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New main chain nonlinear optical polymers with high glass transition temperatures

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Summary

Various 4-methoxy-4'-carbomethoxy-α-amino-α'-cyanostilbenes were prepared as mixtures of E and Z isomers, and polymerized via condensation polymerization using dibutyltin diacetate as catalyst. The resulting low molecular weight homopolymers showed higher glass transition temperatures (168-183°C) than previously reported main chain nonlinear optical (NLO) homopolymers. A high molecular weight ($M_n \simeq 30,200$) copolymer possessed an even higher glass transition temperature of 187°C. The hyperpolarizability of the polymers and a model compound were found by EFISH measurements to be in the range of 61 to 79 x 10^{-48} esu.

Introduction

Copolymers with NLO chromophores aligned in the same direction in the main chain were first synthesized in this Laboratory.[1,2] A large density of NLO-phores can be obtained, which could lead to a material with high second order susceptibility (χ^2). Such films can also exhibit tensile and mechanical properties far superior to the side chain polymers under common study. Moreover, arranging the NLO units in head-to-tail fashion could result in large second order hyperpolarizability enhancement due to cooperative interaction of the aligned dipoles.

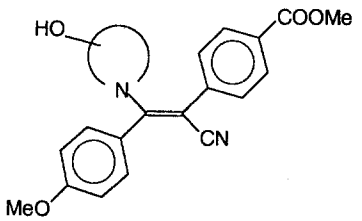
Hall and coworkers synthesized an AB copolymer of α-cyano-m-methoxy-p-(ω-oxypropoxy)-cinnamate with ω-hydroxydodecanoate.[1] This copolymer showed a twenty-fold enhancement of $\mu\beta$ in solution compared to monomeric NLO phores by EFISH measurements.[1] The tg was below room temperature, and films could only be poled at low temperatures. Enhancement was not observed in films of this copolymer, perhaps because alignment of the total main chain chromophores would be difficult due to chain entanglements.

Offsetting the desire for homopolymer so as to achieve higher dipole density is the necessity of forming tractable homopolymers. Researchers at AT&T Bell Laboratories,[4] as well as Hall and coworkers,[5,6,7] have since reported the synthesis of various other main chain chromophore homopolymers. However, these homopolymers have been soluble only in the strongest solvents which are not suitable for spin-casting films. Recently, Stenger-Smith and coworkers reported the synthesis of 4-amino-α-cyanocinnamic polyesters which were soluble in common solvents.[8]

Other important property requirements are a high glass transition temperature and optical clarity. To date, the highest glass transitions reported for homopolymers were 90°C for the cinnamic polyesters synthesized by Stenger-Smith *et al.*,[8] and 92°C in the recent work with main chain *p*-aminophenyl.sulfones by Robello *et al.*[3]

The specific objective of this research is to synthesize homopolymers containing donor/acceptor-substituted stilbenes with high glass transition temperatures. The chosen polymerizable AB stilbene structure is shown below. In general a p-methoxy- and a p-carbomethoxy-substituent form the

donor-acceptor axis, with an α-cyano substituent as an additional acceptor and the α'-amine substituent as additional donor. The latter also contains the hydroxyl function to form the polyester. Comparison of EFISH measurements of the model small molecule with the polymers will be made to establish if dipole enhancement occurred in the latter.

