

Synthesis of new donor-acceptor diarylacetylene chromophores and preparation of corresponding nonlinear optical side-chain polymers

John Wong, Patrick Masson, and Jean-François Nicoud*

Groupe des Matériaux Organiques, Institut de Physique et Chimie des Matériaux, Institut Charles Sadron, 6, rue Boussingault, F-67083 Strasbourg Cedex, France

Summary

New donor-acceptor substituted diarylacetylene hyperpolarizable chromophores bearing an amino group as donor and a methylsulfonyl group as acceptor at each extremities of an azatolane conjugated path have been designed to get a good nonlinearity-transparency trade-off, and synthesized. Corresponding methacrylate esters have been obtained then submitted to free radical polymerization, leading to novel side-chain nonlinear optical polymers and copolymers.

Introduction

In recent years, poled amorphous polymeric materials for second-order nonlinear optical (NLO) properties have been widely investigated (1-3). Typically, such materials incorporate hyperpolarizable chromophores into amorphous polymer or copolymer leading to a guest-host system (4,5) or by attaching them covalently leading to a main-chain (6) or a side-chain polymer (7).

The quadratic NLO properties are obtained only when a noncentrosymmetric alignment of the active chromophores is obtained, usually by electric-field poling above the glass transition temperature T_g , then cooling the matrix below its T_g , while keeping the electric field. The nature of the hyperpolarizable chromophore must be chosen in function of the desired NLO effect with the resulting material. For electrooptical modulation, highly colored chromophores can be used since the modulated laser light is often in the near infrared region, but for second harmonic generation (SHG) the material must have a complete transparency in regards to the second harmonic wavelength. For frequency doubling of the light of common solid-state laser diode emitting between 820 and 900 nm, this implies the use of NLO chromophores whose charge transfer (CT) absorption permits a high transparency in the visible region from 410/450 nm, along with reasonable hyperpolarizability and photochemical stability. We wish to report in this communication, the design and synthesis of novel NLO polymers based on donor-acceptor diarylacetylene chromophores of type **1b** in their side chains (figure 1). **1b** avoids the easy cis/trans isomerism encountered in classical donor-acceptor stilbene or azobenzene chromophores, and its hyperpolarizability and absorption properties should lead to a good nonlinearity/transparency trade-off.

*Corresponding author

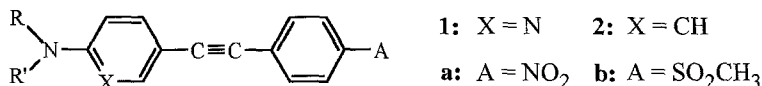
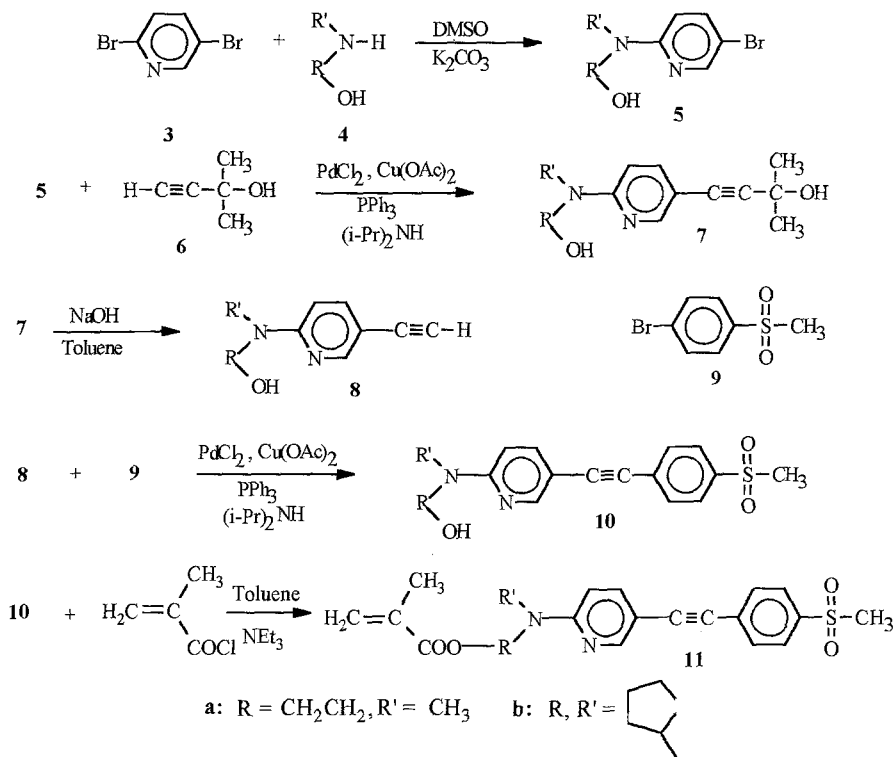


