounds [20 mmol of **3(a,b)** or 10 mmol of **4(a,b)**] and finely ground mol sieves 4 Å (4 g) were stirred in acetonitrile (60 ml). Methacroyl chloride (25 mmol) was added and the mixture heated under reflux (reaction times are given below). The hot reaction mixtures were then suction filtered, solvent and excess methacroyl chloride removed under reduced pressure and the solid residues recrystallized. Relevant characterization data is given below.

4-Dicyanmethyleneamino-*N*-ethyl-*N*-methacroyloxyethyl-aniline 3(a)

Yield 65% (48 h reflux), violet crystals, m.p. (decomp.) 85°C (chloroform/diethyl ether). IR: $\nu = 3650–3000, 3000–2850, 2210, 2200, 1740, 1720, 1610, 1520–1510\ cm^{-1}$. ^1H NMR: $\delta = 1.20$ (t, 3H, CH_3), 1.86 (s, 3H, CH_3), 3.65 (q, 2H, CH_2), 3.90 (t, 2H, N–CH_2), 4.33 (t, 2H, O–CH_2), 5.70 and 6.00 (d, 2H, $=CH_2$), 7.00 (d, 2H, arom. protons), 7.22 (d, 2H, arom. protons) ppm. Uv–vis (acetone) λ_{max} (logε): 487 (4.60) nm. Calculated for $C_{17}H_{18}N_4O_2$: C, 65.8; H, 5.8; N, 18.1; found: C, 65.4; H, 5.6; N, 17.9.

4-(2,2,1-Tricyanethenyl)-*N*-ethyl-*N*-methacroyloxyethyl-aniline 3(b)

Yield 52% (24 h reflux), violet needles, m.p. 120°C (methanol). IR: $\nu = 2215$, 1720, 1715, 1605, 1495 cm^{-1}. ^{1}H NMR: $\delta = 1.19$ (t, 3H, CH_3), 1.85 (s, 3H, CH_3), 3.65 (q, 2H, CH_2), 3.90 (t, 2H, N-CH_2), 4.35 (t, 2H, O-CH_2), 5.70 and 6.00 (d, 2H, $=CH_2$), 7.12 (d, 2H, arom. protons), 7.95 (d, 2H, arom. protons) ppm. Uv–vis (acetone) λ_{max} (logε): 512 (4.66) nm. Calculated for $C_{19}H_{18}N_4O_2$ C, 68.3; H, 5.4; N, 16.8; found: C, 67.9; H, 5.2; N, 16.5. 113 $\mu\beta = 400 \times 10^{-68} Cm^5V^{-1}$.

4-Dicyanmethyleneamino-*N*,*N*-bis(*β*-hydroxyethyl)aniline 4(a)

p-Nitroso-*N*,*N*-bis(*β*-hydroxyethyl)aniline (10 mmol) and malononitrile (10 mmol) were dissolved in absolute ethanol (20 ml) and heated under reflux for 1 h. The product was then either precipitated by addition of water or obtained by removing the solvent *in vacuo*. Yield 50%, black–violet needles, m.p. 145°C (methanol). IR: $\nu = 3500$–3000, 2215, 1610, 1530, 1460, 1450 cm^{-1}. ^{1}H NMR: $\delta = 3.65$ (m, 8H, 4 CH_2), 4.92 (br. s, 2H, OH), 6.99 (d, 2H, arom. protons), 7.73 (d, 2H, arom. protons) ppm. Uv–vis (ethanol) λ_{max} (logε): 493 (4.58) nm; Uv–vis (acetone) λ_{max} (logε): 494 (4.60) nm; UV–Vis (acetonitrile) λ_{max} (logε): 493 (4.67) nm. Calculated for $C_{13}H_{14}N_4O_2$: C, 60.5; H, 5.5; N, 21.7; found: C, 60.7; H, 5.4; N, 21.4.