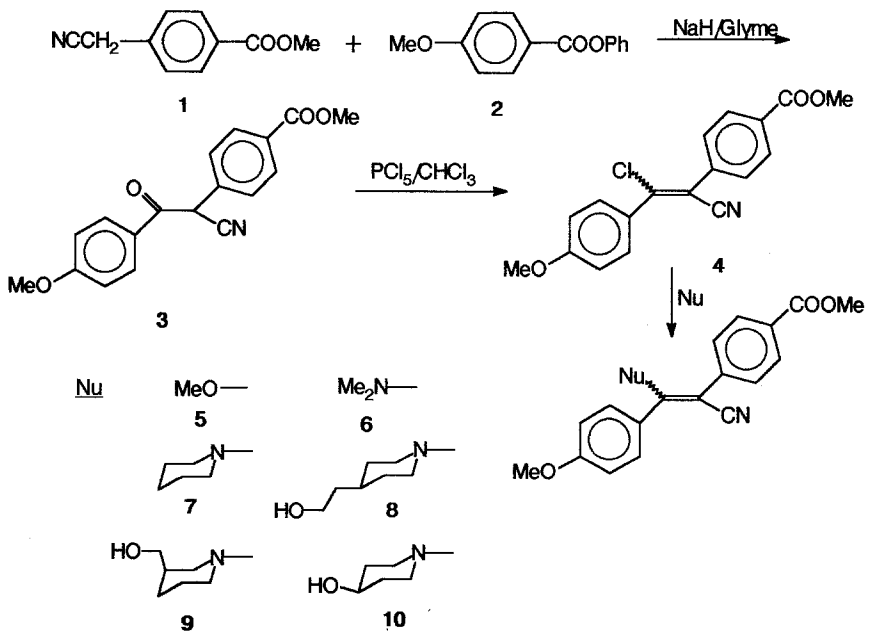


Results and Discussion

Synthesis

The synthesis of the α-amino-α'-cyanostilbene began with a crossed Claisen condensation between methyl p-cyanomethylbenzoate 1 and phenyl p-methoxybenzoate 2 as shown in Scheme 1. After acidic workup and purification a typical yield of 67% was obtained for compound 3. Phenyl ester 2 was used because of its proper reactivity; *p*-anisyl chloride was too reactive and formed the stilbene ester, and methyl *p*-anisate did not undergo the condensation.

Scheme 1



Compound 3 was converted to the α-cyano-α'-chlorostilbene 4 with phosphorus pentachloride in methylene chloride[9,10] in 73% yield. The chlorostilbene derivative 4 then became the keystone compound from which all monomers and model compounds of this series were derived.

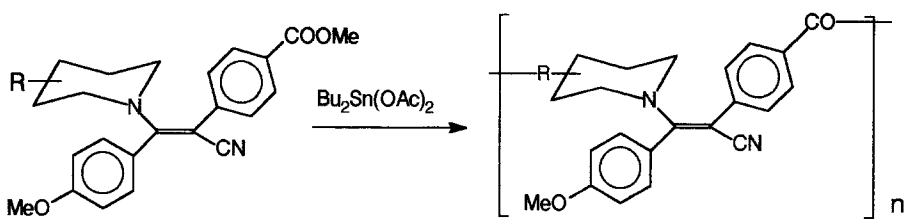
The α-cyano-α'-methoxystilbene 5 was easily prepared in 76% yield as a mixture of E and Z isomers by dissolution of 4 in sodium methoxide/methanol solution followed by reflux. The more prevalent isomer was assumed to be the more stable E isomer ("trans" stilbene). Analogous compounds prepared by Rappoport indicate that the protons on the vinylic methoxy of the Z isomer should be shifted further downfield as compared with the E isomer.[11,12] The minor isomer (C=C-OC$\underline{H}_3$, 3.69ppm) was therefore the Z isomer, and the major product (C=C-OC$\underline{H}_3$, 3.62 ppm) was the E isomer.

Compound 4 was reacted with excess dimethylamine in methylene chloride at room temperature to give the α-dimethylamino-stilbene 6 in very high yield. The product was obtained as an approximately 50/50 mixture of E and Z isomers.

The piperidine analog 7 and the monomers 8-10 were prepared by a similar method.[13] Compound 4 was refluxed in acetonitrile with 2-4 equivalents of the piperidine compounds to give the desired enamines in typical yields of 95%. Compounds 7-10 were isolated as roughly 50/50 mixtures of their E and Z isomers (determined by ^{1}H-NMR). The synthesis of the enamines could be followed very easily by TLC because the products were all bright yellow. All of the compounds synthesized were purified by either chromatography or recrystallization. The compounds were characterized by proton and carbon NMR and infrared spectroscopy.

Polymer Synthesis

The monomers (8-10) were polymerized by condensation polymerizations with loss of methanol. The catalyst, dibutyltin diacetate, was used in a concentration of 2 mole percent. The polymerizations were carried out in a neat melt, two stage polycondensation[6] at 100°C for one hour and then at 170-190°C under high vacuum (about 0.4 mmHg) for several hours. The polymers (11-13) were soluble in chloroform and were purified by precipitation in methanol. No attempt was made to maximize the molecular weights of the homopolymers.