Figure 1: General structure of diarylacetylene NLO chromophore

Results and discussion

The choice of a diarylacetylene type chromophore has been made also hoping that such a rigid rodlike long chromophore would prevent more efficiently the reorientation of the NLO group after the poling process. Rigid side-chain NLO chromophores derived from 4-amino-4'-nitrotolane (**2a**) have been already described for the same reason (8,9). A pyridine ring has been placed on the donor side of the chromophore for transparency reasons. It has been already shown that **1a** presents an hypsochromic shift ($\lambda_{\max} = 384$ nm in EtOH) of the charge transfer band in comparison with **2a** ($\lambda_{\max} = 404$ nm in EtOH) (10). The hyperpolarizability β of tolane and diarylacetylene derivatives is now well documented (11,12), though experimental β value of **1b** is not yet known. From results on **1a**, **2a** and **2b** obtained by EFISHG measurements (11-14), it can be anticipated that the hyperpolarizability β of **1b** should be slightly over the one of 4-nitroaniline derivatives, in the range of 13×10^{-30} esu. The chosen chromophore **1b** bears a classical amino donor group, and a sulfonyl group as an attractor rather than the classical nitro one in order to improve the transparency (**2a**: $\lambda_{\max} = 402$ nm; **2b**: $\lambda_{\max} = 358$ nm) (13). The use of alkylsulfonyl or fluoroalkylsulfonyl acceptor groups has been recently proposed because it allows a certain synthetic flexibility by changing the attached alkyl group without modifying its acceptor properties (15,16). Such hyperpolarizable chromophores of the diarylacetylene type have never been reported in the literature. The synthesis of the monomers is summarized in scheme 1. 2,5-dibromopyridine **3** is substituted in position 2 by a secondary amino alcohol (N-methylaminoethanol **4a** or (S)-(+)-prolinol **4b**) by an aromatic nucleophilic substitution (S_NAr) in DMSO, to give the 2-amino-5-bromopyridine derivatives **5a,b** bearing the desired hydroxylic function for further esterification. The discrepancy of reactivity between the 2-bromo and 5-bromo positions in **3** can be explained by the more activated bromine in ortho position relative to the nitrogen; this had been previously reported for the synthesis of 2-alkyl-5-bromopyridine (17). The ethynylation of **5** in position 5 is made by a palladium-copper coupling reaction with the alkynol **6** to give the heteroalkynols **7a,b**, that were easily deprotected by sodium hydroxide in refluxing toluene (18) to give the free alkyne derivatives **8a,b**. We must point out the straightforward use of the less expensive alkynol **6** as protected acetylene reagent rather than the more classical trimethylsilylacetylene (19). The donor-acceptor diarylacetylenes **10a,b** were prepared by using the same



Scheme 1: Synthetic route to NLO chromophores and corresponding monomers

kind of catalytic cross-coupling reaction between **8a,b** and the commercially available 4-bromophenylmethylsulfone **9**. Finally, the hydroxyl function of the amino alcohol moiety is esterified with methacryloyl chloride. The chromophore **10** is dissolved in anhydrous toluene, then freshly distilled methacryloyl chloride is added dropwise under N_2 at 0°C . The reaction mixture is kept at 0°C , then allowed to stand at room temperature for one day, to yield the monomers **11a** and **11b**.

