



ELSEVIER

1 November 1996

OPTICS  
COMMUNICATIONS

Optics Communications 131 (1996) 301–306

## Diagnostics of femtosecond laser pulses using films of poly(*p*-phenylenevinylene)

B. Luther-Davies<sup>a,\*</sup>, M. Samoc<sup>a</sup>, J. Swiatkiewicza<sup>a,1</sup>, A. Samoc<sup>a</sup>, M. Woodruff<sup>a</sup>,  
R. Trebino<sup>b</sup>, K.W. Delong<sup>b</sup>

<sup>a</sup> *Laser Physics Centre, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia*

<sup>b</sup> *Sandia National Laboratories, Livermore, CA 94551, USA*

Received 12 January 1996; accepted 28 March 1996

### Abstract

Thin films of poly(*p*-phenylenevinylene) have been used to diagnose femtosecond Ti-sapphire laser pulses using frequency resolved optical gating or third order intensity autocorrelation in the self-diffraction geometry; and using a two-photon fluorescence autocorrelation technique.

### 1. Introduction

The recent development of lasers producing picosecond and femtosecond duration pulses and their growing range of applications have underscored the need for methods for fully characterising the amplitude and phase of such short duration pulses. While simple autocorrelation measurements based on second harmonic generation in a nonlinear crystal provide the intensity autocorrelation function of the pulse, a more detailed characterisation is needed in particular to identify linear or nonlinear frequency chirps which could limit the minimum pulse dura-

tion. Frequency Resolved Optical Gating (FROG) [1–4] is a straightforward extension of the common intensity autocorrelation methods which permits the measurement of the temporal evolution of the complex electric field during the laser pulse. The FROG technique can be implemented in several ways but its important difference from methods providing only the intensity autocorrelation function is that either second-order or third-order autocorrelation signals are spectrally resolved to provide the data set for subsequent analysis.

As discussed elsewhere [4], third-order processes have the advantage that they provide FROG signals which can be unequivocally converted into the time dependent frequency or phase of the pulse. Furthermore, the raw data when presented as a ‘map’ representing the variation of the spectrum with time provides a qualitative measure of the basic pulse

\* Corresponding author. E-mail: bld111@rsphysl.anu.edu.au.

<sup>1</sup> On leave from Photonics Research Laboratory, State University of New York at Buffalo, NY 14260, USA.

characteristics (for example the sign and magnitude of any chirp). In general, however, the sensitivity of FROG measurements based on third order autocorrelators is poor because few materials exist with a large instantaneous third order nonlinearity and measurements to date have relied on the use of fused silica as the nonlinear material. In this case the relatively low third-order nonlinear refractive index ( $n_2 = 3 \times 10^{-16} \text{ cm}^2/\text{W}$ ) means that a relatively thick silica plate is needed to obtain any signal and this both limits the sensitivity of the FROG measurement and can lead to problems when very short laser pulses are investigated because of distortion of the pulse by the group velocity dispersion in the silica. Third order FROG measurements using the Kerr-gate geometry using a 1.6 mm thick silica plate as a nonlinear medium were reported in Ref. [1]. Subsequently most FROG measurements have been based on second order nonlinear processes which although providing higher sensitivity do not provide raw data which visually maps the pulse properties nor unequivocally determines the phase and amplitude of the pulse. It is therefore of interest to investigate the use of alternative third order materials which may eliminate some of these difficulties.

We report here on the use of the third-order nonlinear conjugated polymer – poly(*p*-phenylenevinylene) (PPV) as the medium for diagnosing femtosecond laser pulses by several techniques – simple autocorrelation schemes and by a self-diffraction type FROG. The instantaneous third order third-order nonlinearity of PPV is very high [5–11]. The  $|n_2|$  values determined by degenerate four-wave mixing (DFWM) at 800 nm, for example, are in the range  $10^{-12}$ – $10^{-11} \text{ cm}^2/\text{W}$ . We have also shown [9] that the relative contribution of the real (refractive) and imaginary (absorptive) part of the nonlinearity varies with the degree of  $\pi$ -electron conjugation (which depends on the way the polymer films are prepared) and that the two-photon absorption coefficient  $\beta$  in these highly nonlinear PPV films is also quite high, reaching 80 cm/GW.

