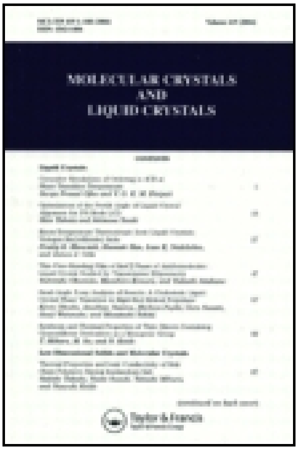


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Third Order Nonlinear Optical Properties of Novel Polythiophene Derivatives

Edward Van Keuren [a] [b] , Vladimir Belov [a] , Wolfgang Schrof [a] , Elmar Mayer [a] , Stanislaw Rozouvan [a] , Hiroki Saitoh [a] , Thorsten Hartmann [a] & Helmutmö Hwald [a]

[a] BASF AG, Polymer Research Laboratory, D-67056, Ludwigshafen, Germany

[b] BASF Advanced Polymer Research, 1-23-2, Kasumi, Yokkaichi, Mie, 510, Japan

Version of record first published: 24 Sep 2006

To cite this article: Edward Van Keuren, Vladimir Belov, Wolfgang Schrof, Elmar Mayer, Stanislaw Rozouvan, Hiroki Saitoh, Thorsten Hartmann & Helmutmö Hwald (1997): Third Order Nonlinear Optical Properties of Novel Polythiophene Derivatives, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 287-290

To link to this article: http://dx.doi.org/10.1080/10587259708032303

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 287–290
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

THIRD ORDER NONLINEAR OPTICAL PROPERTIES OF NOVEL POLYTHIOPHENE DERIVATIVES

EDWARD VAN KEUREN*, VLADIMIR BELOV, WOLFGANG SCHROF,
ELMAR MAYER, STANISLAW ROZOUVAN, HIROKI SAITOH*,
THORSTEN HARTMANN, HELMUT MöHWALD
BASF AG, Polymer Research Laboratory, D-67056, Ludwigshafen, Germany
*BASF Advanced Polymer Research, 1-23-2, Kasumi, Yokkaichi, Mie 510, Japan

Abstract The third order nonlinear optical properties of polythiophene derivatives produced by a novel application of Stille coupling were investigated by degenerate four wave mixing (DFWM) and third harmonic generation (THG). By systematic changes in the substituted side groups, values of the third order susceptibility, $\chi^{(3)}$, reached 1.8×10^{-9} esu (by DFWM) with a figure of merit $\chi^{(3)}/\alpha \sim 7\times10^{-14}$ esu·cm.

INTRODUCTION

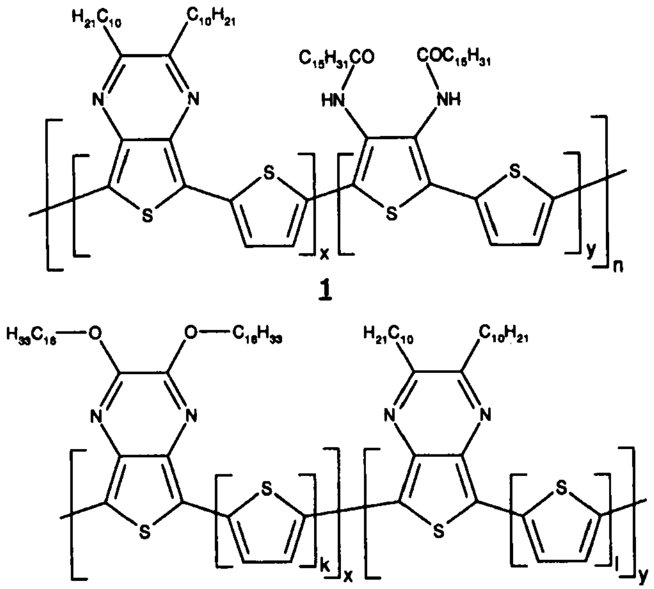
The large third order nonlinear optical susceptibilities, fast response times, and numerous possibilities for alteration have stimulated much interest in polymers such as polyacetylene and polythiophene as potential materials for all-optical switching applications.[1] Recently, we have reported[2] a method for producing novel substituted polythiophene derivatives. By varying both the substituent groups as well as the number of substituted vs. unsubstituted units, we have gained some control over the band gaps and oscillator strengths. Here we report the measurement of the nonlinear optical susceptibilities of some of these materials.

SYNTHESIS

The method of Stille coupling[3] allows one to obtain polythiophene derivatives with minimal structural defects, doping or overoxidation. A wide variety of functional groups including acceptors, donors and π-systems with multiple bonds between the carbon and heteroatoms may be used. Finally, the method allows the synthesis of polymers with alternation of rings with different substitution patterns, e.g., substituted and unsubstituted at positions 3 and 4, or even copolymers with two different thiophene units.

A number of these materials incorporating a thieno[3,4-b]pyrazine unit were investigated with respect to their linear and nonlinear optical properties. The pyrazine ring condensed with the thiophene ring at the 3,4- position provides an alternate conjugation path for the π-electrons and strongly affects the optical properties. Substitution on the pyrazine ring will further affect these properties. The lower steric demands due to alternation of substituted and unsubstituted nuclei should give a planar form for these materials, resulting in longer conjugation lengths compared to, e.g., the low band-gap material poly(5(6)-(di)alkylbenzo[c]thiophene).