Monomers **11a**, **11b** were submitted to free radical polymerization with 2,2'-azobisisobutyronitrile (AIBN) as radical initiator in THF to give polymers **12** and **13**. Copolymerization between **11b** and methylmethacrylate, in 50/50 molar ratio, was made in DMF, giving the copolymer **14**. The characterization data of these polymers are given in table 1. Both monomers are soluble in THF, but precipitation occurs during their homopolymerizations which can explain the low yields obtained. The molecular weight distribution may be compared with those obtained in radical polymerizations. The copolymer composition determined from elemental analysis and from ^1H NMR spectra is the same as the monomer feed composition. DSC analyses show that the glass transition temperature (T_g)

for these polymers lies in the range 110°C/120°C, depending on the structure of the attached NLO chromophore to the polymer backbone. The T_g appear sufficiently high to permit a stable orientation of the chromophore after poling. All the polymers are thermally stable, up to 200°C in nitrogen atmosphere, as observed from the thermogravimetric analysis.

Polymer	monomer	$m_{pol}^{a)}$	Mw ^{b)}	Mw/Mn ^{b)}	Mw ^{c)}	yield (%)	T_g (°C)	λ_{max} (nm)
12	11a	1.00	-	-	85.000	35	112	352
13	11b	1.00	-	-	120.000	39	122	348
14	11b/MMA	0.50	28.000	2.0	30.000	60	118	353

a) mole fraction of NLO chromophore monomer in copolymer

b) measured by GPC in THF, PMMA standards

c) measured by light scattering in DMF (**12,13**) or in THF (**14**)

Table 1: Synthesis and characterization of NLO polymers **12**, **13**, and **14**

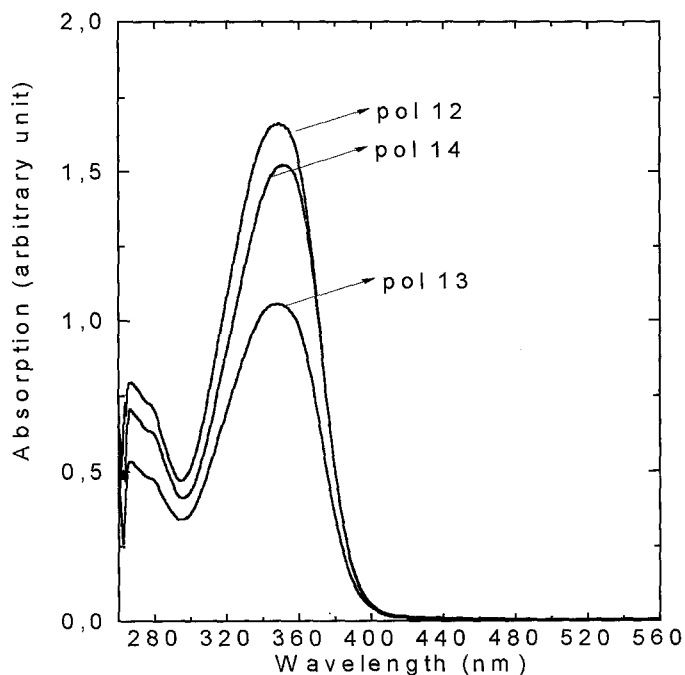


Figure 2: UV/VIS spectra of polymers **12**, **13** and **14** in DMF solutions

The UV/VIS spectra of homo- and co-polymers were recorded in DMF (figure 2). They show typical narrow bands attributed to the charge transfer transition at the origin of the hyperpolarizability of the chromophores. We can

notice the expected blue shift (10) produced by the pyridine ring in chromophores of type **1b** in comparison with **2b**, so that a transparency in the visible region may be expected from 420 nm for these new polymers.

In conclusion novel polymers bearing diarylacetylene NLO chromophores in their side chains have been synthesized. Their transparency qualifies them for frequency doubling of semiconductor laser light. Preparation of new analogous polymers, processing and poling experiments, are currently under investigation.