## 2. PPV film preparation and characterisation

PPV films used in the experiments were prepared to have low scattering and hence provided a low

background for the measurements. The material was prepared according to the precursor polymer route [12–16]. The synthetic procedure performed by us was similar to the one described in Ref. [12] with modifications introduced in Ref. [13]: tetrahydrothiophene instead of dimethyl sulphide was used to react with  $\alpha,\alpha'$ -dichloro-*p*-xylene to form the bis-sulfonium salt monomer. The monomer salt was polymerised in a water:methanol (50:50) solution using sodium hydroxide with 0.9 mol equiv. of base. The viscous polyelectrolyte precursor polymer solution was purified by dialysis against deionised water ( $3 \times 2000 \text{ cm}^3$ ) with Spectra/Por 3 dialysis tubing of the molecular weight cut-off of 3500 Da. The concentration of the precursor polymer was 0.74%. PPV films were obtained by spinning of the solution of the precursor polymer onto silica or Fisher microscope slides and thermally converted under dynamic vacuum at elevated temperatures (150–200°C) for 3–5 hours. We found that we could prepare films of better optical quality if the precursor solution prior to the deposition was diluted with methanol (e.g., 2:1), stored at room temperature for at least 1 day then filtered (0.5  $\mu\text{m}$ ) and concentrated with a rotary evaporator. The influence of methanol on the precursor polymer has been already observed at temperatures 50–60°C [14–16] leading to the precursor partially substituted with methoxy groups possibly acting as defects breaking the conjugation in the rigid rod molecule of poly(*p*-phenylenevinylene) and limiting the tendency for crystallisation. Indeed, the scattering of light in our films was reduced (waveguiding of HeNe laser light was observed). Films were characterised by UV-VIS-NIR spectroscopy, refractive indices and thicknesses measured with a prism coupler. Absorption spectra of the PPV films showed maximum at ca. 420–430 nm, the absorption coefficients at the resonance were in the range  $(1.6\text{--}1.8) \times 10^5 \text{ cm}^{-1}$ . Refractive indices  $n_{\text{TE}}$  and  $n_{\text{TM}}$  were found to be equal to 2.26 and 1.60 at 633 nm and to 2.10 and 1.58 at 810 nm, respectively, indicating anisotropic alignment of the molecules in the films. The index data varied slightly (5%) between samples. The data indicated moderate conjugation length had been introduced into the polymer backbone during the polymerisation and under the processing conditions we applied. The third order optical nonlinearities evaluated with fs degenerate four

wave mixing at 800 nm in these films were in the range  $|n_2| = (2-4) \times 10^{-12} \text{ cm}^2/\text{W}$ .

### 3. The laser system

The laser system used in the investigation comprised of an Ar-ion (Coherent Innova) pumped Ti-sapphire oscillator (Coherent Mira 900D) and an amplifier using the chirped pulse amplification scheme. Single 90 fs pulses from the 76 MHz mode-locked train generated by the oscillator were selected with a Pockels cell and expanded by a factor of about 1000 in a grating decompressor. The pulses were then injected into a Ti-sapphire regenerative amplifier pumped at 30 Hz with frequency-doubled pulses from a Spectra-Physics GCR-130 Nd-YAG laser. After amplification using a fixed number of passes (12) in the regenerative amplifier the pulses were recompressed in a grating compressor. This resulted again in about 90 fs pulses with energies which could be varied in 0.1–100 microjoule range by controlling the delay between the pulse of the Nd-YAG pump and the moment of the injection of the pulse from the Mira oscillator into the amplifier.

### 4. Third-order autocorrelation with PPV films

The simplest way of diagnosing Ti-sapphire pulses with nonlinear effects in PPV films which we found useful for routine diagnostics of pulse duration was third-order autocorrelation by self diffraction. If two short pulses from the same laser overlap within a third order nonlinear material, a transient refractive index grating is formed from which the beams can be individually diffracted. If the film is thin and the nonlinearity very high, significant energy can be diffracted into the first (or higher) order components since, although the interaction is non-phase matched, strong diffraction occurs in a distance (the film thickness) shorter than the coherence length for the interaction. If a delay is introduced between the two pulses then the variation of the diffracted intensity with delay provides a measure of the third order autocorrelation function of the pulse.

Fig. 1 shows a multiple shot autocorrelation trace obtained by self diffraction and fitted by a model

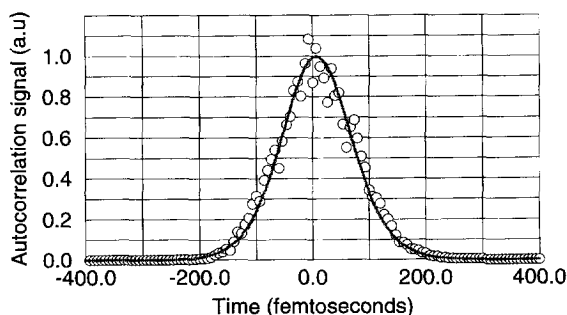


Fig. 1. Multiple shot autocorrelation trace fitted to a 90 fs duration  $\text{sech}^2$  pulse.