4-Dicyanmethyleneamino-*N*,*N*-bis(methacroyloxyethyl)-aniline 5(a)

Yield 59% (48 h reflux), oily residue after evaporation of the solvent; the product solidified on addition of sodium carbonate/water, violet needles, m.p. 83°C (ethanol/water). IR: $\nu = 3950$, 3880, 2215, 1715, 1605, 1495 cm^{-1}. ^{1}H NMR: $\delta = 1.84$ (s, 6H, CH_3), 3.93 (t, 4H, N–CH_2), 4.36 (t, 4H, O–CH_2), 5.68 and 6.00 (d, 4H, $=CH_2$), 7.12 (d, 2H, arom. protons), 7.73 (d, 2H, arom. protons) ppm. Uv–vis (acetone) λ_{max} (logε): 480 (4.63) nm. Calculated for $C_{21}H_{22}N_4O_4$: C, 64.0; H, 5.6; N, 14.2; found: C, 63.6; H, 5.6; N, 13.9. $\mu\beta = 390 \times 10^{-68} Cm^5V^{-1}$.

4-(2,2,1-Tricyanethenyl)-*N*,*N*-bis(methacroyloxyethyl)-aniline 5(b)

Yield 65% (72 h reflux), oily residue after evaporation of the solvent; product solidified on addition of sodium carbonate/water, violet needles, m.p. 102°C (ethanol). IR: $\nu = 2980$, 2960, 2940, 2220, 1720, 1605, 1510, 1500 cm^{-1}. ^{1}H NMR: $\delta = 1.84$ (s, 3H, CH_3), 3.95 (t, 2H, CH_2), 4.35 (t, 2H, CH_2), 5.67 and 5.98 (d, 2H, $=CH_2$), 7.20 (d, 2H, arom. protons), 7.93 (d, 2H, arom. protons) ppm. Uv–vis (acetone) λ_{max} (logε): 503 (4.63) nm. Calculated for

$C_{23}H_{22}N_4O_4$: C, 66.0; H, 5.3; N, 13.4; found: C, 65.5; H, 5.2; N, 13.3. $\mu\beta = 530 \times 10^{-68} Cm^5V^{-1}$.

Preparation of MMA copolymers 6(a-c) and 7(a,b); general procedure

The mixtures of monomers (20 mmol, MMA and dyes [**3(b)**, **5(a)**] in different compositions) and AIBN (0.02 g) were dissolved in acetone (20 ml) and refluxed for 20 h. The mixtures were then cooled to room temperature and the products precipitated by pouring the reaction mixture into methanol (100 ml). The products were collected by suction and dried under vacuum.

6(a) From 0.33 g (1 mmol) **3(b)** and 1.90 g (19 mmol) MMA; yield 60%, $T_g = 183°C$. $M_w = 41300$; IR: $\nu = 2990$, 2950, 2220, 1740, 1730, 1605, 1545, 1510, 1490 cm^{-1}. Uv–vis (acetone) λ_{max} (logε): 512 (4.72) nm. $\mu\beta = 520 \times 10^{-68} Cm^5V^{-1}$.

6(b) From 0.66 g (2 mmol) **3(b)** and 1.80 g (18 mmol) MMA; yield 65%, $T_g = 185°C$. $M_w = 16900$; IR: $\nu = 3600–3300$, 2990, 2950, 2220, 1730, 1605, 1545, 1490 cm^{-1}. Uv–vis (acetone) λ_{max} (logε): 511 (4.61) nm. $\mu\beta = 400 \times 10^{-68} Cm^5V^{-1}$.

6(c) From 1.68 g (5 mmol) **3(b)** and 1.50 g (15 mmol) MMA; yield 62%, $T_g = 211°C$. $M_w = 5800$; IR: $\nu = 2990$, 2940, 2220, 1740, 1730, 1605, 1545, 1490 cm^{-1}. Uv–vis (acetone) λ_{max} (logε): 508 (4.69) nm. $\mu\beta = 330 \times 10^{-68} Cm^5V^{-1}$.

7(a) From 0.78 g (2 mmol) **5(a)** and 1.80 g (18 mmol) MMA; yield 55%, $T_g = 208°C$, $M_w = 6400$; IR: $\nu = 3500–3100$, 3000, 2950, 2220, 2200, 1735, 1730, 1610, 1550, 1515 cm^{-1}. Uv–vis (acetone) λ_{max} (logε): 480 (4.61) nm. $\mu\beta = 520 \times 10^{-68} Cm^5V^{-1}$.

7(b) From 1.18 g (3 mmol) **5(a)** and 1.70 g (17 mmol) MMA; yield 51%, $T_g = 209°C$. $M_w = 4400$; IR: $\nu = 3700–3100$, 2980, 2950, 2220, 2200, 1725, 1610, 1535, 1510 cm^{-1}. Uv–vis (acetone) λ_{max} (logε): 480 (4.63) nm. $\mu\beta = 380 \times 10^{-68} Cm^5V^{-1}$.

