Third order non-linear optical properties of poly-*p*-phenylene benzobisthiazole and its novel composite with Zytel processed via methane sulphonic acid solution extrusion

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It was found that improved optical quality films of poly-*p*-phenylene benzobisthiazole (PBZT) and of a novel composite of PBZT and nylon (Zytel 330) can be produced by extruding below critical concentration solutions in methane sulphonic acid. The linear refractive indices and their dispersion behaviour in these films have been determined by analyses of the interference fringes observed in the optical transmission spectra. A relatively large value of the linear refractive index is obtained for PBZT. The third-order non-linear optical susceptibility, $\chi^{(3)}$, is determined for the films of PBZT and PBZT/Zytel composite using subpicosecond degenerate four-wave mixing. The $\chi^{(3)}$ value observed for this PBZT film is almost an order of magnitude larger than that previously reported for PBZT films of a rather inferior quality processed through polyphosphoric acid solution. This result emphasizes the importance of polymer processing to produce better optical quality films for evaluation of intrinsic $\chi^{(3)}$ values of polymers. The response time of the non-linearity is limited by the laser pulse width, indicating that the non-linear response is derived from the coherent electronic $\chi^{(3)}$. The $\chi^{(3)}$ value of the PBZT/Zytel composite is lower than that for pure PBZT because of the reduced number density. However, determination of the optical loss, α, in these films yields a much lower value of α for the PBZT/Zytel composite film, resulting in an improved value of the often used device figure of merit $\chi^{(3)}/\alpha$. This result suggests that composite structures may be useful for optimizing the $\chi^{(3)}/\alpha$ ratio.

(Keywords: optical properties; poly-*p*-phenylene benzobisthiazole; Zytel; composite)

INTRODUCTION

Non-linear optics is currently at the forefront of research because of its importance in providing the enabling technology for optical processing in the emerging area of photonics. Polymeric structures are now recognized as an important class of non-linear optical materials. Even in the region of their optical transparencies, conjugated polymers show large third-order non-linear optical response characterized by the third-order susceptibility $\chi^{(3)}$ which derives its dominant contribution from the delocalized π electrons. This non-resonant non-linearity also provides the fastest response time in femtoseconds, experimentally limited only by the pulse width of the laser, which is of great significance for photonics. Another advantage of polymeric materials is that they offer tremendous flexibility of structural modifications at both molecular and bulk levels. At the molecular level, molecular engineering is easily achievable in polymers to tailor their backbone and side chain structures in order to enhance the non-linear coefficient $\chi^{(3)}$ and increase solubility in common organic solvents. At the bulk level, polymeric structures allow one to make various polymer composites, and induce the orientation of polymer chains by processing.

Spin coating is the most commonly used technique for preparing optically non-linear polymer films. This technique does not always work well for high molecular weight polymers and can only be used if the polymer is soluble in a suitable solvent. Thus a large number of polymers, for example the rigid rod poly-*p*-phenylene benzobisthiazole (PBZT)[1], are unsuitable for spin coating. This fact renders the $\chi^{(3)}$ measurement of many polymers a difficult task because thin films of desired optical quality and transparency cannot be prepared.

Solutions of sufficiently high viscosity can be extruded

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through dies and the solvent can be removed through coagulation with a non-solvent to form thin films. This technique has been widely used for PBZT[2-4]. The $\chi^{(3)}$ value of a biaxial PBZT film extruded from its polyphosphoric acid solution was measured several years ago[5]; the PBZT film showed an anisotropy in the $\chi^{(3)}$ values which ranged from 5.4×10^{-12} to 7.2×10^{-12} e.s.u., depending on the orientation of the film. These figures underestimate the effective $\chi^{(3)}$ value of PBZT. Besides the relatively low optical quality of the film sample, there were two other factors not precisely known at the time of this earlier publication: the anisotropy of the refractive index and the film thickness. The index of refraction, 1.81, was calculated using crude assumptions made to evaluate molar refraction of the polymer. Based on the work reported in the present paper, the earlier estimated value of refractive index of PBZT was too low. Also, the thickness of the film used in the previous work was not 33 μm as reported there but only 12 μm. If we use the current measured refractive index value for PBZT films and also use the correct thickness, a proper estimate of $\chi^{(3)}$ from the data of reference 5 is $\sim 3 \times 10^{-11}$ e.s.u. Still, the optical quality of the previous films is an issue.

