ELSEVIER

Synthetic Metals 109 (2000) 79–83

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Two-photon and one-photon resonant third-order nonlinear optical properties of π-conjugated polymers

Marek Samoc *, Anna Samoc, Barry Luther-Davies

Australian Photonics Cooperative Research Centre, Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University, Canberra 0200, Australia

Received 26 June 1999; accepted 10 September 1999

Abstract

Third-order nonlinear optical properties of a number of polymers with π-electron conjugated structures have been investigated. For several polymers large negative refractive nonlinearities measured at 800 nm are accompanied by large two-photon absorption coefficients. Very strong nonlinear effects can be achieved in polymers showing linear absorption and absorption saturation effects at 800 nm, the examples of which are polyaniline (salt form) and poly(indenofluorenone).

Keywords: NLO; π-Conjugated polymers; Absorption

1. Introduction

A high density of delocalized electrons present in π-conjugated polymers leads to strong nonlinear optical (NLO) properties of these materials. This paradigm has been known for a relatively long time, but there has been only limited progress in the understanding of the factors determining the NLO response of various materials as well as in determination of the suitability of such materials for applications in photonics. In particular, the use of so-called merit factors to evaluate the suitability of conjugated polymers for use in optical switching has been advocated but the availability of the relevant data in the literature is rather scarce [1,2]. We survey in this paper some recent results on NLO properties of various conjugated polymers. In particular, we concentrate on the issue of the differences in the behaviour of π-conjugated polymers in the regions where the dominant loss mechanism is the two-photon absorption and where the loss is due to one-photon absorption.

* Corresponding author. Fax: +61-2-249-0029; e-mail: marek.samoc@anu.edu.au

2. Third-order NLO properties in the range of two-photon absorption

A substantial part of the experimental effort in the field on π-conjugated NLO polymers was directed at those polymers that have a good transparency in the wavelength range of interest and can therefore be considered for application in waveguide geometries. However, in most cases, the transmission of short laser pulses in such polymers is limited by the presence of nonlinear absorption: two-photon absorption as well as higher order processes that may involve three-photon absorption as well as absorption of light by two-photon induced excited states. The relevant parameter for the case of pure two-photon absorption is the so-called T merit factor, $T=\beta\lambda/Re(n_2)=4\pi Im(n_2)/Re(n_2)$ where n_2 is the (complex) nonlinear refractive index, β is the two-photon absorption coefficient and λ is the wavelength. It is important that investigations of third-order NLO properties of conjugated polymers include the determination of both the real and imaginary part of the third-order nonlinearity (expressed as n_2 or as the degenerate third-order susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$).

We have investigated third-order nonlinear effects in several different conjugated polymer structures, with the

0379-6779/00/$ - see front matter
PII: S0379-6779(99)00201-5

interest in both the fundamental structure–property relations and in merit factors determining the viability of such materials for applications in photonic devices. The NLO properties have been measured using mostly the techniques of femtosecond degenerate four-wave mixing and of Z-scan. We have found that combining these two techniques one can obtain well reproducible results for the nonlinear refractive index and the two-photon absorption coefficient of the investigated polymers [3]. Among the materials investigated by us, poly(*p*-phenylenevinylene) (PPV) [4] and its derivatives appear to have interesting values of the nonlinear refractive index ($|n_2|$ reaching 10^{-11} cm^2/W in the case of unsubstituted PPV at 800 nm) [5,6] as determined by the degenerate four-wave mixing technique. In the case of soluble PPV derivatives the refractive (real part of n_2) and absorptive (imaginary part of n_2) contributions to $|n_2|$ can be conveniently determined by the Z-scan technique, performing measurements of open and closed aperture Z-scans on solutions with varying concentrations of the polymer [3,7,8].