Experimental part

Instrumentation: ^1H and ^{13}C NMR spectral data were obtained on a Bruker AC 200 spectrometer; chemical shifts (δ in ppm) are reported down field from TMS. UV/VIS spectra were recorded on a Beckman DK 2 spectrophotometer. Melting points were determined on a Reichert microscope with a Mettler FP 82 hot stage. Thermogravimetric data were obtained on a Mettler TA 3000 apparatus. Differential scanning calorimetry (DSC) thermograms were recorded on a Perkin Elmer DSC2 and DSC 7 apparatus, with a heating rate of $20^\circ\text{C}/\text{min}$.

Materials: 2,5-dibromopyridine (**3**) (Aldrich), N-methyl-2-aminoethanol (**4a**) (Aldrich), (S)-(+)-prolinol (**4b**) (Aldrich), 2-methyl-3-butyn-2-ol (**6**) (Aldrich), 4-bromophenylmethyl-sulfone (**9**) (Lancaster) were used as received. Methacryloyl chloride (Aldrich) was carefully distilled before use.

Synthesis of chromophores and monomers: The synthesis of chromophores **10a,b** and monomers **11a,b** is summarized in scheme 1. 2-[N-(2-hydroxyethyl)-N'-methylamino]-5-bromopyridine (**5a**) was prepared from 2,5-dibromopyridine (**3**) and N-methyl-2-aminoethanol (**4**). A mixture of 9.9g (41.7 mmol) of **3**, 6.26g (2 equiv.) of aminoalcohol **4** and 3g of K_2CO_3 in suspension in 50 ml of DMSO is stirred overnight at $120\text{--}130^\circ\text{C}$. The reaction mixture is poured in iced water, then extracted with ether, washed with NaCl solution and dried over Na_2SO_4 . Evaporation of the solvent gave **5a** as an oily compound that crystallizes slowly on standing at room temperature (crude yield: 95%).

^1H NMR (CDCl_3): $\delta = 3.05$ (s, 3H), 3.8 (m, 4H), 4.3 (s, 1H), 6.45 (d, 1H, $J = 8.8$ Hz), 7.5 (dd, 1H, $J = 8.8$ Hz, $J = 2.3$ Hz), 8.1 (d, 1H, $J = 2.3$ Hz).

$\text{C}_8\text{H}_{11}\text{N}_2\text{OBr}$ (231.09)	Calc.	C 41.58	H 4.80	N 12.12
	Found	C 41.22	H 4.61	N 12.08

Similarly was obtained **5b** (84% yield) starting from **3** and (S)-(+)-prolinol **4b**.

^1H NMR (CDCl_3): $\delta = 2.10$ (m, 4H), 3.6 (m, 4H), 4.2 (m, 1H), 6.1 (s, 1H), 6.41 (d, 1H, $J = 9$ Hz), 7.5 (dd, 1H, $J = 2.1$ Hz, $J = 9$ Hz), 8.2 (d, 1H, $J = 2.1$ Hz).

$\text{C}_{10}\text{H}_{13}\text{N}_2\text{OBr}$ (257.13)	Calc.	C 46.71	H 5.10	N 10.89
	Found	C 46.71	H 5.05	N 10.86

2-methyl-4-[2-(N-2-hydroxyethyl-N-methylamino)-5-pyridyl]-3-butyn-2-ol (**7a**).

A mixture of 9g (39.0 mmol) of **5a** and 9.8g (3 equiv.) of the alkynol **6** in 50 ml of diisopropylamine was degassed and kept under nitrogen. Then the ingredients of the catalytic mixture, 69 mg of PdCl_2 (1%), 78 mg of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (1%)

and 510 mg of triphenylphosphine (5%), were added. The mixture is heated with stirring under N₂ to 84°C, after what a precipitate of diisopropylammonium bromide occurs. The reaction is complete after 3 hr. The excess amine solvent is evaporated, and the brownish residue thus obtained is flash chromatographed over silica gel (hexane-AcOEt 1/1) to get **7a** as a pale yellow powder (57%). ¹H NMR (CDCl₃): δ = 1.6(m, 6H), 2.5 (s, 1H), 3.0 (s, 3H), 3.8 (m, 4H), 4.3 (s, 1H), 6.4 (d, 1H, J = 8.8 Hz), 7.5 (dd, 1H, J = 8.8 Hz, J = 2.1 Hz), 8.0 (d, 1H, J = 2.1 Hz). C₁₃H₁₈N₂O₂ (234.3)