Efforts in the past have largely focused on finding polymeric structures with enhanced non-linear susceptibility $\chi^{(3)}$. However, the optical quality of the non-linear medium is of immense concern. Not only is excellent optical quality necessary from the device point of view, where extremely low optical loss is a requirement, but it is also of fundamental importance in regard to determining the intrinsic $\chi^{(3)}$ of a material. This point is demonstrated by the results of the study reported here which shows that $\chi^{(3)}$ of these improved optical quality films is higher than the previously reported value for this material. The improved quality films of PBZT for the present work were fabricated by extruding low concentration (below critical concentration) solutions in methane sulphonic acid. The experimental set-up and the procedure used for the present film fabrication were similar to those reported elsewhere for fabricating structural films[4]. The films, even though being extruded from an apparatus that was not designed for optical films, showed improvement in optical quality over those used in the previous measurement[5].

Novel guest-host composite films of PBZT were also prepared with this approach. Zytel 330, an amorphous nylon, 6F-PBO[6] and Lubrizol[7] have been used as the hosts. Among these composites, the PBZT/Zytel 330 composite films are of the best optical quality. This paper reports measurements of both linear refractive index and $\chi^{(3)}$ for PBZT and PBZT/Zytel composite films. The results show that the incorporation of an appropriate host component can produce a film with an enhanced figure of merit $\chi^{(3)}/\alpha$, where α is the total optical loss in the film.

EXPERIMENTAL

Film preparation

The chemical structures of PBZT and Zytel are shown in *Figure 1*. The PBZT sample had an intrinsic viscosity of 16 dl g^{-1} in methane sulphonic acid (MSA), corresponding to an average molecular weight of 27000. The amorphous nylon sample was obtained from DuPont (trade name Zytel 330). The critical concentration of PBZT in methane sulphonic acid was experimentally determined to be 3.6% by weight[7]. A 1% by weight solution in MSA was used. At this concentration the rod content was well below the critical concentration, but the viscosity was within the operational range of our film extrusion apparatus. In the composite film preparation, Zytel (1.5% by weight) and PBZT (1.5% by weight) were codissolved in MSA. The solution was stirred under dry nitrogen atmosphere until it was judged by visual inspection and optical microscopy to be homogeneous (usually after several days).