pulse assumed to have a  $\text{sech}^2$  temporal profile. The Ti-sapphire amplifier output beam was split in two, passed through an adjustable delay line and the two beams were focussed to intersect at an angle of about  $10^\circ$  in a  $200 \mu\text{m}$  diameter spot on a  $3.6 \mu\text{m}$  thick sample of PPV prepared as described above. The diffracted signal was generally visible using an infrared image converter, and at high energies ( $> 10 \mu\text{J}$ ) several diffracted orders could be observed. Typically  $> 100 \text{ nJ}$  of input energy was required to obtain an autocorrelation trace although this value depends, of course, on the experimental geometry. The curve fitting indicated the laser pulse duration was  $\approx 90 \text{ fs}$ .

### 5. FROG by self-diffraction in PPV films

While the intensity autocorrelation is very useful for diagnosing operation of a short pulse laser, it does not, however, provide any information on the degree of frequency chirping that may be present in the pulse. The simple measurement of the intensity autocorrelation function can be extended by spectrally resolving the diffracted light. By measuring the spectrum as a function of delay, input data for a FROG analysis can be obtained. Our experimental arrangement was modified to allow a complete set of FROG data to be obtained from a single laser pulse. The incoming beams were focussed using a cylindrical lens to form two overlapping line foci at the PPV (see Fig. 2). Diffraction only occurs from those regions where the pulses from the two different directions overlap in time, and hence the intensity autocorrelation function can be measured by imaging

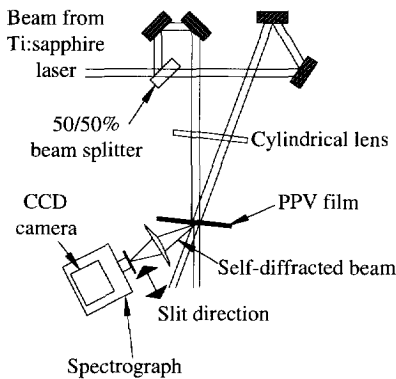


Fig. 2. Apparatus used to record single shot FROG traces.

the diffracted emission as a function of distance along the line focus. The emission can be spectrally resolved in a direction orthogonal to the time "axis" allowing single shot recording of the FROG trace.

We used a cooled CCD camera (Photometrics Imagepoint) connected to a framegrabber and computer to record the two-dimensional information in the frequency–time plane. By optimising the system (we chose the length of the line focus to be equivalent to  $\approx 5 \times$  the pulse duration and used a  $\approx 30 \mu\text{m}$  wide line), FROG data could be recorded using single pulse energies as small as 200 nJ in 90 fs. This represents a factor of five better sensitivity than achieved in previous FROG measurements using other third order nonlinear media [1].

The FROG data was used to recover the phase and intensity profile of the laser pulse using algorithms that have been described elsewhere [3]. Fig. 3

shows an example of raw FROG data for a  $1 \mu\text{J}$  pulse compared with a reconstructed frequency–time distribution obtained from the FROG analysis whilst Fig. 4 shows the intensity and phase profiles of the pulse. As is evident, the pulse is not perfectly transform limited and contains a nonlinear chirp which prevents compression below 90 fs.

One of the most useful features of a FROG image obtained from a third order autocorrelation trace is the qualitative link that exists between the shape of the image and the pulse characteristics [4]. Any residual chirp arising from incorrect setting of the grating pulse compressor at the output of the regenerative amplifier appeared as an elongation of the FROG image along an axis inclined in the time–frequency plane. The slope changes sign as the chirp varies from positive to negative. As a result of the high FROG sensitivity using self-diffraction from PPV it was possible to easily optimise the compressor for minimum pulse duration and chirp.

To determine the ultimate sensitivity available from a PPV autocorrelator we attempted to record FROG data using the train of 10 nJ, 90 fs unamplified pulses direct from the MIRA oscillator. Self-diffraction could, in fact, be observed but scattering and/or the growth of a permanent grating in the film obscured the FROG signal. Thus although changing from 200 nJ single pulses to a 76 MHz, 10 nJ pulse train allowed the  $20^3$  reduction in the self-diffracted signal to be partially compensated by the high repetition rate of the pulses, our present PPV would not produce a useable FROG trace using the oscillator