Calc.	C	66.64	H	7.74	N	11.96
Found	C	66.59	H	7.69	N	11.92

Similarly was obtained **7b** (70%) as yellow crystals from hexane-AcOEt; m.p. 99-100°C. ¹H NMR (CDCl₃ + DMSO d₆): δ = 1.61 (m, 6H), 2.05 (m, 4H), 2.54 (s, 1H), 3.55 (m, 4H), 4.3 (m, 1H), 6.38 (d, 1H, J = 8.8 Hz), 7.5 (dd, 1H, J = 2.24 Hz, J = 8.8 Hz), 8.15 (d, 1H, J = 2.1 Hz).

C ₁₅ H ₂₀ N ₂ O ₂ (260.34)	Calc.	C	69.20	H	7.74	N	10.76
	Found	C	69.16	H	7.70	N	10.75

The arylalkynes **8** are obtained by deprotection of the alkynols **7**. A solution of the alkynol **7a** (5.9g, 22.6 mmol) in 80 ml of dry toluene is refluxed in a Dean-Stark apparatus with 0.5g of powdered NaOH. After 25 ml of toluene is removed the deprotection is complete as seen by TLC. The reaction mixture is filtered over silica gel, evaporated to give **8a** as thick oil (66%).

¹H NMR (CDCl₃): δ = 2.04 (s, 1H), 3.08 (s, 3H), 3.75 (m, 4H), 4.5 (s, 1H), 6.45 (d, 1H, J = 8.9 Hz), 7.5 (dd, J = 2.3 Hz, J = 8.9 Hz), 8.2 (d, 1H, J = 2.1 Hz).

Similarly **8b** was obtained as a thick oil. ¹H NMR (CDCl₃): δ = 1.9 (s, 1H), 2.05 (m, 4H), 3.55 (m, 4H), 4.3 (m, 1H), 6.2 (s, 1H), 6.35 (d, 1H, J=8.8 Hz), 7.5 (dd, 1H, J=2.2 Hz, J=8.8 Hz), 8.2 (d, 1H, J = 2.2 Hz).

2-[N-(2-hydroxyethyl)-N-methylamino]-5-(4-methylsulfonylphenylethynyl)-pyridine (10a): A mixture of 1.3g of **8a** (7.3 mmol) and 1.65g of 4-bromophenylmethylsulfone **9** in 25 ml of diisopropylamine is degassed and stirred under nitrogen. Then the catalytic mixture is added (13 mg of PdCl₂, 15 mg of Cu(OAc)₂·H₂O and 97 mg of PPh₃) and the reaction flask is heated to 84°C while stirring. After 3 hrs the reaction is complete, the excess amine is removed and the solid residue is chromatographed over silica gel to give **10a** as a yellow solid (63 %). ¹H NMR (CDCl₃): δ = 3.08 (s, 3H), 3.13 (s, 3H), 3.84 (m, 4H), 4.3 (s, 1H), 6.55 (d; 1H; J=9,1 Hz), 7.65 (m, 3H), 7.9 (m, 2H), 8.28 (d, 1H, J = 1.7 Hz).

UV/VIS (DMF): λ_{max} = 356 nm.

C ₁₇ H ₁₈ N ₂ O ₃ S (330.4)	Calc.	C	61.80	H	5.49	N	8.48
	Found	C	61.79	H	5.45	N	8.41

Similarly *2-[2-(hydroxymethyl)pyrrolidinyl]-5-(4-methylsulfonylphenylethynyl)-pyridine (10b)* was obtained as yellow crystals (71%). ¹H NMR (CDCl₃) δ = 1.76 (m, 1H), 2.07 (m, 3H), 3.07 (s, 3H), 3.57 (m, 4H), 4.36 (m, 1H), 6.16 (s, 1H), 6.43 (d, 1H, J = 8.9 Hz), 7.6 (m, 3H), 7.9 (m, 2H), 8.25 (d, 1H, J = 1.8 Hz).