8 R = 4-CH_2CH_2OH
9 R = 3-CH_2OH
10 R = 4-OH

11 R = 4-CH_2CH_2O-
12 R = 4-CH_2O-
13 R = 4-O-

The copolymerization between monomers 8 and 9 was carried out under conditions designed to produce high molecular weight copolymer 14. Less catalyst was used (0.3 mole percent dibutyltin diacetate) and the heating sequence consisted of three steps. The first step and second step reaction times and temperatures were similar to those used in the homopolymerizations. To help increase molecular weight a third step was added, heating at 220°C under vacuum. Copolymer of higher molecular weight was obtained in 90% yield as shown in Table I.

The polymers were purified by precipitation and characterized by proton and carbon NMR, and infrared spectroscopies, as well as differential scanning calorimetry and size exclusion chromatography. The polymerizations

Table 1. Physical and Nonlinear Optical Characteristics of NLO Polymers.

Monomer	Polymer	M_w	M_n	PDI	T_g (°C)	Yield (%)	$\mu\beta/N$ x 10^{-48}esu
8	11	6270	4860	1.3	167	80	74
9	12	6750	5190	1.3	176	72	61
10	13	4720	3960	1.2	183	43	63
8/9	14	30200	12800	2.4	187	92	79

did supply material with the physical properties that were desired; the results are listed in Table 1. All the homo- and copolymers were readily soluble in chloroform and acetone. The copolymerization was run under harsher conditions and using less catalyst and gave polymer of molecular weight 30,200. Recent work by Robello *et al.*[3] indicates that molecular weights of this magnitude may be optimal. Lower molecular weights give more brittle polymers, and higher molecular weights make it too difficult to pole the bulk polymer.[3]

All polymers showed glass transitions which were very high (above 160°C) as shown in Table I. In fact, these are the highest glass transitions reported to date for a NLO polymer with the chromophore in the main chain. The differential scanning calorimeter (DSC) characterization of polymer 13 showed decomposition exotherms above 220°C. Polymers 11, 12, and 14 were all stable to at least 300°C (the materials were not evaluated above 300°C).

EFISH Measurements

EFISH measurements made on the polymers were carried out in fresh chloroform solutions, probing at 1.9μm. The results are included in Table 1. The EFISH measurements show that all three homopolymers as well as the copolymer have approximately the same hyperpolarizability in solution. The value obtained for the monomeric dimethylamino analog 6 was 144 x 10^{-48} esu at 1.064 μm. Dispersion effects might reduce $\mu\beta$ by a factor of two. Therefore there is no apparent enhancement, as the polymers have basically the same hyperpolarizability as the monomeric model compound.

Experimental

General Methods

Melting points are corrected and determined on a Thomas Hoover melting point apparatus. Nuclear magnetic resonance spectra were recorded on a 250 MHz Bruker WM-250 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Elemental analyses were performed by Desert Analytics of Tucson, Arizona. Differential scanning calorimetry (DSC) data were collected using a Perkin-Elmer DSC-4. Molecular weights were determined by size exclusion chromatography (SEC) using a UV detector, Phenomenex SEC columns, and polystyrene standards.

Starting Materials

Methyl p-cyanomethylbenzoate 1 was synthesized according to a literature procedure[14] starting from p-toluic acid by successive bromination, esterification and substitution by cyano. Phenyl p-methoxybenzoate 2 was prepared by esterification of p-anisyl chloride in phenol/pyridine.[15]

4'-Carbomethoxy-4-methoxy-α'-cyano-α-hydroxystilbene (3) was synthesized following a literature procedure[16] and was recrystallized twice from methanol to give a 67% yield of white crystalline product. Compound 3 is a

mixture of E and Z enol isomers (mp=120-125°C). ^{1}H-NMR (d_6-DMSO) Major isomer: δ 8.0 (d, 2H), 7.92 (d, 2H), 7.65 (d, 2H), 7.08 (d, 2H), 3.84 and 3.83 (2s, 6H). Minor isomer: δ 7.75 (d, 2H), 7.25 (d, 2H), 7.11 (d, 2H), 6.90 (d, 2H), 3.79 (s, 3H), 3.75 (s, 3H). ^{13}C-NMR (d_6-DMSO) d 170.0, 166.0, 161.3, 138.3, 131.0, 130.5, 130.3, 129.4, 127.5, 127.2, 120.7, 114.0, 113.8, 87.0, 55.5, 52.1. ^{1}H-NMR ($CDCl_3$) d 7.96 (d, 2H), 7.87 (d, 2H), 7.46 (d, 2H), 6.85 (d, 2H), 5.70 (s, 1H), 3.83 (s, 3H), 3.77 (s, 3H). ^{13}C-NMR ($CDCl_3$) d 186.6, 165.9, 164.5, 135.4, 131.7, 131.6, 130.4, 128.2, 125.9, 116.3, 114.2, 55.4, 52.1, 45.7. IR (KBr) 3063, 2217, 1712, 1589, 1512, 1280 cm^{-1}. Analysis Calculated: C 69.90%, H 4.85%, N 4.53%. Found: C 69.87%, H 4.81%, N 4.44%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-chlorostilbene (4) was synthesized following the literature.[9,10]