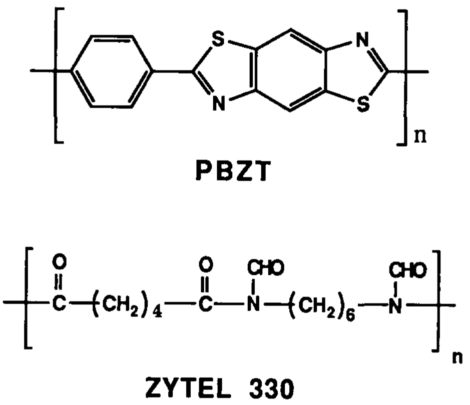

Figure 1 Chemical structures of PBZT and Zytel 330

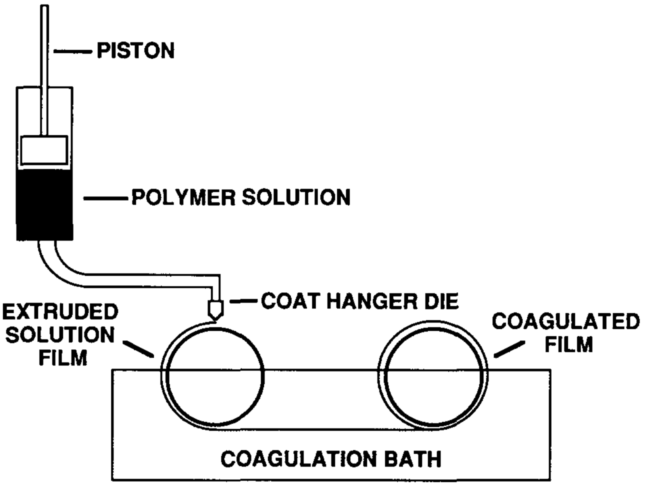

Figure 2 Schematic of the film extrusion–coagulation apparatus

The solution was transferred into the extrusion reservoir and was degassed under vacuum overnight. The schematic of the extrusion apparatus is shown in *Figure 2*. The solution was extruded through a coat hanger die with a slit dimension of 0.457 × 38.1 mm. The extruded film was coagulated in water. The film was left in water for several days to wash off the residual acid. Good optical quality sections of the film were selected for specimen preparation and drying. A ring mount configuration was selected for this study. The rings were glass collars made by cutting a ~19 mm diameter glass tube into sections. The wet film was mounted taut on a collar like a drum and air-dried at room temperature.

Measurement of refractive index

The refractive index of the ring-mounted films was determined from the optical transmission spectra recorded for each sample. Shimadzu spectrophotometers (model numbers UV-265FW and UV-3101PC) were used for recording the spectra. The wavelength range was limited by the absorption edge of the samples, near 500 nm, and by the longest wavelength available in the spectrophotometer, 3000 nm in the case of the UV-3101PC model. From the unpolarized beam the *s* component was selected using a Glan-Thompson calcite polarizer. The samples were oriented with a principal optical axis parallel to the electric field vector of the incident beam and the surface of the film was normal to the beam.

The transmission spectra revealed the extremes caused by the interference of the light at a particular wavelength. These interference fringes were used for calculating the refractive index of the film[8]. The thickness of the film was measured with a Shieffield Universal Slide Spectre profilometer (RLU model 1) and the results were used in the calculations of the refractive index and non-linear optical susceptibility, $\chi^{(3)}$.

Measurement of the third-order non-linear optical susceptibility, $\chi^{(3)}$

The degenerate four-wave mixing (DFWM) technique was used for the determination of $\chi^{(3)}$. This technique is described in detail elsewhere[9–12]. The DFWM experiment was performed in the standard phase conjugate geometry[13]. The film was aligned normal to the counter-propagating laser beams. Polarizations of all three beams were parallel and vertical to the incidence plane.

The laser system used for the study included an oscillator and an amplifier. The oscillator consisted of a cw mode-locked Nd–Yag laser (Spectra Physics model 3800). The pulses from the laser were compressed in a fibre optic pulse compressor (Spectra-Physics model 3690), frequency doubled in a KTP crystal, and used to pump a dye laser (Spectra-Physics model 375B). The pulses from the dye laser were amplified in a three-stage dye amplifier (Spectra-Physics model PDA-1) pumped by a 30 Hz nanosecond Nd–Yag laser (Quantum Ray Model DCR-2A). The amplified pulses were about 400 fs wide with the wavelength for the present study centred at 602 nm.

The effective $\chi^{(3)}$ value was calculated from the DFWM signal recorded for the polymer film, which was referenced to the signal recorded under the same condition for carbon disulphide. This method is described elsewhere[5,11,12]. An important assumption made in this analysis was that under the experimental conditions used, higher order interactions, such as multiphoton absorption processes, were not manifested. Often at very high intensities of laser pulses, the time-resolved response indicates an increasingly distinct long-lived signal, possibly due to the involvement of a non-instantaneous multiphoton absorption process. These circumstances were specifically avoided in our experiment by selecting the laser intensity within the range where no delayed response was observed.

RESULTS

Specimen quality

The specimens used for this study were selected on the basis of their optical quality. *Figure 3* shows a diagram of a typical good quality specimen. Four types of defect have been reported for this type of film[14]. They are:

(1) 20 μm voids;
(2) 1 μm particles;
(3) lines transverse to the extrusion direction;
(4) lines parallel to the extrusion direction.

However, in the films prepared for the present study, only three types of defect could be detected. The voids and the particles were present, but in very low density. There were extrusion direction lines present in the specimens, but no detectable transverse lines.