$C_{19}H_{20}N_2O_3S$ (356.44)	Calc.	C 64.02	H 5.66	N 7.86
	Found	C 64.02	H 5.69	N 7.59

2-[*N*-(2-methacryloyloxyethyl)-*N*-methylamino]-5-(4-methylsulfonylphenylethynyl)-pyridine (**11a**): To 1.23g (3.71 mmol) of **10a** dissolved in 60 ml of freshly distilled anhydrous toluene under N_2 atmosphere, are added 0.5ml of freshly distilled NEt_3 , then dropwise, 0.36ml of freshly distilled methacryloyl chloride. The reaction mixture is stirred at $0^\circ C$ during one hour, then allowed to stand at room temperature for one day while stirring. After evaporation of the solvent, the reaction mixture is chromatographed over silica gel, to yield the monomer **11a** that is recrystallized in ethylacetate (55%).

1H NMR ($CDCl_3$): δ = 1.92 (s, 3H), 3.07 (s, 3H), 3.15 (s, 3H), 3.94 (t, 2H, J = 5.6 Hz), 4.37 (t, 2H, J = 5.6 Hz), 5.56 (t, 1H, J = 1.6 Hz), 6.07 (s, 1H), 6.52 (d, 1H, J = 8.9 Hz), 7.62 (m, 3H), 7.9 (m, 2H), 8.34 (d, 1H, J = 1.8 Hz).

^{13}C NMR ($CDCl_3$): δ = 18, 36.7, 43.4, 62.1; 88.6, 91.9, 105.2, 126, 127.4, 128.2, 131.6, 135.7, 139.7, 139.9, 151.2, 157.6, 166.5.

UV/VIS (EtOH): λ_{max} = 349 nm.

$C_{21}H_{22}N_2O_4S$ (398.48)	Calc.	C 63.30	H 5.56	N 7.03
	Found	C 63.32	H 5.54	N 6.93

2-(2-methacryloyloxymethylpyrrolidinyl)-5-(4-methylsulfonylphenylethynyl)-pyridine (**11b**). Obtained with 49% yield as above.

1H NMR ($CDCl_3$): δ = 1.95 (s, 3H), 2.12 (m, 4H), 3.07 (s, 3H), 3.54 (m, 2H), 4.12 (m, 1H), 4.39 (m, 2H), 5.5 (d, 1H, J = 1.5 Hz), 6.11 (s, 1H), 6.5 (d, 1H, J = 8.8 Hz), 7.6 (m, 3H), 7.9 (d, 2H, J = 8.3 Hz), 8.35 (d, 1H, J = 2.1 Hz).

^{13}C NMR ($CDCl_3$): δ = 18, 22.8, 27.8, 43.4, 47.3, 55.7, 63.9, 88.6, 92, 105.4, 106.7, 126, 127.3, 128.1, 131.5, 135.7, 139.6, 139.7, 151.5, 156.1, 166.5.

UV/VIS (DMF): λ_{max} = 355 nm

$C_{23}H_{24}N_2O_4S$ (424.51)	Calc.	C 65.08	H 5.70	N 6.60
	Found	C 64.96	H 5.76	N 6.42

Synthesis of polymers

The homopolymerizations were carried out in THF solution under argon atmosphere at $60^\circ C$ in the presence of 5 mol % of AIBN for 48 hours. Precipitation occurs during polymerization. After polymerization THF was evaporated, the polymer was dissolved in DMF and precipitated in ethanol. This was repeated three times, then the solid was dried. Copolymerization was carried out under the same conditions, except that DMF was the solvent. Methacrylate monomer **11b** and methyl methacrylate were introduced in the same molar ratio.