Compound 4 was isolated as a yellow solid which contained a mixture of E and Z isomers. The product, obtained in a 73% yield, had mp=89-105°C. ^{1}H-NMR ($CDCl_3$) Major isomer: δ 7.93 (d, 2H), 7.29 (d, 2H), 7.19 (d, 2H), 6.75 (d, 2H), 3.90 (s, 3H), 3.79 (s, 3H). Minor isomer: δ 8.12 (d, 2H), 7.79 (d, 2H), 7.69 (d, 2H), 6.98 (d, 2H), 3.95 (s, 3H), 3.88 (s, 3H). ^{13}C-NMR ($CDCl_3$) δ 166, 162 and 161.6, 148.9, 138 and 137.4, 131.4 and 130.6, 130.2, 129.9 and 129.8, 129.3, 128.5 and 126.7, 118 and 117.3, 113.9, 111.5, 55.4 and 55.3, 52.2. IR (KBr) 2213, 1719, 1602, 1285, 1262, 1188 cm^{-1} Analysis Calculated: C 65.96%, H 4.31%, N 4.27%, Cl 10.82%. Found: C 65.68%, H 4.10%, N 4.15%, Cl 11.02%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-methoxystilbene (5):

Compound 4 (0.2 g, 0.6 mmole) was treated with a sodium methoxide/methanol solution following a literature procedure.[11] Compound 5 was isolated as a yellow solid, mp=104-114°C, in 76% yield. ^{1}H-NMR ($CDCl_3$) d 8.02 (d, 2H), 7.80 (d, 2H), 7.47 (d, 2H), 7.02 (d, 2H), 7.10 and 6.80 (2d from the minor isomer), 3.90 (s, 3H), 3.84 and 3.79 (s, 3H), 3.69 and 3.62 (s, 3H). ^{13}C-NMR ($CDCl_3$) δ 171.8, 166.5, 161.7, 137.0, 130.8 and 131.5, 129.7 and 129.0, 128.8, 128.0, 123.8, 119.8, 114.6 and 114.4, 94.8, 59.1, 55.5, 52.2. IR (KBr) 2958, 2204, 1712, 1279, 1251 cm-^{1}. Analysis Calculated: C 70.58%, H 5.30%, N 4.33%. Found: C 70.66%, H 5.13%, N 4.24%. Pure E isomer of 11 was obtained by recrystallization from ethanol to yield white crystals, mp=117-118°C, in a 55% recovery. ^{1}H-NMR ($CDCl_3$) δ 8.02 (d, 2H), 7.80 (d, 2H), 7.47 (d, 2H), 7.01 (d, 2H), 3.91 (s, 3H), 3.86 (s, 3H), 3.63 (s, 3H).

4'-Carbomethoxy-4-methoxy-α'-cyano-α-(N,N-dimethylamino)stilbene (6):