Unfortunately, the use of Z-scan for the determination of the NLO parameters of thin films is often quite difficult because of the possibility of film damage and high sensitivity of closed aperture Z-scans to film non-uniformities. Therefore, one may need to employ alternative measurement techniques capable of the determination of the refractive and absorptive nonlinearity. An example of such a technique is the simultaneous measurement of phase-matched and non-phase-matched degenerate four-wave mixing signal [3,9] for different thicknesses (and/or concentrations of the NLO component in the case of NLO composites) of the film deposited on a transparent substrate of low nonlinearity (e.g., glass or silica). The superposition of the DFWM signal from the substrate with the signal from the thin film will lead to different behaviour for the phase matched and non-phase-matched interactions: the substrate contribution being important for the phase-matched interaction, but (in the case of the nonlinearity of the film being much bigger than the nonlinearity of the substrate) negligible for the phase-mismatched interaction. A convenient way of presenting the results of such a study is in a form of a plot of $I_{PM}/I_{PM,substr}$ vs. $(I_{NPM}/I_{PM,substr})^{1/2}$ where I_{PM} is the phase-matched DFWM signal intensity, I_{NPM} is the non-phase-matched signal intensity and $I_{PM,substr}$ is the intensity of the phase-matched signal from the substrate without the nonlinear film. One can show that the resulting plot should be a quadratic curve with an equation of the form $y = ax^2 + bx + 1$ where $x = (I_{NPM}/I_{substr})^{1/2}$, $y = I_{PM}/I_{substr}$ and $b \propto Re(\chi^{(3)}_{film})/|\chi^{(3)}_{film}|$. Fig. 1 shows an example of such a plot for a series of PPV composites [10].

The important conclusion from the results presented in Fig. 1 is that the *b* parameter in the fit curve equation is negative, implying a negative real part of $\chi^{(3)}$ for the investigated PPV composites at 800 nm. This behaviour is typical for many conjugated polymers, and in particular, substituted PPV derivatives, investigated at 800 nm. Table 1 shows examples of data obtained for some polymers investigated in our laboratory.

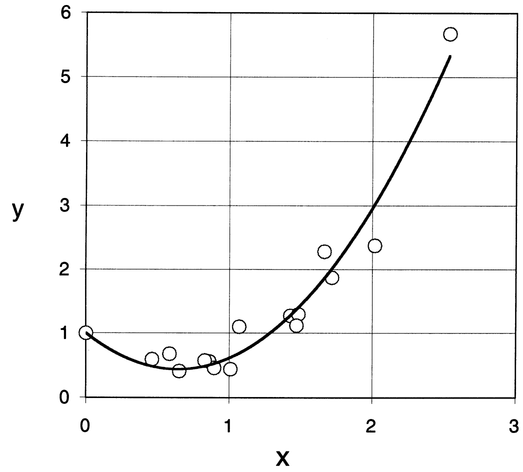


Fig. 1. A plot of $y = (I_{PM}/I_{PM,substr})$ vs. $x = (I_{NPM}/I_{PM,substr})^{1/2}$ for a series of films of PPV/polyvinylpyrrolidone composites with different thicknesses and PPV concentrations. The least-squares fit equation is $y = 1.3629x^2 - 1.7508x + 1$.

One notices that the refractive nonlinearity (the real part of n_2) is negative for some polymers but positive for others and varies in a wide range of values. The presence of two-photon absorption seems to be an important factor determining the magnitude and sign of the real part of n_2. In general, all conjugated polymer materials investigated by us that have high refractive nonlinearities at 800 nm are also strong two-photon absorbers.

An interesting issue is that the strong two-photon absorption in these polymers may of interest on its own because of possible applications of two-photon absorbing materials [11–14], e.g., for 3-D information storage. One notes that a two-photon absorption coefficient of $\beta = 8 \times 10^{-8}$ cm/W for unsubstituted PPV at 800 nm corresponds to the two-photon absorption cross-section $\sigma_2 = \hbar\omega\beta/N = 3 \times 10^{-48}$ cm^4 s (where $\hbar\omega$ is the photon energy and *N* is the concentration of molecules) per repeat unit of the polymer which is a relatively high value if one compares it with other two-photon absorbers [11–14] taking into account the relative two-photon absorption strengths expressed by σ_2/M values (*M* being the molecular weight) rather than just the two-photon cross-sections.

Very high effective nonlinearities can be achieved in some π-conjugated polymers under the conditions of one-photon resonances. Usually, interest in these nonlinearities is limited because the high one-photon absorption may make them unsuitable for use in waveguide devices. However, there may be cases where the high absorption is not an obstacle and then the nonlinearities related to one-photon absorption may be of practical importance. We have investigated in some detail two conjugated polymers that absorb strongly at 800 nm: polyaniline (in several different forms) [15–17] and polyindenofluorene [8,18]. Not unexpectedly, we find that high nonlinearities in these materials result mostly from absorption saturation effects. In the case of polyaniline, the salt form absorbs strongly at 800 nm. Z-scan and pump-probe experiments [15–17] show clearly that the main nonlinear effect is the absorption bleaching. Within the investigated range of experimental parameters we have found that the bleaching can be described by a simple linear intensity dependence of the absorption coefficient on intensity, that is $\alpha = \alpha_0 - \beta I$ where α_0 is the absorption coefficient at zero light intensity and β is the absorption bleaching coefficient. We have determined $Im(n_2) = -4.4 \times 10^{-11}$ cm^2/W for polyaniline sulphate [3,16] which gives $\beta = 7 \times 10^{-6}$ cm/W for the bleaching coefficient (extrapolated to pure polyaniline).