Polymer **12**: $(C_{21}H_{22}N_2O_4S)_n$ (398.48)_n Calc. C 63.30 H 5.56 N 7.03
Found C 62.32 H 5.58 N 6.77

1H NMR ($CDCl_3$) δ = 1.3 (8H), 3.0 (4H), 3.95 (3H), 6.5 (1H), 7.55 (3H), 7.8 (2H), 8.3 (1H).

Polymer **13**: $(C_{23}H_{24}N_2O_4S)_n$ (424.51)_n Calc. C 65.08 H 5.70 N 6.60

Found C 63.22 H 5.76 N 6.01

^1H NMR (CDCl_3) δ = 1.05 (3H), 2.02 (6H), 3.04 (3H), 3.8 (5H), 6.39 (1H), 7.56 (3H), 7.82 (2H), 8.24 (1H).

Copolymer **14**, soluble in DMF, was obtained in the same manner by precipitation in ethanol.

Calc. for 50/50 molar ratio: C 64.10 H 6.15 N 5.34 O 18.30 S 6.11

Found: C 63.56 H 6.14 N 5.31 O 18.09 S 6.19

^1H NMR (CDCl_3) δ = 0.94 (6H), 1.89 (8H), 3.06 (3H), 3.85 (8H), 6.45 (1H), 7.6 (3H), 7.85 (2H), 8.3 (1H).

References

1. Ulrich DR (1988) *Mol Cryst Liq Cryst* 160: 1
2. Staring EJ (1991) *Rec Trav Chim Pays-Bas* 110: 492
3. Buckley A (1992) *Adv Mater* 4: 153
4. Williams DJ (1987) p.405 in Chemla DS, Zyss J (eds) "Nonlinear Optical Properties of Organic Molecules and Crystals", Vol.I, (Academic Press, Orlando)
5. Singer KD, Sohn JE, Lalama SJ (1986) *Appl Phys Lett* 49: 248
6. Willand CS, Williams DJ (1987) *Ber Bunsenges Phys Chem* 91: 1304
7. Stamatof J, DeMartino R, Haas D, Holland WR, Katz HE, Dirk CW, Schilling ML (1990) *Angew Makromol Chem* 183: 151
8. Jungbauer D, Teraoka I, Yoon DY, Reck B, Swalen JD, Twieg RJ, Wilson CG (1991) *J Appl Phys* 69: 8011
9. Zentel R, Jungbauer D, Twieg RJ, Yoon DY, Wilson CG (1993) *Makromol Chem* 194: 859
10. Nicoud JF, (1988) in "Nonlinear Optical Properties of Organic Materials", Khanarian G (ed), *Proc. SPIE* 971: 68
11. Stiegman AE, Graham E, Perry KJ, Khundkar LR, Cheng LT, Perry JW (1991) *J Am Chem Soc* 113: 7658
12. Barzoukas M, Fort A, Klein G, Boeglin A, Serbutoviez C, Oswald L, Nicoud JF (1991) *Chem Phys* 153: 457
13. Twieg RJ, Burland D, Lux M, Moylan C, Nguyen C, Walsh P, Wilson CG, Zentel R (1991) *Polym Preprint* 32 (3): 80
14. Zyss J, Ledoux I, Nicoud JF (1993) "Advances in Molecular Engineering for Quadratic Nonlinear Optics" in Zyss J (ed) "Molecular Optoelectronics: Materials, Physics and Devices" (Academic Press, Boston)
15. A. Ulman A, Willand CS, W. Köhler W, Robello DR, Williams DJ, Handley L (1990) *J Am Chem Soc* 112: 7083
16. Nijhuis S, Rikken GLJA, Havinga EE, Hoeve W ten, Wynberg H, Meijer EW (1990) *J Chem Soc Chem Commun* 1990: 1093
17. Tilley JW, Zawoiski S (1988) *J Org Chem* 53: 386
18. Onopchenko, ET Sabourin, Selwitz CM, (1979) *J Org Chem* 44: 1233
19. Ames DE, Bull D, Takundwa C (1983) *Synthesis* 1983: 312