Compound 4 (0.2 g, 0.61 mmole) was dissolved in 1 ml of 3 M dimethylamine/methylene chloride solution at 0°C. After 2 hours 9 ml more of the 3 M dimethylamine solution was added, and the mixture was allowed to warm to room temperature. This solution was stirred overnight, and then filtered through a plug of silica gel, rinsing with acetonitrile. After evaporation of the solvent, the product was purified by chromatography (30% ethyl acetate in hexanes) to give a 90% yield of 6. Compound 6 was isolated as a mixture of E and Z isomers. The yellow solid had mp=158-160°C. ^{1}H-NMR ($CDCl_3$) δ 7.93, 7.60, 7.41, 7.19, 7.06, 6.90, 6.70 (7d, 8H), 3.84, 3.78, 3.75, 3.71 (4s, 6H), 3.06 and 2.64 (2s, 6H). ^{13}C-NMR ($CDCl_3$) δ 166.9, 166.7, 165.3, 163.5, 161.8, 161.3, 142.2, 141.7, 132.7, 132.1, 129.4, 129.0, 128.1, 127.6, 126.8, 126.1, 125.5, 123.4, 121.8, 114.1, 82.6, 80.9, 55.3, 55.2, 52.0, 51.7, 43.6, 43.1. IR (KBr) 2933, 2183, 1713, 1272 cm^{-1} Analysis Calculated: C 71.41%, H 5.99%, N 8.33%. Found: C 71.23%, H 6.03%, N 8.02%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-piperidinostilbene (7):
Compound 4 (0.20 g, 0.61 mmole) was dissolved in 1 ml of acetonitrile (anhydrous) with 0.12 g of piperidine (2.1 eq.). This solution was refluxed for 3 hours under argon. After cooling, the reaction mixture was filtered through a plug of silica gel, rinsing with acetonitrile to insure complete recovery. The solvent was then evaporated, and the product was purified by chromatography. A 90% yield of compound 7 was obtained as a mixture of E and Z isomers. The product was a yellow solid, mp=161-162°C. ^{1}H-NMR ($CDCl_3$) δ 8.02, 7.68, 7.55, 7.25, 7.18, 7.00, 6.78 (7d, 8H), 3.91, 3.86, 3.83, 3.78 (4s, 6H), 3.42 and 2.84 (2bs, 4H), 1.72 and 1.59 (2bs, 6H). ^{13}C-NMR ($CDCl_3$) δ 167.2, 167.0, 165.8, 164.0, 162.2, 161.6, 142.4, 142.0, 132.5, 131.9, 129.6, 129.1, 128.4, 128.1, 127.5, 126.9, 126.7, 125.8, 123.5, 121.9, 114.2, 83.4, 81.6, 55.4, 55.3, 52.7, 52.2, 52.0, 51.9, 26.8, 26.6, 24.0, 23.8. IR (KBr) 2932, 2181, 1709, 1276, 1251 cm^{-1} Analysis Calculated: C 73.38%, H 6.43%, N 7.44%. Found: C 72.89%, H 6.66%, N 7.12%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-(4-ethanolpiperidino)stilbene (8):
The procedure was the same as for the synthesis of compound 7: 1 g (3 mmole) of 4 and 1.2 g (3 eq.) of 4-piperidinoethanol were dissolved in 20 ml anhydrous acetonitrile under argon. The solution was refluxed for 48 hours, and then worked up as in the previous procedure. After purification by chromatography a 95% yield of yellow solid, mp=77-78°C, was obtained. Compound 8 was isolated as an approximately 50/50 mixture of the E and Z isomers. ^{1}H-NMR ($CDCl_3$) δ 7.94, 7.62, 7.47, 7.18, 7.10, 6.92, 6.72 (7d, 8H), 3.85, 3.80, 3.77, 3.67 (4s, 6H), 3.5-3.7 (m, 3H), 3.15 (bt, 1H), 2.99 (bd, 1H), 2.62 (bt, 1H), 2.02 (bs, 1H), 1.1-1.8 (m, 7H). ^{13}C-NMR ($CDCl_3$) d 166.8, 166.7, 165.1, 163.5, 161.9, 161.3, 142.2, 141.6, 132.4, 131.8, 129.4, 129.0, 128.1, 127.4, 126.8, 126.5, 125.5, 123.3, 121.8, 114.1, 83.4, 81.7, 60.2, 59.7, 55.2, 55.1, 51.9, 51.7, 51.3, 38.8, 38.7, 33.0, 32.9, 32.0, 31.7. IR (KBr) 3441, 2925, 2183, 1712, 1601, 1503, 1278, 1254, 1017 cm^{-1} Analysis Calculated: C 71.41%, H 6.71%, N 6.66%. Found: C 71.15%, H 6.71%, N 6.63%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-(3-hydroxymethylpiperidino)-stilbene (9):
The procedure was the same as for the synthesis of compound 7: 1 g (3 mmole) of 4 and 1.13 g (3.2 eq.) of 3-piperidinomethanol were dissolved in 20 ml anhydrous acetonitrile, under argon. The solution was refluxed for 48 hours, and then worked up as for compound 7. After purification by chromatography a 95% yield of yellow solid was obtained, mp=86-90°C. Compound 9 was isolated as an approximately 50/50 mixture of the E and Z isomers. ^{1}H-NMR ($CDCl_3$) δ 8.00, 7.67, 7.52, 7.24, 7.15, 6.97, 6.77 (7d, 8H), 3.91, 3.85, 3.82, 3.77 (4s, 6H), 2.9-3.6 (m, 4H), 2.4-2.7 (m, 1H), 2.14 (bs, 1H), 1.5-2.0 (m, 4H), 1.1-1.4 (m, 1H). ^{13}C-NMR ($CDCl_3$) d 166.9, 166.7, 165.4, 163.7, 161.9, 161.3, 142.1, 141.6, 132.4, 131.8, 129.5, 129.0, 128.1, 127.3, 126.9, 126.4, 125.5, 123.3, 122.2, 114.1, 83.7, 81.6, 64.9, 64.7, 55.2, 55.1, 54.9, 52.4, 51.9, 51.7, 39.8, 39.5, 26.8, 26.4, 25.7, 25.4. IR (KBr) 3447, 2933, 2184, 1713, 1601, 1508, 1433, 1278, 1253 cm^{-1} Analysis Calculated: C 70.92%, H 6.45%, N 6.89%. Found: C 70.64%, H 6.42%, N 6.64%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-(4-hydroxypiperidino)stilbene (10):
The procedure was the same as for the synthesis of compound 7: 1 g (3 mmole) of 4 and 1.0 g (3.2 eq.) of 4-hydroxypiperidine were dissolved in 20 ml anhydrous acetonitrile, under argon. The solution was refluxed for 48 hours, and then worked up as for compound 7. After purification by

