Third-order non-linear optical properties of oriented films of poly(p-phenylene vinylene) investigated by femtosecond degenerate four wave mixing

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The third-order non-linear optical susceptibility, $\chi^{(3)}$, has been investigated at wavelengths of 602 and 580 nm for a 10:1 stretch-oriented uniaxial film of poly(p-phenylene vinylene) using femtosecond degenerate four wave mixing. A relatively large $\chi^{(3)}$ with a subpicosecond response is observed. A large anisotropy in the $\chi^{(3)}$ value is found, the largest component of $\chi^{(3)}$ being along the draw direction.

INTRODUCTION

Interest has been shown recently in π-conjugated polymers which exhibit relatively large non-resonant third-order optical non-linearities[1,2]. The third-order non-linear optical processes are expected to play important roles in all optical communication and signal processing. Since the third-order non-linear optical susceptibility $\chi^{(3)}$ is a fourth rank tensor, it can exhibit a large anisotropy in an ordered polymer. Based on this anisotropy, device structures using the concept of orientational bistability have been proposed[3]. However, very few studies of $\chi^{(3)}$ in oriented polymers have been made[4,5]. One group of ordered polymers is rigid-rod aromatic heterocyclic polymers such as poly(p-phenylene benzobisthiazole) (PBT) where the anisotropy of $\chi^{(3)}$ has been investigated[5]. Progress has been made in processing of PBT, but high optical quality films are difficult to obtain.

Recently high optical quality films of ordered poly(p-phenylene vinylene) have been produced using a soluble precursor route. This method is described in detail elsewhere[6]. The oriented PPV film appears to be a highly promising $\chi^{(3)}$ material for the following reasons:

(1) the PPV polymer can readily be synthesized to yield high molecular weight polymer of relatively high purity and narrow molecular weight distribution;

(2) they can conveniently be processed into various shapes using a water-soluble precursor route;

(3) PPV films can be stretch-oriented to produce highly ordered films in which the conjugated chains align in the stretch direction;

(4) the oriented films have good optical quality and optical transparency over a wide range; they have good mechanical strength such that even a 2 μm thick free-standing film can be prepared;

(5) in contrast to polyacetylene which is extremely air sensitive, the environmental stability of the PPV film is excellent. The film also exhibits high optical damage threshold under picosecond and femtosecond pulse illumination;

(6) in the stretched films, doping can produce high electrical conductivity along the draw direction[6], indicating a high effective π-conjugation in this polymer—a criterion needed for large $\chi^{(3)}$. A recent third-harmonic generation study of an unoriented PPV film suggests a large $\chi^{(3)}$ (ref. 7).

Because of these desirable features, we have investigated the $\chi^{(3)}$ behaviour of a uniaxial stretch-oriented PPV film by femtosecond degenerate four wave mixing.

EXPERIMENTAL

The laser system used is based on a mode-locked Nd–Yag laser. The pulses are compressed in a fibre compressor, frequency doubled and then used to sync-pump a dye laser. The dye pulses are subsequently amplified in a three-stage amplifier pumped by a 30 Hz pulse Nd–Yag laser. The resulting amplified pulses are ~400 fs with a pulse energy of 0.5 mJ. The wavelengths used are 602 and 580 nm. The beam is split in three parts and used in a backward wave geometry to conduct the degenerate four wave mixing experiment which has been discussed in detail elsewhere[4]. The film is mounted on a precision

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rotational stage so that it can be rotated to get the orientational anisotropy of $\chi^{(3)}$. CS_2 is used as a reference with the reported value of 6×10^{-13} esu for its $\chi^{(3)}$ obtained with picosecond pulses[8]. This method of referencing with CS_2 has also been described in detail elsewhere[5]. The calculation also requires the measurement of the thickness of the film and its refractive index. The film used had a 10:1 draw ratio. The refractive indices and film thickness were determined by using the m-line technique described elsewhere[9]. The film was found to be $\sim 2\,\mu m$ thick. The refractive indices parallel and perpendicular to the draw direction are 1.60 and 1.59, respectively. The published u.v. visible spectra[10] show that our wavelengths of measurement (580 and 602 nm) are below the band gap and should yield a non-resonant $\chi^{(3)}$ value.

RESULTS AND DISCUSSION

The DFWM signal at 602 nm obtained as a function of the backward beam time delay and with the electric vectors of all the waves parallel to the draw direction is shown in *Figure 1*. The behaviour at 580 nm is basically the same. The rise time is clearly very fast, limited by the rise time of the optical pulse. The decay of the signal is initially fast, again, within the autocorrelation width. Therefore, a subpicosecond response of $\chi^{(3)}$ is observed as expected under non-resonant conditions. However, there is also the presence of a weak tail with a longer time constant which we attribute to the presence of absorbing impurities. Therefore, even the apparent non-resonant regime (below the band gap) is not completely free of absorption. The $\chi^{(3)}$ value along the draw direction is $\sim 4 \times 10^{-10}$ esu at both 602 and 580 nm, which is relatively high.