REFERENCES

1. Marder, S. R., Tiemann, B. G., Perry, J. W., Cheng, L. T., Tam, W., Schaefer, W. P. and Marsh, R. E., In *Materials for Nonlinear Optics, Chemical Perspectives,* vol. 455 eds S. R. Marder, E. J. Sohn and G. D. Stucky. American Chemical Society, Washington, 1991, 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. and Rikken, G. L. J. A., In *Materials for Nonlinear Optics Chemical Perspectives* vol. 455 eds S. R. Marder, J. E. Sohn and G. D. Stucky. American Chemical Society, Washington, 1991, pp. 158–169.

3. Eaton, D. F., In *Materials for Nonlinear Optics, Chemical Perspectives* vol. 455, eds S. R. Marder, J. E. Sohn and G. D. Stucky. American Chemical Society, Washington, 1991, pp. 128–156.
4. Marder, S. R., Sohn, J. E. and Stucky, G. D. eds *Materials for Nonlinear Optics, Chemical Perspectives*. American Chemical Society, Washington, 1991.
5. Lindsay, G. A., *Acs of Symposium Ser.*, 1995, **601**, 1–19.
6. Katz, H. E., Singer, K. D., Sohn, J. E., Dirk, C. W., King, L. A. and Gordon, H. M., *Journal of the American Chemical Society*, 1987, **109**, 6561–6563.
7. Rao, V. P., Jen, A., Wong, K. Y. and Drost, K. J., *Journal of the Chemical Society Chemical Communications*, 1993, 1118–1120.
8. Jen, A., Rao, V. P., Wong, K. Y. and Drost, K. J., *Journal of the Chemical Society Chemical Communications*, 1993, 90–92.
9. Jen, A. K.-Y., Rao, V. P., Drost, K. J., Wong, K. Y. and Cava, M. P., *Journal of the Chemical Society Chemical Communications*, 1994, 2057–2058.
10. Drost, K. J., Rao, V. P. and Jen, A., *Journal of the Chemical Society Chemical Communications*, 1994, 369–371.
11. Jen, A., Drost, K. J., Cai, Y., Rao, V. P. and Dalton, L. R., *Journal of the Chemical Society Chemical Communications*, 1994, 965–966.
12. Rao, V. P., Cai, Y. M. and Jen, A., *Journal of the Chemical Society Chemical Communications*, 1994, 1689–1690.
13. Jen, A. K.-Y., Liu, Y.-J., Cai, Y., Rao, V. P., and Dalton, L. R., *Journal of the Chemical Society Chemical Communications*, 1994, 2711–2712.
14. McKusick, B. C., Heckert, R. E., Clairns, T. L., Coffman, D. D. and Mower, H. F. *Journal of the Chemical Society Chemical Communications*, 1958, **80**, 2806–2815.
15. Lambert, R. L., Jr, *Ger. Offen. 2,918,685*. Minnesota Mining and Mfg. Co., Germany, 1979, 35 pp.
16. JPN *Kokai Tokkyo Koho JP 60 31563 (85 31563)*. Mitsubishi Chemical Industries C., Ltd., Japan, 1985, 6 pp.
17. Dworczak, R., Fabian, W. M. F., Kieslinger, D. and Junek, H., *Dyes and Pigments*, 1997, **34**, 13–23.
18. Seymour, R. B. and Carraher, C. E. *Polymer Chemistry—An Introduction*, 2nd edn. Marcel Dekker, Inc., New York and Basel, 1988, 670 pp.
19. Banks, A. R., Fibiger, R. F. and Jones, T., *Journal of Organic Chemistry*, 1977, **42**, 3965–3966.
20. Moylan, C. R., Miller, R. D., Twieg, R. J. and Lee, V. Y., *ACS Symposium Series*, **601**, 1995, 66–81.
21. Kieslinger, D. W., Master thesis, Institute Experimental Physics, University of Graz, 1995.
22. Sheeren, G., Persoons, A., Rondou, P., Wiersma, J., Vanbeylen, M. and Samyn, C., *Makromolecular Chemistry Macro. Chemistry and Physics*, 1993, **194**, 1733–1744.
23. Rondou, P., Vanbeylen, M., Samyn, C., Sheeren, G. and Persoons, A. *Makromolecular Chemistry Macro. Chemistry and Physics*, 1992, **193**, 3045–3055.
24. Calabrese, J. C., Cheng, L. T., Green, J. C., Marder, S. R. and Tam, W., *Journal of the American Chemical Society*, 1991, **113**, 7227–7232.
25. Marder, S. R., Beratan, D. N. and Cheng, L. T. *Science*, 1991, **252**, 103–106.
26. Marder, S. R., Gorman, C. B., Tiemann, B. G. and Cheng, L. T. *Journal of the American Chemical Society*, 1993, **115**, 3006–3007.

