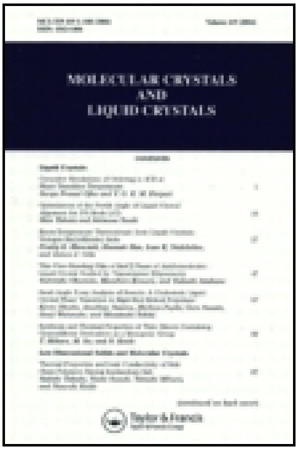


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Azo Chromophore Functionalized Polythiophenes. Synthesis and Nonlinear Optical Properties

Malgorzata Zagórska [a] , Torsten Gase [b] , François Kajzar [b] , Paul Raimond [b] , Irena Kulszewicz-Bajer [a] & Adam Pron [a]

[a] Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warszawa, Poland

[b] LETI- Technologies Avancees, DEIN/SPE/GCO, CEA Saclay, 98191 Gif-Sur-Yvette, Cedex, France

Version of record first published: 24 Sep 2006

To cite this article: Malgorzata Zagórska, Torsten Gase, François Kajzar, Paul Raimond, Irena Kulszewicz-Bajer & Adam Pron (2000): Azo Chromophore Functionalized Polythiophenes. Synthesis and Nonlinear Optical Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 354:1, 493-501

To link to this article: http://dx.doi.org/10.1080/10587250008023643

*Mol. Cryst. and Liq. Cryst.*, 2000, Vol. 354, pp. 493-501
Reprints available directly from the publisher
Photocopying permitted by license only

# Azo Chromophore Functionalized Polythiophenes. Synthesis and Nonlinear Optical Properties

MALGORZATA ZAGÓRSKA[a], TORSTEN GASE[b],
FRANÇOIS KAJZAR[b], PAUL RAIMOND[b],
IRENA KULSZEWICZ-BAJER[a] and ADAM PRON[a]

[a]*Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00–664 Warszawa, Poland and* [b]*LETI- Technologies Avancees, DEIN/SPE/GCO, CEA Saclay, 98191 Gif-Sur-Yvette, Cedex, France*

New polythiophene derivatives containing azo dye side group were prepared via copolymerization of 3-alkylthiophenes and Disperse Red 1 substituted thiophenes. The presence of chromophore groups in the polymers was confirmed by NMR and FTIR spectroscopies as well as by elemental analysis. The obtained soluble polymers were processed into thin films by spin coating technique and their nonlinear optical properties were studied by the optical second harmonic generation technique and by quadratic electro-optic Kerr effect. The second order nonlinear optical coefficients are : $d_{sp} = 6.8$ pm/V and $d_{pp} = 28.3$ pm/V at 1064 nm fundamental wavelength. The quadratic electro-optic Kerr coefficient is about three times larger for the unfunctionalized polymer than for unfoncionalized.

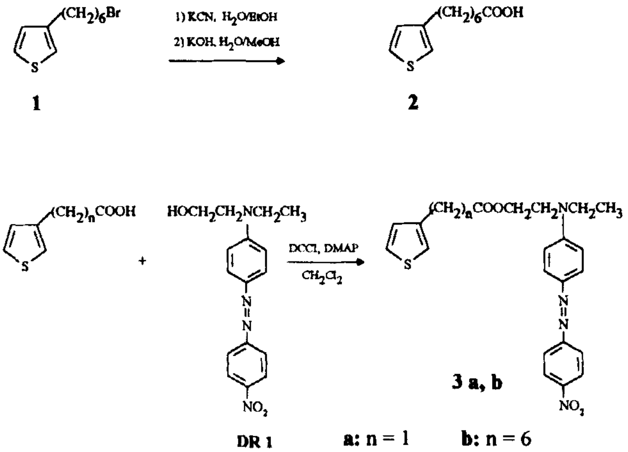
*Keywords:* functionalized polythiophenes; poly(3-alkylthiophenes); nonlinear optical properties; second harmonic generation; quadratic Kerr effect

## INTRODUCTION

Polythiophenes can be functionalized giving new materials which combine physical properties characteristic of polyconjugated backbone with specific properties of a substituent.

In addition to peculiar electrochemical and transport properties, polyconjugated systems exhibit interesting third order non-linear optical behaviour. From this point of view it is interesting to functionalize polythiophene with an appropriate second order NLO chromophore. Such functionalization allows to combine second and third order NLO properties in one material.