Some examples of the materials investigated are shown in Figure 1. Details of the synthesis are published elsewhere[2]. The reactivities of the monomers used were found to be similar, allowing the synthesis of copolymers of two different units. Linear absorption measurements showed a large shift of the band edge to longer wavelengths compared to 3-alkylsubstituted polythiophene. In addition, the shapes of the absorption spectra as well as the absorption coefficients could be markedly altered by introducing



1

2

FIGURE 1 Polythiophene derivatives (polymer 1-a: x/y = 9:1; polymer 1-b: x/y = 8:2; polymer 2: x/y=85:15, k,l = 2 (85%); = 1 (15%).

additional unsubstituted spacers between the thieno[3,4-b]pyrazine units and/or by using two substituted units with different groups attached to the pyrazine rings.

RESULTS AND DISCUSSION

The third order nonlinear optical susceptibilities, $\chi^{(3)}$, were measured by third harmonic generation (THG) and degenerate four wave mixing (DFWM). The THG fundamental (wavelength 1.2 μm to 2.4 μm) was provided by a BBO-crystal optical parametric oscillator pumped by the tripled frequency pulse of a Nd:YAG laser. Details of the experimental setup and analysis are given elsewhere.[4] In table I, the maximum values of $\chi^{(3)}$ are given for the materials shown in Figure 1. The incorporation of the thieno[3,4-b]pyrazine unit significantly increased the value of $\chi^{(3)}$ $(-3\omega;\omega,\omega,\omega)$ compared to materials without, e.g., alkyl-substituted polythiophene.

TABLE I $\chi^{(3)}$ from THG [TH wavelength of maximum] and DFWM (at 800 nm) and figure of merit $(\chi^{(3)}_{DFWM}/\alpha)$ for polythiophene derivative films.

Sample number	Absorption λ_{max} (nm)	$\chi^{(3)}$ $(-3\omega;\omega,\omega,\omega)$ (THG) (esu)	$\chi^{(3)}$ $(-\omega;\omega,-\omega,\omega)$ (DFWM) (esu)	$\chi^{(3)}/\alpha$ (10^{-14} esu·cm)
1-a	764	2.14×10^{-11} [800 nm]	0.49×10^{-9}	2.7
1-b	732	8.98×10^{-12} [800 nm]	0.55×10^{-9}	2.9
2	670	3.32×10^{-11} [675 nm]	1.81×10^{-9}	6.7

DFWM experiments were performed using a mode-locked Ti:Sapphire laser (Coherent MIRA 900F). The 100 fs output pulses were tunable in the range 720 to 900 nm with variable repetition rate down to 100 kHz (using a pulse picker). Alternately, the output could be further amplified by a regenerative Ti:Sapphire amplifier (Coherent RegA 9000), giving 250 femtoseconds pulses at 800 nm with a 250 kHz repetition rate. The lower repetition rate reduced problems with thermal grating buildup.

A typical result is shown in Figure 2. All three materials showed rapid response times on the order of picoseconds. The values for both $\chi^{(3)}$ and figures of merit $\chi^{(3)}/\alpha$ are also given in Table I. The relative strength of the C=C stretching bands in these materials, as measured by Raman spectroscopy, suggests long conjugation lengths, corroborating the large values of $\chi^{(3)}$. This again illustrates the importance of the

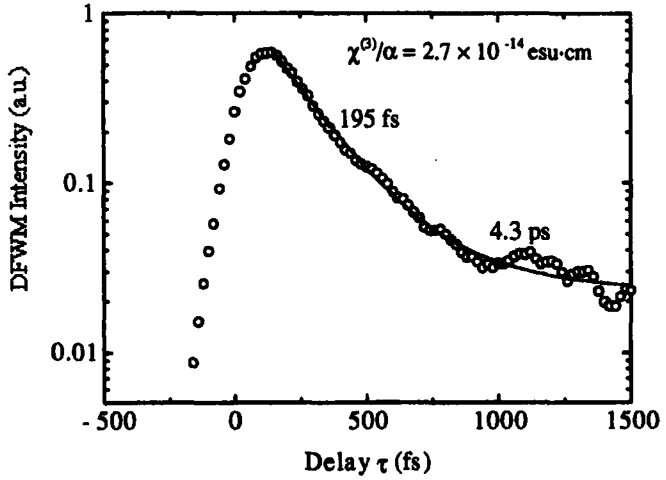


FIGURE 2 DFWM signal from polythiophene derivative 1-a.

pyrazine rings in reducing twisting of the chains. The long conjugation along the main chain, as well as the additional conjugation path(s) through the pyrazine ring and resonance structures possible, have significant effects on the electronic and optical properties of these materials. Current synthetic work involves more extensive investigation of copolymer materials such as 1 and 2. By control of the band gap and increase of both conjugation length and anharmonicity of the electronic potential, we hope to be able to produce materials suitable for device applications.

ACKNOWLEDGMENTS

This work was performed by BASF AG under the management of the Japan High Polymer Center as part of the Research and Development Project on Basic Technologies for Future Industries supported by the New Energy and Industrial Technology Development Organization.

REFERENCES

1. see, e.g., P. Prasad and D. Williams, Introduction to Nonlinear Effects in Molecules and Polymers (John Wiley & Sons, New York, 1991).
2. H. Möhwald, V. Belov and W. Schrof, Polymer Preprints, Japan, 45, 79 (1996).
3. J. K. Stille, Angew. Chem. Int. Ed. Engl., 25, 508 (1986).
4. A. Gierulski, H. Naarman, W. Schrof and A. Ticktin, Proc. SPIE, 1560, 172 (1991).