27. Risser, S. M., Beratan, D. N. and Marder, S. R., *Journal of the American Chemical Society*, 1993, **115**, 7719–7728.
28. Bourhill, G., Bredas, J. L., Cheng, L. T., Marder, S. R., Meyers, F., Perry, J. W. and Tiemann, B. G., *Journal of the American Chemical Society*, 1994, **116**, 2619–2620.
29. Sen, R., Majumdar, D., Bhattacharyya, S. P. and Bhattacharyya, S. N., *Journal of Physics and Chemistry*, 1993, **97**, 7491–7498.
30. Matsuzawa, N. and Dixon, D. A., *Journal of Physics and Chemistry*, 1992, **96**, 6232–6241.
31. Frisch, M. J., Trucks, G. W. Schlegel, H. B., *et al*., *Gaussian 94, Revision B.3*. Gaussian, Inc., Pittsburgh PA, 1995.
32. Dewar, M. J. S., Zoebisch, E. G., Healy, E. F. and Stewart, J. J. P., *Journal of the American Chemical Society*, 1985, **107**, 3902–3909.
33. Clark, T., *VAMP 4.4, Erlangen Vectorized Molecular Orbital Package*. Computer-Chemie-Centrum, University Erlangen-Nürnberg, 1992.
34. Meyers, F. and Bredas, J. L. *International Journal of Quantum Chemistry*, 1992, **42**, 1595–1614.
35. Kanis, D. R., Ratner, M. A. and Marks, T. J., *Chemical Reviews*, 1994, **94**, 195–242.
36. Docherty, V. J., Pugh, D. and Morley, J. O., *Journal of the Chemical Society Faraday Transactions*, 1985, **81**, 1179–1192.
37. Morley, J. O., Docherty, V. J. and Pugh, D., *Journal of the Chemical Society Perkin Transactions*, 1987, 1351–1355.
38. Morley, J. O., Docherty, V. J. and Pugh, D., *Journal of the Chemical Society Perkin Transactions*, 1987, 1357–1360.
39. Morley, J. O., Docherty, V. J., Pugh, D., *Journal of Molecular Electronics*, 1989, **5**, 117–121.
40. Morley, J. O., Pugh, D. and Pavlides, P., *Journal of the Chemical Society Faraday Transactions*, 1989, **85**, 1789–1798.
41. Hurst, M., Munn, R. W. and Morley, J. O., *Journal of Molecular Electronics*, 1990, **6**, 15–19.
42. Morley, J. O., *Journal of the American Chemical Society*, 1988, **110**, 7660–7663.
43. Morley, J. O., Pavlides, P. and Pugh, D., *International Journal of Quantum Chemistry*, 1992, **43**, 7–26.
44. Morley, J. O., *Journal of the Chemical Society Perkin Transactions*, 1989, 103–106.
45. Morley, J. O., *International Journal of Quantum Chemistry*, 1993, **46**, 19–26.
46. Morley, J. O., *Journal of the Chemical Society Faraday Transactions*, 1991, **87**, 3009–3013.
47. Morley, J. O., *Journal of the Chemical Society Faraday Transactions*, 1991, **87**, 3015–3019.
48. Morley, J. O., Pugh, D., *Journal of the Chemical Society Faraday Transactions*, 1991, **87**, 3021–3025.
49. Morley, J. O., *Journal of the Chemical Society Faraday Transactions*, 1994, **90**, 1849–1852.
50. Morley, J. O., *Journal of the Chemical Society Faraday Transactions*, 1994, **90**, 1853–1855.
51. Albert, I. D. L., Morley, J. O. and Pugh, D., *Journal of Chemical and Physics*, 1993, **99**, 5197–5210.