chromatography a 100% yield of yellow solid, mp=93-97°C, was obtained. Compound **10** was isolated as an approximately 50/50 mixture of the E and Z isomers. ^{1}H-NMR ($CDCl_3$) δ 8.01, 7.69, 7.53, 7.26, 7.16, 6.78 (6d, 6H), 6.96-7.01 (m, 2H), 3.6-4.0 (m, 7H), 3.3 (m, 1H), 3.1 (m, 1H), 2.7 (m, 1H), 2.5 (bd, 1H), 1.5-2.1 (m, 5H). ^{13}C-NMR ($CDCl_3$) δ 166.9, 166.7, 165.1, 163.4, 162.0, 161.4, 141.9, 141.5, 132.4, 131.7, 129.6, 129.0, 128.1, 128.0, 127.4, 127.1, 126.3, 125.7, 123.2, 121.7, 114.2, 83.9, 82.4, 66.4, 66.0, 55.3, 55.2, 52.0, 51.8, 48.7, 48.3, 34.8, 34.6. IR (KBr) 3431, 2946, 2183, 1714, 1600, 1508, 1278, 1253 cm^{-1} Analysis Calculated: C 70.39%, H 6.16%, N 7.14%. Found: C 70.26%, H 6.17%, N 7.23%.

4'-Carbomethoxy-4-methoxy-α'-cyano-α-aminostilbene Polyesters (**11-13**):

A dry 10 ml conical flask was fitted with a distilling adapter and a capillary argon bubbler. The arm of the distilling adapter was connected to a three way stopcock which could be switched between a bubbler and vacuum. The monomer (**8**, **9**, or **10**; 1.2 mmole) and 6 μl (24 μmole) of dibutyltin diacetate were mixed in the flask, and the argon flowed through the mixture and apparatus. Polymerization was then allowed to occur at 100°C for 1 hour. The mixture was then heated to 170-190°C, and the pipet removed and the top of the adapter stoppered. The reaction was placed under vacuum (about 0.4 mmHg). The polymerization was allowed to proceed for 1.5-6 hours. After this time, the polymer was cooled and dissolved in 5 ml of chloroform. The polymer was precipitated into 50 ml of methanol. The product was filtered and dried under vacuum.