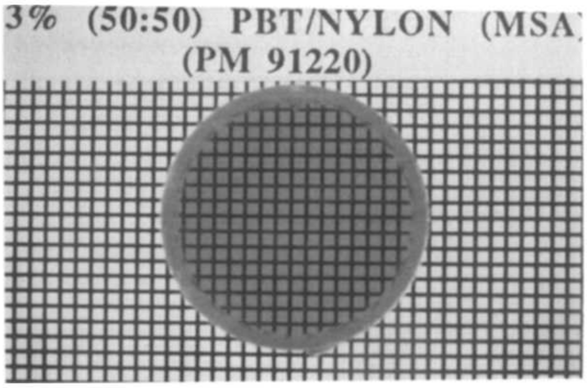

Figure 3 Diagram of a ring-mount sample with the transparent polymer film wrapped taut on a glass collar

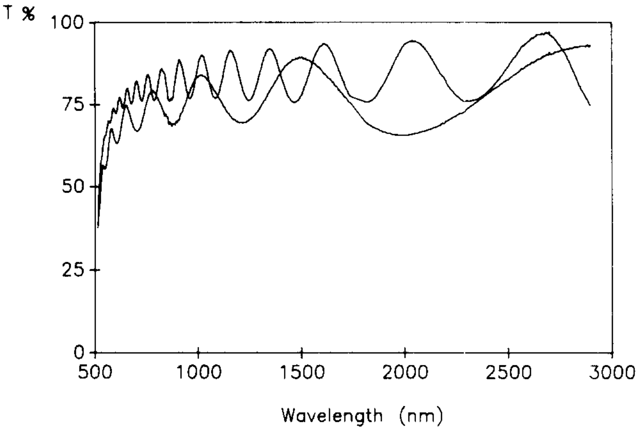

Figure 4 Transmission spectra of PBZT (lower curve), and PBZT/Zytel composite (upper curve)

Refractive index

Typical transmission spectra of the PBZT film and the PBZT/Zytel composite film are shown in *Figure 4*. Both films were birefringent, but only one spectrum of each sample is shown for illustration. We assumed negligible dispersion of the refractive indices within the long wavelength range above 1500 nm. The order of interference was estimated for the extremes (an integer for maxima and a half-integer for minima of the transmission spectrum), by applying the following equation:

$$2nd = m\lambda \qquad (1)$$

where n is the refractive index, d is the thickness of the film, λ is the wavelength at which the extreme is observed and m is the corresponding interference order. For example, the maximum at the longest wavelength for PBZT/Zytel was assigned as $m = 3$, whereas that for the PBZT film was $m = 1$. The consecutive maxima have the

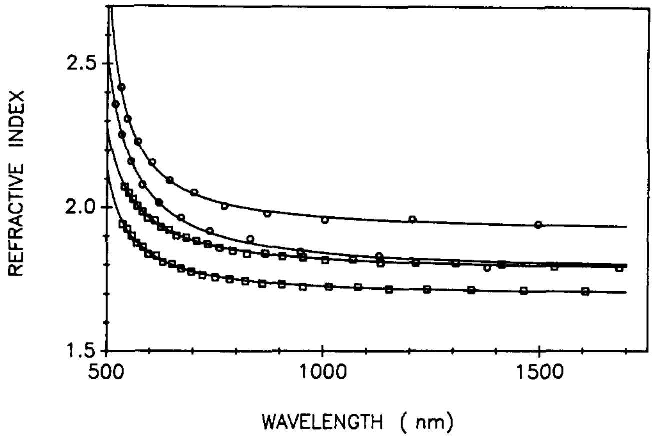

Figure 5 Refractive index as a function of wavelength for two principal directions in the polymer film: ○, PBZT film; □, PBZT/Zytel film

Table 1 Thickness, refractive index, optical loss and the third-order non-linear optical susceptibility, $\chi^{(3)}$, of free standing films of PBZT and its composite with Zytel 330

Sample	d (μm)	n	$\alpha \times 10^{-3}$ (cm^{-1})	$\chi^{(3)} \times 10^{10}$ e.s.u.
PBZT	0.77 (7)	2.16 (20) 2.04 (20)	5.2 (5) 4.7 (5)	4.5 (9) 3.3 (7)
PBZT/Zytel	2.35 (1)	1.98 (2) 1.83 (2)	1.2 1.2	2.0 (3) 1.2 (2)

The values in parentheses represent the estimated error

interference order incremented by one. Since the thickness of the sample was determined from an independent measurement, equation (1) was used for calculating the refractive index for all wavelengths, corresponding to the countable extremes. The dispersion curves, $n(\lambda)$, for PBZT and PBZT/Zytel samples, measured in two perpendicular directions, are shown in *Figure 5*.