52. Kanis, D. R., Marks, T. J. and Ratner, M. A., *International Journal of Quantum Chemistry*, 1992, **43**, 61–82.
53. Li, D. Q., Ratner, M. A. and Marks, T. J., *Journal of the American Chemical Society*, 1988, **110**, 1707–1715.
54. Kanis, D. R., Ratner, M. A., Marks, T. J. and Zerner, M. C., *Chemistry of Materials*, 1991, **3**, 19–22.
55. Dibella, S., Fragala, I. L., Ratner, M. A. and Marks, T. J., *American Chemical Society*, 1993, **115**, 682–686.
56. Li, D. Q., Marks, T. J. and Ratner, M. A., *Journal of Physical Chemistry*, 1992, **96**, 4325–4336.
57. Kanis, D. R., Ratner, M. A. and Marks, T. J., *Journal of American Chemical Society*, 1990, **112**, 8203–8204.
58. Di Bella, S., Ratner, M. A. and Marks, T. J., *Journal of the American Chemical Society*, 1992, **114**, 5842–5849.
59. Di Bella, S., Marks, T. J. and Ratner, M. A., *Journal of the American Chemical Society*, 1994, **116**, 4440–444.
60. Dehu, C., Meyers, F., Hendrickx, E., Clays, K., Persoons, A., Marder, S. R. and Bredas, J. L., *Journal of the American Chemical Society*, 1995, **117**, 10127–10128.
61. Jain, M. and Chandrasekhar, J., *Journal of Physical Chemistry*, 1993, **97**, 4044–4049.
62. Yoshimura, T., *Physical Reviews B Cond. Matter*, 1989, **40**, 6292–6298.
63. Yoshimura, T., *Applied Physics Letters*, 1989, **55**, 534–536.
64. Yoshimura, T., *Molecular Crystals and Liquid Crystallography*, 1990, **182**, 43–50.
65. Pierce, B. M., *Journal of Chemical and Physics*, 1989, **91**, 791–811.
66. Andraud, C., Brotin, T., Garcia, C. *et al.*, *Journal of the American Chemical Society*, 1994, **116**, 2094–2102.
67. Dehu, C., Meyers, F. and Bredas, J. L., *Journal of the American Chemical Society*, 1993, **115**, 6198–6206.
68. Dirk, C. W., Twieg, R. J. and Wagniere, G., *Journal of the American Chemical Society*, 1986, **108**, 5387–5395.
69. Ulman, A., Willand, C. S., Kohler, W., Robello, D. R., Williams, D. J. and Handley, L., *Journal of the American Chemical Society*, 1990, **112**, 7083–7090.
70. Itoh, Y., Isogai, M., Kakuta, A. and Oono, K., *Molecular Crystals and Liquid Crystallography*, 1989, **170**, 259–272.
71. Ohno, K., Itoh, Y., Hamada, T., Isogai, M. and Kakuta, A., *Molecular Crystals and Liquid Crystallography*, 1990, **182**, 17–31.
72. Ridley, J. E. and Zerner, M. C., *Theoretica Chimica Acta*, 1973, **32**, 111–134.
73. Zerner, M. C., *ZINDO, A Comprehensive Semiempirical Quantum Chemistry Package*, Quantum Theory Project, Gainesville, 1993.
74. Tapia, O. and Goscinski, O., *Molecular Physics*, 1975, **29**, 1653–1661.
75. Karelson, M. M. and Zerner, M. C., *Journal of Physical Chemistry*, 1992, **96**, 6949–6957.
76. Szafran, M., Karelson, M. M., Katritzky, A. R., Koput, J. and Zerner, M. C., *Journal of Computational Chemistry*, 1993, **14**, 371–377.
77. Yu, J. and Zerner, M. C., *Journal of Physics*, 1994, **100**, 7487–7494.
78. Fabian, W. M. F., *Journal of Computational Chemistry*, 1988, **9**, 369–377.
79. Adachi, M., Murata, Y. and Nakamura, S., *Journal of the American Chemical Society*, 1993, **115**, 4331–4338.

80. Adachi, M., Murata, Y. and Nakamura, S., *Journal of Organic Chemistry*, 1993, **58**, 5238–5244.
81. Cheng, L. B., Chen, X., Hou, Y. and Griffiths, J., *Dyes and Pigments*, 1989, **10**, 123–140.