Poly(indenofluorene) (PIF) is another example of a material showing strong absorption bleaching (absorption saturation) [8,18,19]. In this polymer, however, the dependence of the absorption coefficient on light intensity cannot be described by a simple linear relation. Thus, PIF shows a strong non-Kerr behaviour. In effect, the nonlinearity calculated from linear dependencies would be intensity-dependent itself. Surprisingly, the absorption saturation in PIF was found to be relatively well described by an empirical formula: $\alpha = \alpha_0(1/(1 + (I/I_{sat})^{0.5}))$ where I_{sat} is the saturation intensity (the intensity at which the absorption coefficient decreases to half of its low intensity value) [18].

An interesting feature of both polyaniline and poly(indenofluorenone) is that the changes of absorption exhibit relatively short lifetimes, on the order of a few picoseconds. This feature makes these materials attractive when compared to, e.g., semiconductors with strong resonant nonlinearities but long carrier lifetimes. An interesting question is whether the absorption saturation in conjugated polymers can be described in terms of a standard two-level

Table 1
Selected experimental results of the determinations of the third-order nonlinearity for conjugated polymers with 100 fs pulses at 800 nm [3,5–8,17,20]

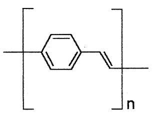
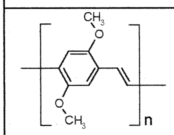
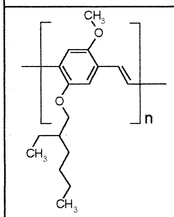
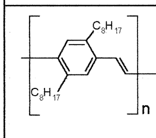
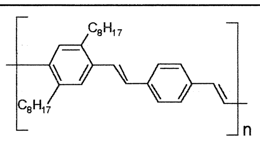
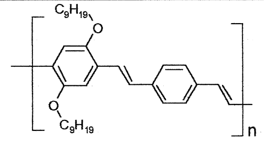
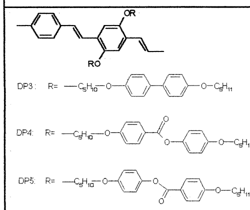
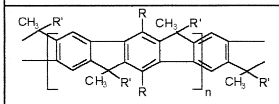
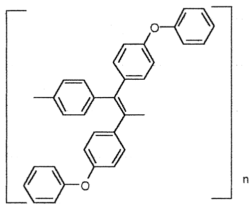
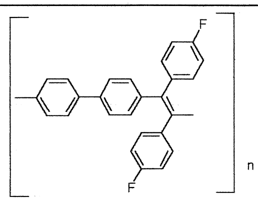
Polymer	n_2 (cm^2/W)	β (cm/W)	Method	Ref
	$\|n_2\|= 1\times10^{-12}-1\times10^{-11}$	Up to 8×10^{-8}	DFWM, power-dependent transmission	[5,6]
	$Re(n_2)= -4\times10^{-12}$	$2.5-8\times10^{-8}$	DFWM, Kerr gate	[17], unpublished
	$Re(n_2)= -3\times10^{-12}$ $\|n_2\|= 1.8\times10^{-12}$	1.8×10^{-7}	Z-scan DFWM	[3,8]
	$Re(n_2)= -0.6\times10^{-12}$	4×10^{-8}	Z-scan	[3,8]
	$Re(n_2)= -1.1\times10^{-12}$ $\|n_2\|= 1.1\times10^{-12}$	4×10^{-8}	Z-scan DFWM	[3,8]

Table 1 (continued)

	$Re(n_2)= -2.2x10^{-12}$ $\|n_2\|= 1.7x10^{-12}$	$4.4x10^{-8}$	Z-scan DFWM	[3,8]
	$Re(n_2)=$ $-0.158x10^{-12}$ $-0.18x10^{-12}$ $-0.088x10^{-12}$	 $4.6x10^{-8}$ $7.4x10^{-8}$ $7.4x10^{-8}$	Z-scan	[8]
	$\|n_2\| = 4\text{-}7x10^{-13}$	 $5x10^{-9}$	DFWM Z-scan	[20]
	$Re(n_2)= 8.4\ x10^{-15}$ $\|n_2\|=$ $(0.7 - 1.3)\ x10^{-14}$	$1.3x10^{-10}$	Z-scan DFWM	[7]
	$Re(n_2)= 8.3\ x10^{-15}$ $\|n_2\|=$ $(1.0 - 1.5)\ x10^{-14}$	$1.0x10^{-10}$	Z-scan DFWM	[7]

model. A crucial parameter in this model is the coherence time (T_2). Our preliminary measurements for polyindenofluorene indicate that T_2 may be relatively long in this material, on the order of 100 fs.

