Synthesis of Polymers Containing Second Order NLO-Active Thiophene and Thiazole Based Chromophores

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Summary: Grounding on the evidence that thiophene or thiazole rings in donor-acceptor chromophoric systems promote enhancement of charge transfer and nonlinear optical responses, in this work NLO properties have been investigated of organic polymers containing azoic chromophores based on dinitrothiophene or nitrothiazole moieties. It has been carried out the azo coupling reaction directly between a series of copolymers and diazonium salts containing the etherocyclic group at different grafting percentages.

Keywords: NLO; polymers; thiazole; thiophene

Introduction

During the past decade, heteroaromatic compounds have attracted widespread interest because it was experimentally[1,3] and theoretically[4,5] demonstrated that they increase the second-order molecular NLO properties of push-pull chromophores respect to the corresponding aryl analogues. In fact, since the delocalization energy of heteroaromatics, such as thiophene or thiazole, is lower than that of benzene, their presence in push-pull chromophores is expected to result in enhanced charge-transfer properties and NLO responses, in comparison with related systems containing benzenoid rings. Thus, one of the most recent approaches to the design of highly NLO-active systems is based on the presence of a five-membered heterocyclic ring in a push-pull donor-acceptor chromophore.

Moreover, heterocyclic based chromophores appear to be more easily processable compared with more extended conjugated compounds containing benzenoid rings, which are often insoluble in most common organic solvents. Accordingly, recent trends[3] in tailoring second order NLO materials deal with push-pull chromophores with relatively short conjugated paths containing heterocycles.

In the present paper we report the synthesis and characterization, including EFISH measurements, of two functionalised chromophores which can be incorporated in polymeric backbones. The chromophores have a nitro-thiazole or a dinitro-thiophene acceptor group and a substituted amino-benzene donor group linked by a conjugated system containing one azo-bridge.

We also prepared a series of new NLO active side-chain polymers, containing thiophene or thiazole-based chromophores, by using a "post-azo coupling" reaction[6] on the amino-benzenic unit of different co-polyacrylates and/or polymethacrylates. In this case the post-functionalization method of preformed polymeric backbones proved to be more effective than the common synthetic methods for preparation of NLO addition polymers from functionalized vinylic monomers. The easiness and repro-

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ducibility of the synthesis are the major advantages of the adopted procedure.

Experimental Section

Materials and Instruments

The structures of chromophores and intermediates were confirmed by ^{1}H-NMR. The spectra were recorded using Varian Spectrometers operating at 200 MHz and 300 MHz. Optical observation were performed by using a Zeiss Axioscop polarizing microscope equipped with FP90 Mettler temperature heating stage. Phase transition temperatures and enthalpies were measured using a DSC scanning calorimeter Perkin Elmer Pyris with a scanning rate of 10 °C/min, under nitrogen flow. UV-Vis absorption spectra were recorded at room temperature by use of a Jasco V-560 Spectrophotometer. Thermogravimetric analysis were performed in air by a TA Instruments SDT 2960 Simultaneous DTA-TGA. Inherent viscosities of N,N-dimethylformamide solutions (0.500g/dL) of polymers at 25.00 °C were measured using an Ubbelohde viscosimeter.

The molecular quadratic optical non linearities of the chromophores **C1(b)** and **C2(b)** (see Figure 1) were experimentally determined by the EFISH[7] technique, especially suited for rod-like push-pull molecules in solution. The set-up allows the determination of the scalar $\mu\beta$ product where μ is the dipole moment and β the vector part of the quadratic hyperpolarizability tensor. The measurements were performed at 1.907 μm and calibrated relative to a quartz wedge whose quadratic susceptibility $d_{11} = 1.2\ 10^{-9}$ esu at 1.064 μm was extrapolated to $1.1\ 10^{-9}$ esu at 1.907 μm. The $\mu\beta(0)$ values, where $\beta(0)$ is the static quadratic hyperpolarizability, were calculated by using a simple dispersion relationship in the two-level approximation, and are reported in Table 3.