The refractive indices for the wavelength $\lambda = 602$ nm were evaluated from the data shown in *Figure 4*, and they are collectively presented in *Table 1*. The table also contains the measured thicknesses of the films and an estimate of the optical loss, α.

Third-order optical non-linearity

Degenerate four-wave mixing experiments were performed on the polymer films and on liquid carbon disulphide as the reference. The film and the reference measurements were carried out under identical conditions (laser pulse duration, the intensity as well as the geometry of the arrangement). The intensities of the DFWM signal from the sample and the reference were recorded. These values were applied in the following formula to calculate the effective $\chi^{(3)}$:

$$\chi^{(3)}_{\rm eff} = (n/n_r)^2 \cdot d_r/d \cdot (I/I_r)^{1/2} \cdot A \cdot \chi^{(3)}_r \qquad (2)$$

where n is the refractive index, d is the thickness of the sample and I is the DFWM signal intensity. The corresponding parameters with subscript r refer to the reference, CS_2. Here we have used $\chi^{(3)}_r = 6.8 \times 10^{-13}$ e.s.u. as reported by Xuan *et al.*[15], $d_r = 0.2$ mm (the thickness of the cuvette containing the CS_2) and $n_r = 1.63$. The term A on the right hand side of equation (2) stands for the optical loss correction factor[9]:

$$A = \alpha d / [\exp(-\alpha d/2)(1 - \exp(-\alpha d))] \qquad (3)$$

where α is the total optical loss assumed to lead to an exponential decay of intensity in the sample (i.e. it obeys Beer's law). Additional parameters needed for equations (2) and (3) are listed in *Table 1*. The results of the calculations are shown in the last column of the table.

DISCUSSION

The values of the third order non-linear optical susceptibility, $\chi^{(3)}$, (*Table 1*), are surprisingly large compared with the value reported by Rao *et al.*[5]. The optical quality of the films used in this study is improved in terms of the loss parameter. This parameter contains not only scattering losses but also the absorption loss. Actually, in our experiment, the measured value refers to a preresonant condition since the wavelength used is near the band edge or within its exponential tail. Near an electronic resonance, the DFWM signal is derived from two types of non-linear response[9]; a coherent electronic $\chi^{(3)}$ which shows an instantaneous response (or limited by the laser pulse width) and an incoherent population grating diffraction which is non-instantaneous, its decay being determined by the excited state relaxation. Under the experimental conditions of our study we observe only instantaneous response (*Figure 6*) indicating that the non-linear response is derived from the coherent electronic $\chi^{(3)}$.

This large value of $\chi^{(3)}$ for the present film compared to that reported earlier[5] may be a result of improved optical quality of the films, which allows a better assessment of the intrinsic non-linearity of PBZT. Even though the optical loss correction factor A is supposed to correct for optical losses, it assumes that the loss obeys Beer's law. In these samples, where the predominant loss mechanism may be scattering due to inhomogeneities, the quantity A as described by equation (3) may not be adequate. Another possible cause for this difference between the present study and that of reference 5 may be associated with the possible residual MSA solvent in the present films, which can partially protonate PBZT. Theoretical calculation suggests that a protonated PBZT model compound has a higher second hyperpolarizability (microscopic third-order non-linear coefficient) than that of the unprotonated form[16]. The susceptibility of the protonated PBZT is currently being measured to confirm the theoretical prediction and to provide some insight on this issue.