4-nitro-4'-(N-ethyl-N-2-hydroxyethyl)aminoazobenzene, known as Dispersed Red 1 (DR1), is one of NLO chromophores most frequently attached to classical polymers. In this communication we report the preparation of Disperse Red 1 functionalized polythiophenes (scheme 1).



*Scheme 1*

## EXPERIMENTAL

### Synthesis of monomers

The synthesis of Disperse Red 1 functionalized thiophenes is depicted in Scheme 1. ω-Bromohexylthiophene (**1**) and 7-(thienyl-3-yl)heptanoic acid (**2**) were prepared according to the method of Baüerle et al [1][2].

Monomers **3** were obtained from 3-thiopheneacetic acid (**3a**) or (7-(thienyl-3-yl)heptanoic acid (**3b**) in the estrification reaction with DR1, in the presence of dicyclohexylcarbodiimide (DCCI) and a catalytic amount of dimethylaminopyridine (DMAP).

### Synthesis of copolymers of 3-alkylthiophenes with monomer 3

The polymerization process was carried out in the presence of $FeCl_3$ in the mixture of chloroform and nitromethane (7:1 v/v). DR functionalized thiophenes were copolymerized with 3-alkylthiophenes, where alkyl group was butyl, octyl or decyl.

More synthetic details have been given elsewhere [3].

## RESULTS

### Characterization of the obtained polymers

All obtained copolymers are partially soluble in such organic solvents as chloroform or toluene. The solubility of the product depends on the length of alkyl group. The insoluble part of the polymer is always enriched in Disperse Red substituted thiophene units as compared to the soluble fraction.

The ratio of 3-DR-2,5-thienylene units to 3-alkyl-2,5-thienylene units in $CHCl_3$ fraction varies from 1:5 to 1:13 depending on slight differences in the copolymerization procedure and on the alkyl substituent size. The composition of the copolymers can be determined from the analytically measured N/S ratio.

Spectral features of the ester derivative of DR are clearly seen in the FTIR spectrum of copolymers, in particular the band at 1740 $cm^{-1}$, which can be ascribed to C=O stretching. In the region of 2000 - 600 $cm^{-1}$ the bands originating from the chromophore dominate the spectrum (1600, 1515, 1387, 1338, 1135, 824 $cm^{-1}$). The copolymerization process is manifested by the disappearance of the band at 768 $cm^{-1}$ which is characteristic of C-H deformation in monosubstituted thiophene ring.

$^1$H NMR spectra of the copolymers show following lines corresponding to the protons of the chromophore: 1.19 ppm ($-CH_3$), 3.44 ppm ($-CH_2-CH_3$), 3.68 ppm ($-CH_2-N$), 3.84 ppm ($CH_2-COO-$), 4.34 ppm ($-O-CH_2-$), 6.73, 7.85 and 8.28 ppm (protons of phenylene groups). The integration of the lines originating from the protons of DR substituent and the lines corresponding to the alkyl group in the co-monomer confirms the composition of the polymer, which has been determined from the elemental analysis.

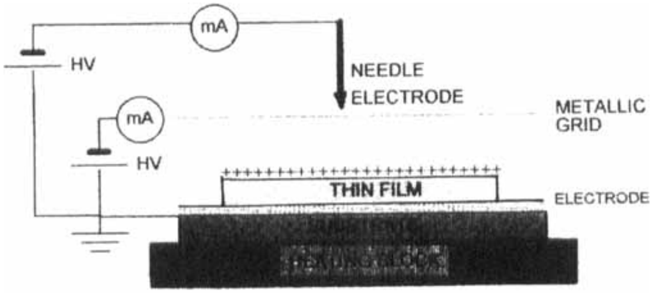


Fig. 1. Schematic presentation of the corona poling apparatus.

Thin films were prepared on glass substrates by spinning technique from polymer solution inchloroform. The chromophore orientation was performed by corona discharge technique made in air. The needle electrode, made from tungsten, was located about 2 cm from the thin film surface. The metallic grid (cf. Fig. 1 ) placed between the discharge needle and the thin film surface allows a control of the poling current and homogenization of poling. A corona voltage of 6kV was applied. The film with substrate is put on a heating element and then heated to the polymer glass transition temperature. In order to determine the time necessary to orient chromophores some of the SHG experiments were performed *in situ*. Due to the relatively low glass transition temperature of these polymers and high rotational mobility of chromophores a saturation in SHG signal was observed after 2-3 minutes. The chromophore orientation was frozen by cooling thin film under the applied poling field to the glass transition temperature.