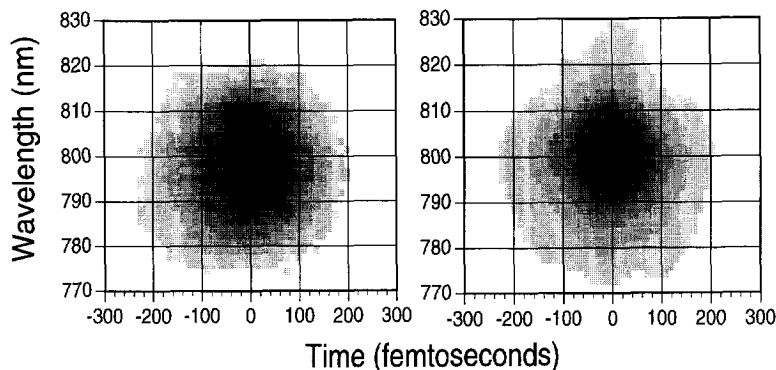


Fig. 3. Raw single shot FROG data (left) compared with reconstructed data (right) from a  $1 \mu\text{J}$ , 90 fs duration laser pulse. The fringes on the experimental data are an artifact.

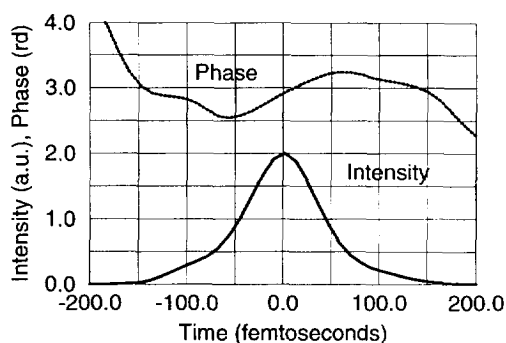


Fig. 4. Intensity and phase profiles of the pulse obtained from the FROG data of Fig. 3.

beam alone. Can, therefore, FROG traces be obtained with lower energy pulses that currently demonstrated? For a given experimental geometry the self diffracted energy is proportional to the ratio of the  $(\text{pulse energy})^3/(\text{pulse duration})^2$ , thus, shorter pulses should produce FROG traces more easily.

## 6. Autocorrelation by two-photon induced fluorescence in PPV

Whilst FROG analysis provides the most quantitative information on the pulse another property of PPV proved useful for qualitative analysis. PPV shows quite strong two-photon induced fluorescence when exposed to short pulses around 800 nm. This efficient fluorescence is the result of the high value of  $\beta$  combined with the fact that a substantial fraction of excited states of PPV decay in a radiative way. Using the same geometry as for single shot FROG analysis, a simple single-shot autocorrelator

can be constructed where two photon fluorescence from PPV is imaged with the CCD camera to provide an autocorrelation trace. Autocorrelation can readily be observed using single pulses of a few microjoules energy from the Ti-sapphire amplifier. The traces could be analysed as discussed e.g. in Refs. [17,18], however, the accuracy of the autocorrelation profiles relies on the time-integrated two-photon fluorescence intensity depending quadratically on the laser intensity. In fact, measurements from degenerate four-wave mixing in PPV at high intensities (around  $100 \text{ GW/cm}^2$ ) indicate that the decay time for the two-photon induced excited species becomes power dependent [11]. This leads to deviation from the desired quadratic dependence making it difficult to obtain quantitative information from this autocorrelation signal.

Nevertheless, the convenience of this visible fluorescence signal should not be underestimated since it is a considerable aid when aligning the other forms of autocorrelator or setting up experiments on degenerate four wave mixing where three ultra-short pulses must be brought into time coincidence at a sample. A typical two-photon fluorescence autocorrelator signal is shown in Fig. 5.

## 7. Discussion

The advantage of the use of PPV for autocorrelation lies in both the sensitivity and convenience afforded by the use of this material. The demanding FROG analysis benefits from the use of a third order interaction since the FROG traces qualitatively reproduce the main pulse characteristics (e.g. chirp)

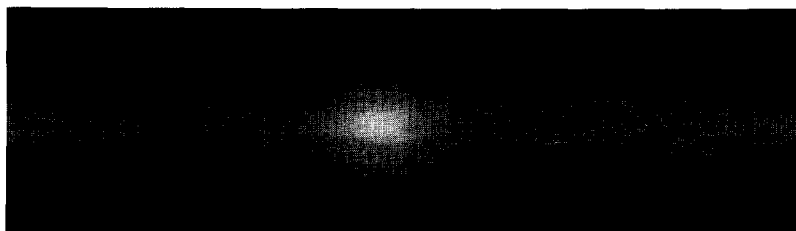


Fig. 5. Two-photon fluorescence autocorrelator signal from PPV. The window width is 2 ps.

which is masked when FROG data are recorded from a second harmonic autocorrelator. Self-diffraction from PPV has also provided a five fold increase in sensitivity compared with earlier results obtained using the Kerr gate geometry with silica as the nonlinear medium. Our 3  $\mu\text{m}$  thick PPV films have, for example, an equivalent “nonlinearity” to  $> 20$  mm of fused silica and they should provide fs temporal resolution where thick media may be limited.