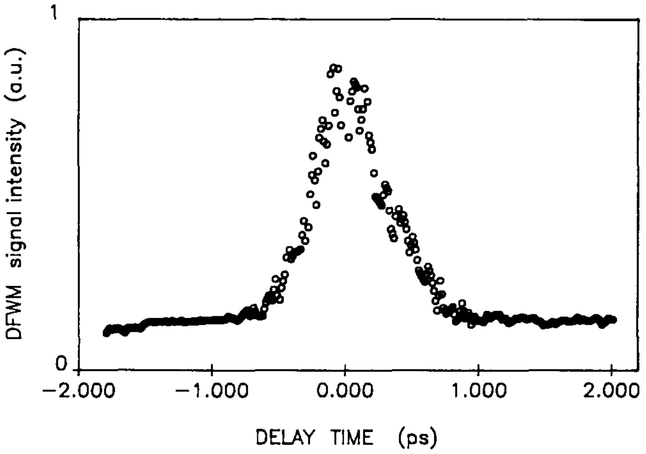

Figure 6 Time-resolved DFWM response from the PBZT film

The PBZT sample used in this study was from a batch used extensively for molecular composite studies. The structure was well characterized and its rod-like structure was confirmed by its ternary phase diagram[17]. The phase diagram agrees very well with the theoretical treatment of Flory[18]. Such data were not available for the PBZT sample used in the previous measurement[5]. Therefore it is not clear if any differences (e.g. molecular structure and/or molecular weight) between the two batches of polymers could be contributing to the discrepancy.

It is interesting to note that a biaxially oriented PBZT film*, recently prepared via polyphosphoric acid (PPA) in a way very similar to the film studied by Rao *et al.*[5], gave a $\chi^{(3)}$ value of 0.4×10^{-10} e.s.u. This value is in reasonable agreement with the corrected $\chi^{(3)}$ value using the previously reported data[5]. For PPA film processing, all the PPA solutions were above the critical concentration, in contrast to the MSA solutions used in the present study, where they were below the critical concentration. It is also possible that molecular packings in the films processed from these two types of solutions are different, possibly contributing to the difference in their $\chi^{(3)}$ values.

Considering the solution concentration, the viscosity and the shear rate used in the extrusion, the molecular orientations in the MSA films were expected to be much less ordered than in the PPA films. The $\chi^{(3)}$ ratio between the two optical axes are, however, not much different from that reported in reference 5.

The $\chi^{(3)}$ value for the molecular composite film, within experimental uncertainties, is consistent with that of the PBZT film. Because of the lower PBZT number density, the $\chi^{(3)}$ value of the composite is lower than that of pure PBZT. The advantage of the composite film can be illustrated when the figure of merit, $\chi^{(3)}/\alpha$ is considered. The PBZT film has a value of $\chi^{(3)}/\alpha = 0.86 \times 10^{-13}$ e.s.u. cm^{-1}, while that of the PBZT/Zytel is about 1.67×10^{-13} e.s.u. cm^{-1}. As pointed out previously, α is not merely due to molecular absorption; defects in poor optical quality films can increase α by scattering. The difference between the α values of the PBZT film and the composite film can only be attributed to differences in their optical qualities. The flexible nature of the nylon molecule has provided a host medium that enables a more optically homogeneous dispersion (not necessarily molecular dispersion) of the rods in the coagulated films. The optical qualities of these films have definitely been improved through processing via the present approach. It is recognized that there is much room for improvement. If the optical quality of the films is a contributing factor for the discrepancy of the $\chi^{(3)}$ values between this study and the previous one[5], then it is not clear if the measured $\chi^{(3)}$ value in this study truly represents the intrinsic third-order non-linearity of PBZT.

CONCLUSION

This paper reports a new $\chi^{(3)}$ value for PBZT which is an order of magnitude higher than the previously reported value. The films used in this study were processed via MSA solutions below the critical concentration. The resultant films are of much better optical quality than the film used in the previous study[5]. The possible sources of this discrepancy are still under investigation, but the importance of processing considerations in the development of $\chi^{(3)}$ polymers is evident from the results of this study. The composite film has a slightly lower $\chi^{(3)}$ value because of the lower number density of PBZT, but the improvements achieved by the reduction in optical loss can sufficiently offset the difference and yield a film with a better $\chi^{(3)}/\alpha$ ratio, which is an important parameter for device consideration.

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