## NONLINEAR OPTICAL PROPERTIES

### Second harmonic generation

Second harmonic generation were performed using a Q switched Nd:YAG laser operating at 1064 nm fundamental wavelength with 13 ns pulse duration and 10 pps repetition rate. The film on glass substrate was mounted on a rotation stage between two crossed polarizers. As for poled thin films there are two nenzero d tensor components: the off diagonal $d_{sp}$ and the diagonal $d_{pp}$ ones, they were determined by doing SHG experiments in two different fundamental - harmonic beam polarization configurations: s-p and p-p. In the first case one determine directly the $d_{sp}$ component, whereas the second configuration allows determination of $d_{pp}$ component injecting into corresponding formulas the value obtained for $d_{sp}$ (for details see e.g. ref. [4]). The SHG intensities were calibrated by SHG measurements on an y-cut a-quartz single crystal slab, done at the same conditions. Using for quartz the value d = 0.5 pm/V, as determined by Choy and Byer [5] we have obtained $d_{sp}$ = 6.8 pm/V and $d_{pp}$ = 28.3 pm/V. These values are quite reasonable for these low charged in active chromophore polymer films. They are underestimated due to the observed fast decay of the induced noncentrosymetry in this polymer.

### Quadratic electro-optic measurements

The third-order NLO properties of polymer solutions were studied by the quadratic Kerr effect in toluene solutions. The correspondence between the square of the applied electrical field and the difference of the achieved refractive index changes $\Delta n_\perp$ and $\Delta n_{||}$ parallel and perpendicular to the plane of incidence, respectively, to the applied electrical field is expressed by the Kerr constant B with

$$B = (\Delta n_\perp - \Delta n_{//})\frac{E^2}{\lambda}. \qquad (1)$$

The achieved phase shift $\partial\Phi$ of the light traveling between electrodes of the length l is then

$$\partial\Phi = \Delta k l = \frac{2\pi}{\lambda} l(\Delta n_\perp - \Delta n_{||}) = 2\pi l B E^2. \qquad (2)$$

Here, k is the wavenumber. For many applications it is convenient to apply an ac electrical field with $E(t) = E_\sim \sin(\omega t)$, where $E_\sim$ is the amplitude and $\omega$ is the circular frequency we get a phase shift of

$$\partial\Phi = 2\pi l B[\frac{1}{2}E_\sim^2 - \frac{1}{2}E_\sim^2\cos 2\omega t]. \qquad (3)$$

That means, beside a time independent phase shift, there exists a phase shift at the frequency $2\omega$.

The apparatus for measuring the quadratic electro-optic Kerr effect consists on set of two parallel electrodes, with space between filled with measured compound and placed between crossed polarizers. The axis of the polarizer and the orthogonal analyzer are set at $\pi/4$ with respect to the electrodes so that the electric field is at $\pi/4$ with respect to both the polarizer and the analyzer. The intensity of the light going through the set up is detect by a Si-photodiode connected to a current-voltage converter. In front of the photodiode a monochromator is placed to avoid the influence of disturbing light. The optical signal S behind the crossed polarizer is given by

$$G=\frac{n^2\sqrt{1-\frac{\sin^2}{n^2}\arcsin\left(\frac{\sin\beta}{n_g}\right)}}{n} \tag{8}$$

where $n_g$ is the refractive index of the used glass and β is the angle of incidence on the glass plate. So, we get for B in the case of parallel glass plates

$$B=\frac{G}{\pi}\frac{S_{\sim}}{S_{=}}\left(\frac{d}{U^2}\right). \tag{9}$$

For our measurements we used two glass sheds that where covered by a ~ 50 nm thick Indium Tin Oxide (ITO) - layer. The distance between these two glass sheds was 20 μm. The measurements were carried out as described above.

The quadratic electro-optic Kerr constant B was measured for pure poly(3-octylthiophene) and for poly(3-octylthiophene) functionalized with Disperse Red 1 (P(OT-co.-DRT)). In both cases the polymer concentration was 22 g/l with toluene as solvent. As already mentioned, the measurements were carried out at the wavelength λ = 632.8 nm. The applied AC-voltage was $V_{\sim}$ = 7.5 V and the DC signal of the photo diode was $S_{=}$ = 1V. The results, in function of the frequency of modulating field, are shown in Fig. 2. For both polymers one observes very high quadratic-electro-optic Kerr coefficient B, about one order of magnitude larger than for the reference material which is nitrobenzene (B = 4.4 pm/$V^2$ [7]). This is obviously purely rotational part. What is interesting is that for the fonctionalized polymer the quadratic-electro-optic Kerr coefficient B is about 3 times larger than for the unfonctionalized one. This is presumably due to the large rotational mobility of DR 1 chromophore. It corroborates very well with the high gain obtained with photorefractive structures based on these two polymers [8]. Indeed the exponential gain coefficient Γ for the functionalized polymers is about 3 times larger than for the second one (Γ = 2600 $cm^{-1}$ [8] and Γ = 1000 $cm^{-1}$ [9], respectively).