Finally we comment on the wavelength range over which PPV can be employed. Our as yet unpublished DFWM results indicate that  $|n_2|$  for the most nonlinear form of PPV  $> 2 \times 10^{-12}$   $\text{cm}^2/\text{W}$  for wavelengths  $< 1$   $\mu\text{m}$  (no measurements have yet been made at longer wavelengths). The range where the two-photon absorption of PPV may be used for autocorrelation is roughly from the one-photon absorption edge at 500 nm to the two-photon absorption edge at about 950 nm (the two-photon absorption spectrum of PPV was published in Ref. [19]). However, we were also successful in using single-shot two-photon fluorescence autocorrelation in a thick PPV film (about 10  $\mu\text{m}$ ) for amplified 1 ps pulses at 1.06  $\mu\text{m}$ . Thus we expect PPV to be useful as an autocorrelator material at least throughout the entire Ti:sapphire tuning band. We also expect that FROG measurements should be possible within a similar wavelength range, however, tuning limitations of our Ti-sapphire oscillator/decompressor/regenerative amplifier/compressor system (set for 800 nm) have not allowed us to investigate directly how the sensitivity of a FROG system based on self diffraction in a PPV film changes with the wavelength.

### Acknowledgements

Parts of this research have been supported by the Harry Triguboff AM Research Syndicate. We ac-

knowledge the technical assistance of Mrs. R.M. Krolikowska.

### References

- [1] D.J. Kane and R. Trebino, *Optics Lett.* 18 (1993) 823
- [2] R. Trebino and D.J. Kane, *J. Opt. Soc. Am. A* 10 (1993) 1101
- [3] K.W. DeLong and R. Trebino, *J. Opt. Soc. Am. A* 11 (1994) 2429
- [4] K.W. DeLong, R. Trebino and D.J. Kane, *J. Opt. Soc. Am. B* 11 (1994) 1595
- [5] B.P. Singh, P.N. Prasad and F.E. Karasz, *Polymer* 29 (1988) 1940.
- [6] C. Bubeck, A. Kaltbeitzel, A. Grund and M. LeClerc, *Chem. Phys.* 154 (1991) 343.
- [7] Y. Pang, M. Samoc and P.N. Prasad, *J. Chem. Phys.* 94 (1991) 5282.
- [8] J. Swiatkiewicz, P.N. Prasad and F.E. Karasz, *J. Appl. Phys.* 74 (1993) 525.
- [9] A. Samoc, M. Samoc, B. Luther-Davies and M. Woodruff, *Optics Lett.* 20 (1995) 1241.
- [10] A. Samoc, M. Samoc, M. Woodruff and B. Luther-Davies, *Proc. American Chemical Society Division of Polymeric Materials, Science and Engineering*, 72 (1995) 224.
- [11] B. Luther-Davies, M. Samoc, A. Samoc and M. Woodruff, *Nonlinear Optics* 14 (1995) 161.
- [12] D.R. Gagnon, J.D. Capistran, F.E. Karasz, R.W. Lenz and S. Antoun, *Polymer* 28 (1987) 567.
- [13] R.W. Lenz, C-C Han, J. Stenger-Smith and F.E. Karasz, *J. Polym. Sci., Part A, Polym. Chem. Ed.* 26 (1987) 3241.
- [14] S. Tokito, T. Momii, H. Murata, T. Tsutsui and S. Saito, *Polymer* 31 (1990) 1137.
- [15] P.L. Burn, D.D.C. Bradley, R.H. Friend, D.A. Halliday, A.B. Holmes, R.W. Jackson and A. Kraft, *J. Chem. Soc., Perkin Trans. 1* (1992) 3225.
- [16] D.A. Halliday, P.L. Burn, D.D.C. Bradley, R.H. Friend, O.M. Gelsen, A.B. Holmes, A. Kraft, J.H.F. Martens and K. Pichler, *Advanced Materials* 5 (1993) 40.
- [17] J.H. Bechtel and W.L. Smith, *J. Appl. Phys.* 46 (1975) 5055.
- [18] P. Sperber and A. Penzkofer, *Optical Quantum Electron.* 18 (1986) 145.
- [19] C.J. Baker, O.M. Gelsen and D.D.C. Bradley, *Chem. Phys. Lett.* 201 (1993) 127.