Synthesis of the Chromophores C1(a, b) and C2(a, b)

The starting aniline derivatives 2-(N,N′-methylphenylamino)ethylester of 2-propenoic and 2-methyl propenoic acid have been previously described.[8,9]

The four chromophores (Figure 1) have been obtained by the same general procedure. As an example the synthesis of **C1(b)** is described.

To the solution of 1.00g of commercial (95%) 2-amino-3,5-dinitrothiofene in 10 mL of acetic acid, cooled in an ice bath and stirred, 0.7 mL of 40% nitrosyl sulphuric acid are added dropwise. The color of the mixture changes from yellow to reddish brown. After 10 minutes stirring 1.08g of the acrylic aniline derivative dissolved in 10mL of dry THF are added dropwise at 4 °C. An intense blue color is observed immediately.

The reaction mixture is poored in cold water and the crude product precipitates as a gummy black "tar" which is separated by filtration. The precipitate is dissolved in chloroform. Addition of hexane affords a

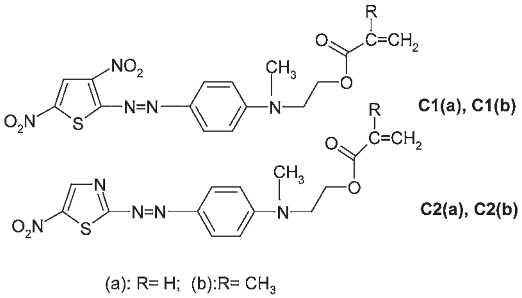

Figure 1.

black solid. This is dissolved in a minimum amount of acetone and the solution is adsorbed on about 3g of florisil 100–200 mesh. The solvent is removed by mild warming in an oven, and the solid is layered on the top of a column containing about 200g of florisil 100–200 mesh. Elution with chloroform affords first a yellowish red fraction, and then the blue fractions containing the product. This is recovered by concentrating the blue solution to a small volume (about 10 mL) and adding hexane as black crystals whose melting was also observed by optical microscopy.

1H-NMR data for the chromofores are reported below:

C1(a): δ_H (200 MHz; $CDCl_3$: Me_4Si) 1.56 (3H, s), 3.25 (3H, s), 3.87 (2H, t, *J* 6.0), 4.44 (2H, t, *J* 5.7), 5.87 (1H, dd, *J* 17.2, *J* 1.4), 6.01 (1H, dd, *J* 10.8, *J* 6.6), 6.44 (1H, dd, *J* 10.5, *J* 1.6), 6.88 (2H, d, *J* 9.2); 7.97 (2H, d, *J* 9.1), 8.36 (1H, s).

C1(b): δ_H (200 MHz; $CDCl_3$: Me_4Si) 1.91 (3H, s), 3.26 (3H, s), 3.88 (2H, t, *J* 5.8), 4.43 (2H, t, *J* 5.7), 5.59 (1H, d, *J* 1.1), 6.07 (1H, d, *J* 1.2), 6.87 (2H, d, *J* 9.3), 7.97 (2H, d, *J* 9.6), 8.36 (1H, s).

C2(a): δ_H (200 MHz; $CDCl_3$: Me_4Si) 2.16 (3H, s), 3.22 (3H, s), 3.84 (2H, t, *J* 6.0), 4.44 (2H, t, *J* 5.8), 5.84 (1H, dd, *J* 18, *J* 1.4), 6.00 (1H, dd, *J* 10.6, *J* 6.4), 6.40 (1H, dd, *J* 10.1, *J* 1.4), 6.84 (2H, d, *J* 9.3); 7.95 (2H, d, *J* 9.2), 8.60 (1H, s).

C2(b): δ_H (200 MHz; $CDCl_3$: Me_4Si) 1.87 (3H, s), 3.35 (3H, s), 4.06 (2H, t, *J* 6.0), 4.47 (2H, t, *J* 5.7), 5.61 (1H, d, *J* 1.1), 6.03 (1H, d, *J* 1.2), 7.11 (2H, d, *J* 9.3), 7.93 (2H, d, *J* 9.6), 8.69 (1H, s).

On the same sample of **C1(b)** employed in EFISH measurements elemental analysis was performed. This was in good agreement with the theoretical composition: calc: C = 48.68%, H = 4.08%, N = 16.99%; S = 7.64%; experim: C = 48.31%, H = 4.18%, N = 16.75%; S = 8.34%.