3. Conclusions

Our studies indicate that, apart from the refractive component of the third-order nonlinearity of conjugated polymers, the absorptive (nonlinear absorption or absorption saturation) component may be of real interest on its own. Studies directed at the optimization of two-photon absorption in such materials and the utilization of this property may therefore be of importance. In the case of absorption saturation, the effects are even stronger and conjugated polymers may be an attractive alternative for other well-known types of saturable absorbers as, e.g., semiconductors.

References

[1] G.I. Stegeman, W.E. Torruellas, Philos. Trans. R. Soc. London, Ser. A 354 (1996) 745.

[2] B. Luther-Davies, M. Samoc, Curr. Opin. Solid State Mater. Sci. 2 (1997) 213.

[3] M. Samoc, A. Samoc, B. Luther-Davies, Z. Bao, L. Yu, B. Hsieh, U. Scherf, J. Opt. Soc. Am. B 15 (1998) 817.

[4] A. Samoc, M. Samoc, M. Woodruff, B. Luther-Davies, in: D.L. Wise, G.E. Wnek, D.J. Trantolo, T.M. Cooper, J.D. Gresser (Eds.), Photonic Polymer Systems, Fundamentals, Methods and Applications, Marcel Dekker, New York, 1998, p. 373.

[5] A. Samoc, M. Samoc, M. Woodruff, B. Luther-Davies, Polym. Mater. Sci. Eng. 72 (1995) 224.

[6] A. Samoc, M. Samoc, M. Woodruff, B. Luther-Davies, Opt. Lett. 20 (1995) 1241.
[7] A. Samoc, M. Samoc, B. Luther-Davies, H. Liebegott, R. Stockmann, H.-H. Hoerhold, Proc. SPIE 3473 (1998) 79, Third-Order Nonlinear Optical Materials.
[8] M. Samoc, A. Samoc, B. Luther-Davies, Z. Bao, S.K. Deb, L. Yu, B. Hsieh, U. Scherf, Nonlinear Opt. 20 (1999) 183.
[9] F.P. Strohkendl, L.R. Dalton, R.W. Hellwarth, H.W. Sarkas, Z.H. Kafafi, J. Opt. Soc. Am. B 14 (1997) 92.
[10] A. Samoc, M. Samoc, B. Luther-Davies, Proc. SPIE-Int. Soc. Opt. Eng. 3147 (1997) 166.
[11] J.W. Perry, K. Mansour, I.Y.S. Lee, X.L. Wu, P.V. Bedworth, C.T. Chen, D. Ng, S.R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, Science 273 (1996) 1533.
[12] J.D. Bhawalkar, G.S. He, P.N. Prasad, Rep. Prog. Phys. 59 (1996) 1041.
[13] M. Albota, D. Beljonne, J.L. Bredas, J.E. Ehrlich, J.Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Marder, D. McCord-maughon, J.W. Perry, H. Rockel, M. Rumi, C. Subramaniam, W.W. Webb, I.L. Wu, C. Xu, Science 281 (1998) 1653.
[14] B.A. Reinhardt, L.B. Lawrence, S.J. Clarson, A.G. Dillard, J.C. Bhatt, R. Kannan, L. Yuan, G.S. He, P.N. Prasad, Chem. Mater. 10 (1998) 1863.
[15] M. Samoc, A. Samoc, B. Luther-Davies, J. Swiatkiewicz, C.Q. Jin, J.W. White, Opt. Lett. 20 (1995) 2478.
[16] A. Samoc, M. Samoc, B. Luther-Davies, C.Q. Jin, J.W. White, International Quantum Electronics Conference IQEC'96, Sydney, 1996.
[17] M. Samoc, A. Samoc, B. Luther-Davies, M. Woodruff, Pure Appl. Opt. 5 (1996) 681.
[18] M. Samoc, A. Samoc, B. Luther-Davies, H. Reisch, U. Scherf, Opt. Lett. 23 (1998) 1295.
[19] M. Samoc, A. Samoc, B. Luther-Davies, H. Reisch, U. Scherf, Nonlinear Opt. 22 (1999) 305.
[20] M. Samoc, A. Samoc, B. Luther-Davies, U. Scherf, Synth. Met. 87 (1997) 197.