The change in $\chi^{(3)}$ value (actually the square root of DFWM signal) as a function of film rotation with respect to the incident electric field vector yields a polar plot shown in *Figure 2*. The highest value of $\chi^{(3)}$ is obtained when the electric vectors of all the four waves are parallel to the draw direction. The minimum value for $\chi^{(3)}$ is for the orientation when all the electric vectors are perpendicular to the draw direction. The $(\chi^{(3)})_{\parallel}/(\chi^{(3)})_{\perp}$ ratio is 37 which is a very high degree of orientational anisotropy. The X-ray study of such stretch-oriented PPV films shows a high degree of polymer chain alignment along the draw direction[11]. Our result then provides confirmation that the largest component of $\chi^{(3)}$ (and hence microscopic nonlinearity γ) tensor is along the chain direction as is expected from any theoretical calculation of miscroscopic nonlinearity in π-conjugated polymeric (or oligomeric) structures[4].

To explain the observed polar plot, we use a simple transformation of the fourth rank tensor $\chi^{(3)}$ from the film-based co-ordinate to the laboratory-based co-ordinate system. This relationship has been discussed in detail elsewhere[4]. Since we are making the film in-plane anisotropic measurement, this transformation reduces to

$$\chi^{(3)}_{1111,L} = \chi^{(3)}_{1111,F}\cos_4\theta + \{\chi^{(3)}_{1122,F} + \chi^{(3)}_{1221,F} + \chi^{(3)}_{2211,F} + \chi^{(3)}_{2122,F}$$

$$+ \chi^{(3)}_{1212,F} + \ldots\}\cos^2\theta \sin^2\theta$$

$$+ \chi^{(3)}_{2222,F} \sin^4\theta \qquad (1)$$

In the above equation, $\chi^{(3)}_{1111,L}$ is the $\chi^{(3)}$ of the film in the laboratory co-ordinate, when all the beam polarizations are vertical. $\chi^{(3)}_{1111,F}$ is the $\chi^{(3)}$ component along the draw direction, and $\chi^{(3)}_{2222,F}$ is the component perpendicular to the draw direction. The other components are the in-plane off-diagonal terms. The angle θ is the angle between the electric polarization vector (vertical in our measurement) and the draw direction. The solid line in the figure represents the theoretical fit using equation (1). The experimentally observed data points are adequately described by the theoretical curve.

CONCLUSIONS

In summary, we have obtained a large non-resonant $\chi^{(3)}$ value with a subpicosecond response for a stretch-oriented uniaxial film of PPV. A large orientational anisotropy in $\chi^{(3)}$ values parallel and perpendicular to the
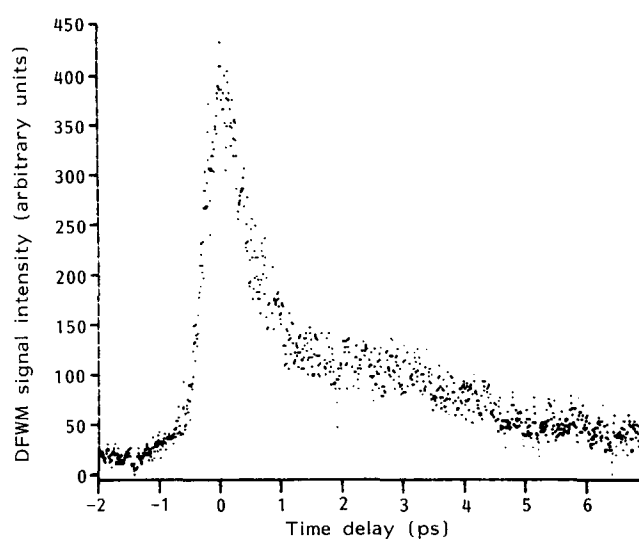
Figure 1 Degenerate four wave mixing (DFWM) signal observed for PPV as a function of the backward beam delay. The wavelength is 602 nm, the pulses are ~ 400 fs, and the film thickness is $\sim 2\,\mu m$ with a draw ratio of 10:1. The intensity on the y-axis is in arbitrary units
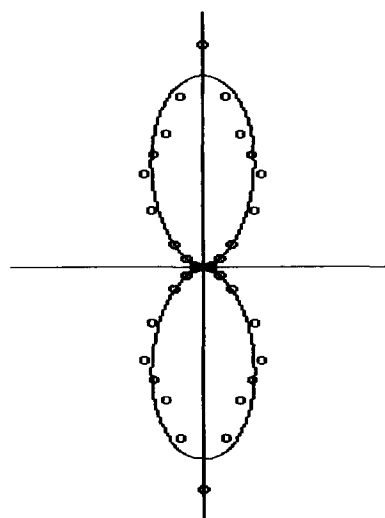
Figure 2 Observed polar plot (orientational anisotropy) of the square root of the degenerate four wave mixing signal intensity (proportional to $\chi^{(3)}$) for the 10:1 stretch-oriented PPV film. □, Observed data points; ———, theoretical fit

draw direction is observed. The largest value of $\chi^{(3)}$ is along the draw direction along which the polymeric chains are oriented. The observed polar plot of $\chi^{(3)}$ is explained by the fourth-rank tensor property of $\chi^{(3)}$.

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