Synthesis of the Pre-Polymers

The same type of procedure was used for the three pre-polymers (see Figure 2). As an example, synthetic details for **P1** are given. In a vial are added 2.000g of methylmethacrylate, 1.024g of 2-(N,N′-methylphenylamino)ethylester of 2-propenoic acid and 0.060g of α,α'-azoisobutyronitrile (AIBN) to 3mL of dry N,N′-dimethylformamide (DMF). After three cycles of freeze-and-thaw the vial is sealed and kept 24 hours at 70 °C. After cooling, the gummy whitish polymer is precipitated by addition of methanol. The crude product is dissolved in dichloromethane and precipitated with hexane two times, and finally washed three times with hexane and dried at 70 °C. Yield 80%.

The characterization of the pre-polymers was made by DSC, DTA-TGA analysis, ^{1}H-NMR and UV-Vis spectra and viscosity measurements (see Table 4 below).

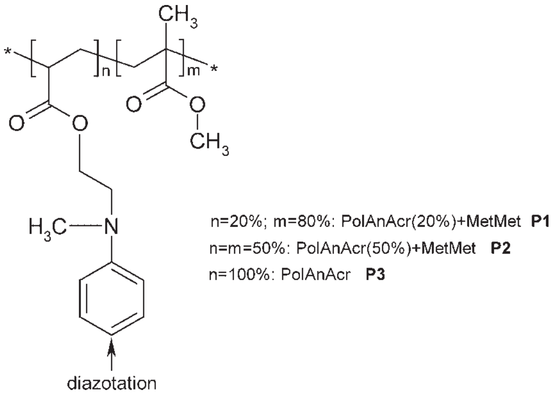

Figure 2.

Synthesis of the Polymers P1-3 (x%)

The synthesis of polymers **P1-3 (x%)** was attained by the same general procedure. As an example, the detailed preparation of polymer **P1 (6%)** is reported.

In 8 mL of acetic acid commercial (95%) 0.760g of 2-amino-3, 5-dinitrothiophene is dissolved. After cooling in an ice bath 0.5 mL of a solution of nitrosyl sulfuric acid (40% in sulfuric acid) are added dropwise under stirring, while the colour of the solution shifts from yellow to brownish red. After 10 minutes stirring the solution is added slowly with stirring to a cold (5 °C) solution of 2.42g of **P1** in 80 mL of a mixture (1:1 by volume) of dry tetrahydrofurane (THF) and dry DMF (only DMF for **P3(x%)** samples) The colour shifts further to deep blue. After 15 min the polymer is precipitated by addition of ethanol (ethanol/water 1:1 for **P3(x%)** samples). The solid is recovered by filtration, it is dissolved in a minimum amount of DMF and precipitated with water, then washed with ethanol. After drying at 40 °C a 70% yield is determined.

The characterization of the polymers was made by DSC, DTA-TGA analysis, ^{1}H-NMR and UV-Vis spectra and viscosity measurements (see Table 4 below).

Results and Discussion

The synthesis and characterization of chromophores **C1(a)** and **C2(a)** in Figure 1 including EFISH measurement, have been obtained in the present investigation.

The two chromophores are acryl derivatives and have a nitro-thiazole or a dinitro-thiophene acceptor group and a substituted amino-benzene donor group, linked by a conjugated system made up of one azo-bridge. Two analogous chromophores i.e. **C1(b)** and **C2(b)**, respectively the methacryl derivatives, have also been prepared by strictly similar procedures. The attainment chromophores of the type of **C1** and **C2** has been already reported in literature,[10,11] where the synthesis of substituted thiazole or thiophene chromophoric compounds with diazo linkages was reported. We have followed a different pathway of synthesis respect to the one previously described and here we report on thermo-chemical and optical characterization of the new chromophores **C1-2**.