## DISCUSSION

We have synthesized a new, soluble and processable polymer which shows interesting second and third-order NLO properties. This polymer can be processed into good optical quality thin films and the attached chromophores can be oriented by the applied static field. With polymers charged at 10% mol of DR 1 we obtain the second-order NLO susceptibilities of $d_{sp}$ = 6.8 pm/V and $d_{pp}$ = 28.3 pm/V.

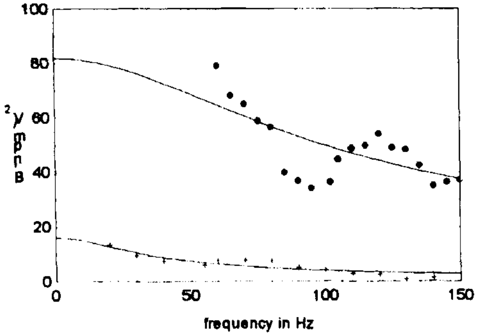


Fig. 2. Frequency dependence of the Kerr constant of two different polymers. ● P(OT-co.-DR) (22 g/l in Toluene); + POT (22g/l in Toluene).

The polymer solutions show also interesting third order NLO properties which were studied by the quadratic electro-optic Kerr effect. The low frequency Kerre constant fo 22 g/l polymer solution is about one order of magnitude larger than those for the référence material - nitrobenzene. Also the functionalized polymer exhibit about 3 times larger response than the unfonctionalized one. The measured frequency variation of the Kerr constant B values was fitted with a Lorentz function and the the following results were obtained.

For poly(3-octylthiophene) :

$$B / (\mathrm{pm} / V^2) = 16 / \sqrt{1 + (2 \times 0.0191 \times f / (\mathrm{Hz}))^2} \qquad (12)$$

For poly(3-octylthiophene) functionalized with DR 1.

$$B / (\mathrm{pm} / V^2) = 103 / \sqrt{1 + (2 \times 0.00946 \times f / (\mathrm{Hz}))^2} \qquad (13)$$

The cut-off frequency is $f_{co}$=52.3 Hz and $f_{co}$=105.7 Hz for POT and P(OT-co.-DRT), respectively. These low frequency response is most likely due to the intramolecular motions of the polymer backobones, as observed in gels of polydiacetylene [9]. The larger response in the case of functionalized polymer may be attributed to high rotational mobility of the attached chromophore.

## References

[1] P. Baüerle, F. Wurthner, and S. Heid, *Angew. Chem.*, **29**, 419 (1990).

[2] P. Baüerle, M. Hiller, S. Scheib, M. Sokolowski, and E. Umbach, *Adv. Mater.*, **8**, 214 (1996).

[3] M. Zagórska, I. Kulszewicz-Bajer, A. Proñ, J. Sukiennik, P. Raimond, F. Kajzar, A.-J. Attias, and M. £apkowski, *Macromolecules*, **31**, 9146 (1998).

[4] J. Swalen and F. Kajzar, Introduction, in Organic Thin Films for Waveguiding Nonlinear Optics, F. Kajzar and J. Swalen Eds, Gordon & Breach Publishers, Amsterdam 1996, , pp. 1–44.

[5] M. Choy and R. L. Byer, *Phys. Rev. B*, **4**, 1693(1976).

[6] B. Kippelen, Sandalphon, K. Meerholz, and N. Peyghambarian, *Appl. Phys. Lett.* **68**, 1748 (1996).

[7] A. D. Buckingham, in Molecular Electro-optics, C. T. O'Konski, Ed., Marcel Dekker, Inc., New York 1976, pp. 27–62.

[8] S. Bartkiewicz, F. Kajzar, A. Miniewicz and M. Zagorska, *Appl. Optics*, **37**, 6871(1998).

[9] A. Miniewicz, S. Bartkiewicz and F. Kajzar, *Nonl. Optics*, **19**, 157(1998).

[10] A. Kapitulnik, S. Casalnuovo, K. C. Lim and A. J Heeger, *Phys. Rev. Lett.* **53**, 469(1972).