Poly{4'-carbo-4-methoxy-α'-cyano-α-(4-piperidinoethoxy)stilbene} (**11**):

An 80% yield of yellow polymer was obtained (see Table 1). ^{1}H-NMR ($CDCl_3$) δ 7.99 (t, 1H), 7.67 (t, 1H), 7.52 (bd, 1H), 7.1-7.3 (m, 2H), 7.00 (bd, 2H), 6.8 (m, 1H), 4.35 (bt, 2H), 3.7-4.0 (m, 4H), 3.0-3.3 (m, 2H), 2.7 (bs, 1H), 1.3-2.0 (m, 7H). ^{13}C-NMR ($CDCl_3$) δ 166.0, 165.8, 164.9, 163.2, 161.7, 161.1, 142.0, 141.5, 132.2, 131.6, 129.2, 128.7, 127.8, 127.5, 127.2, 126.7, 126.2, 125.3, 123.1, 121.5, 113.9, 83.3, 81.7, 62.0, 61.9, 55.1, 51.5, 51.0, 34.7, 32.6, 32.4, 32.1. IR (KBr) 2925, 2184, 1711, 1601, 1503, 1271 cm^{-1}.

Poly{4'-carbo-4-methoxy-α'-cyano-α-(3-piperidinomethoxy)stilbene} (**12**):

A 72% yield of yellow polymer was obtained (see Table 1). ^{1}H-NMR ($CDCl_3$) δ 6.7-8.0 (m, 8H), 1.2-4.3 (m, 14H). ^{13}C-NMR ($CDCl_3$) δ 165.8, 165.6, 165.1, 163.2, 161.8, 161.3, 142.1, 141.8, 141.5, 132.3, 131.7, 129.7, 129.3, 128.8, 127.9, 127.3, 126.5, 126.3, 126.2, 125.3, 125.0, 122.9, 121.3, 114.0, 83.5, 82.2, 65.9, 64.6, 55.2, 54.5, 54.1, 53.9, 52.2, 51.8, 36.6, 26.5, 26.3, 25.5, 25.3. IR (KBr) 2936, 2185, 1712, 1602, 1508, 1268 cm^{-1}

Poly{4'-carbo-4-methoxy-α'-cyano-α-(4-piperidinoxy)stilbene} (**13**):

A 43% yield of yellow polymer was obtained (see Table 1). ^{1}H-NMR ($CDCl_3$) d 8.0, 7.7, 7.5, 7.1-7.3, 7.0, 6.8 (7m, 8H), 5.0-5.3 (m, 1H), 2.7-3.9 (m, 7H), 1.6-2.2 (m, 4H). ^{13}C-NMR ($CDCl_3$) δ 165.3, 165.1, 165.0, 164.9, 163.3, 162.0, 161.4, 142.1, 141.5, 132.3, 131.7, 129.6, 129.0, 128.2, 127.9, 127.7, 127.5, 127.3, 126.1, 122.8, 121.5, 114.2, 69.1, 68.7, 55.2, 48.8, 48.7, 48.3, 48.0, 34.7, 31.4. IR (KBr) 3477, 2948, 2186, 1712, 1602, 1505, 1256 cm^{-1}

Poly{4'-carbo-4-methoxy-α'-cyano-α-[(4-piperidinoethanoxy) and (3-piperidinomethoxy)stilbene} copolymer (**14**):[6]

The same experimental setup was used as in the homopolymerizations. Compounds **8** (0.26 g, 0.62 mmole) and **9** (0.25 g, 0.62 mmole) were mixed with

2 μl (4 μmole) of dibutyltin diacetate. A three stage polymerization was done by first heating to 100°C for 2 hours, with an argon flow. Vacuum was applied and the sample heated at 190°C for 2.5 hours. Finally, while still under vacuum (0.4 mmHg) the sample was heated at 220°C for 2 hours. The polymer was allowed to cool under vacuum overnight. The copolymer was purified by dissolution in chloroform and precipitation into methanol. After filtration and drying the product under vacuum a 92% yield of yellow copolymer 14 was obtained (see Table 1). IR (KBr) 3441, 2931, 2186, 1711, 1602, 1537, 1503, 1267 cm^{-1}.

EFISH Measurements

Solutions were made from filtered chloroform (n=1.446, ϵ=4.81) and stored in the dark. The laser source was a hydrogen gas Raman-shifted Nd:YAG lazer with a wavelength of 1.9 μm. Polarization and intensity of the light was controlled using a half wave plate and polarizer. High voltage (6kV) pulses with a duration of 100 μ/sec applied to the cell and synchronized with timing pulses from the laser. The design of the sample cell is critical and has been discussed in great detail.[17]

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