It has been observed that the presence of the heterocyclic ring in **C1-2** increases the hyperpolarizability coefficient, affording $\mu\beta$ values ca. triplicated respect to those pertaining to benzenoid chromofores of analogous structure. Moreover, $\mu\beta$ values are near the value attained by chromophores including three benzene rings and two azo bridges (of best performance to date). Since the last ones display lower solubility in organic solvents than **C1-2**, and require more cumbersome synthesis, two advantages appear to be related to the use of the chromophores here investigated. Finally, we note that although azo chromophores have been widely investigated, up to now chromophores with heteroaromatic rings have been mainly employed in guest-host systems, while very few examples of main-chain and side-chain polymers have been reported.

The four chromophores C1(a, b) and C2(a, b) are crystalline, greenish gray solids, affording blue (C1) or violet (C2) solutions in chloroform. The DSC curves show the endothermic signals related to melting. Thermodynamic data are reported in Table 1.

All the compounds undergo thermal polymerization as indicated by a broad esothermic signal above 220 °C, related to the reaction of the double bond. Decomposition occurs together with thermal

Table 1.
Thermodynamic data for the chromophores.

Sample	T_m(°C)	ΔH(J/g)	T_{dec}(°C)[a]
C1(a)	135.8[b]; 158.5	31.6; 48.9	222
C1(b)	175.2	93.9	225
C2(a)	120.1	75.8	205
C2(b)	188.3	97.5	210

[a] Decomposition temperature, calculated as the 5% weight loss temperature.

[b] Solid-solid transition temperature.

Table 2.
UV-Vis data for model chromophores.

Sample	*Solvent*	μ (D)[a]	λ_{max} (nm)[b]	ε(L/cm · mol)[c]
C1(b)	Chloroform	1.01	611	43500
	Acetone	2.88	623	47600
	N,N-Dimethylformamide	3.82	645	52600
C2(b)	Chloroform	1.01	557	41100
	Acetone	2.88	565	43600
	N,N-Dimethylformamide	3.82	584	49200

[a] Solvent dipole moment by Handbook of Chemistry and Physics, 59TH Edition, CRC Press, Inc.
[b] Wavelength of UV-VIS absorbance maximum.
[c] Molar absorbance coefficient.

polymerization, as confirmed by thermogravimetrical analysis.

^{1}H-NMR spectra give evidence of high purity of the produced chromophores. Relevant features of the spectra are the singlet at 8.36 ppm pertaining to the thiophene proton and the singlet at 8.68 ppm due to the thiazole proton. These distinct signals can be separately integrated and allow to assess both the copulation reaction advancement and the percent of chromophore contained in the chain after the diazotization step.

The last evaluation can be performed also by UV-Visible spectroscopy, as discussed below. UV-Visible data of the chromophores in solvents with different polarity (see Table 2) show the existence of a relevant solvatochromic shift as well as low levels of optical absorption at some typical operating wavelengths.

EFISH values of μβ for the model chromophores are reported in Table 3. Comparison with related reported data[5,12] shows that our chromophores are characterized by generally higher μβ values.

The well known method of radical polymerization, applied for 48 hours to the mixture of **C1(b)** or **C2(b)** and methyl methacrylate, has afforded mixtures of monomers and oligomers. Thus, we adopted a different procedure to prepare NLO active polymers containing the above monomers. At first, three ‘‘pre-polymers’’ have been obtained by reacting the suited N-ethanolaniline bearing an acrylic group and methyl methacrylate (see formulas in Figure 2).

Table 3.
NLO properties of two model chromophores.

	$\mu_g\beta/10^{-48}$ esu[a]	$\mu_g\beta(0)/10^{-48}$ esu[b]
C1(b)	2180	1345
C2(b)	1825	1299

[a] Measured by EFISH technique in chloroform solutions at 1.907 μm.
[b] Extrapolated to zero frequency by the two level model.

Subsequently the pre-polymer was coupled to the diazotized dinitroaminothiophene or nitroaminothiazole moieties.

Thus, according to this procedure, the pre-polymer **P3**, i.e. the homopolymer derived from the 2-(methylphenylamino)ethyl ester-2-propenoic acid alone, and the pre-polymers **P1** and **P2**, copolymers of the aniline and methyl methacrylate including respectively 20% and 50% of the first reagent, were prepared. Data concerning the composition of the copolymers **P1-2** are reported in Table 4.

The subsequent addition of the suited diazonium salt led to the attainment ‘‘in situ’’ of the chromophores, and thus to the wanted polymers, indicated below as Pn-Cm(x%), where Pn is the pre-polymer and x% is the weight percent content of chromophore in the polymer.

The most profitable features of the adopted procedure can be shortly noted: i) easiness and promptness of the ‘‘post-coupling’’ reaction, ii) direct availability of characterization data of the pre-polymers, making easier the control of molecular weight. In fact, as indicated by viscosity values, these attain fairly high values; iii)

Table 4.
Composition of the pre-polymers **P1** and **P2**.

	Theorical composition[a)]	Experimental composition[b)]
P1	20% AnAcr-80% MetMet	19% AnAcr-81% MetMet
P2	50% AnAcr-50% MetMet	48% AnAcr-52% MetMet

[a)] Expected molar fraction of each monomer.
[b)] Experimental molar fraction calculated from ^{1}H-NMR data.

good chance of regulating the chromophore content within a fairly ample range and tuning relevant properties (as glass transition temperature).

In Table 5 it is reported the content of chromophore achieved for the homopolymer and the two copolymers.

The evaluation of the chromophore content was obtained by the comparison of the UV-Visible absorbance registered on solutions of known concentration of the polymers in chloroform with that displayed from the chromophore, as well as by the comparison of the intensity of the ^{1}H-NMR signal of the heterocycle proton with the total intensity of the aromatic signals. We wish also to note that on comparison of inherent viscosities of pre-polymers with the corresponding coupled compounds it is observed a general increase of viscosity, more consistent for higher chromophore content (Table 5)

DSC analysis results are shown in Table 5. It is found that T_g values are higher for the polymers than for the pre-polymers. This increase is related to the type of pre-polymer and, within the range of the attained chromophore content (up to 12% molar fraction, i.e. ca. 30% weight percent) the increase is more relevant for higher chromophore insertion.

The three pre-polymers are amorphous, with high decomposition temperature. The high glass transition (more than 110 °C) of the polymers **P2(x%)** e **P3(x%)** prompts potential applicative interest on these materials. This interest stems also from the consideration that the high weight percent of chromophore (respectively ca. 30% and 20%) supports the expectation of a relevant NLO activity. It is to note that for guest-host systems the typical chromophore content does not exceed 10% by weight.

A few preliminary attempts to obtain thin layers on glass of **P1-C1(6%)** e **P2-C1(12%)** have been carried out by spin-coating technique. To this purpose solutions (5% by weight) of the polymers have

Table 5.
More relevant data for the pre-polymers and the polymers.

Polymer	Reaction ratio[a)]	X(%)[b)]	T_g(°C)[c)]	T_{dec}(°C)[d)]	η_{inh}(g/dL)[e)]
P1	0	0	35	255	0.18
P1-C1(x%)	1	6	77	238	0.20
	2	11	85	232	0.27
P1-C2(x%)	1	6	95	240	0.20
	2	10	103	236	0.22
P2	0	0	29	252	0.26
P2-C1(x%)	1	13	115	239	0.29
P2-C2(x%)	1	14	134	236	0.22
P3	0	0	13	255	0.20
P3-C1(x%)	1	13	120	230	0.23
P3-C2(x%)	1	13	140	224	0.29

[a)] Molar ratio diazonium salt/aniline in the reacting system.
[b)] Molar fraction of chromophore in the polymer, calculated from UV-VIS and ^{1}H-NMR data.
[c)] Glass transition temperature.
[d)] Decomposition temperature, calculated as the 5% weight loss temperature.
[e)] Inherent viscosity measured at 25.00 °C and C = 0.500g/dL.

been obtained by use of N,N dimethylformamide. Removal of the solvent at 70 °C afforded thin, homogeneous and isotropic films.

Conclusions

This study, as previous ones in this field, grounds on the high second order NLO activity displayed by chromophores including thiophene or thiazole moieties. The polymers here described are easily prepared by coupling of a preformed polymer with the suited diazonium heterocycle derivative. They reveal higher NLO activity, solubility and stability than the common chromophores including two benzenoid rings, thus deserving potential interest for applications.

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