Nonlinear optical figures of merit of processible composite of poly(2-methoxy,5-(2′-(ethyl)hexyloxy)-*p*-phenylene vinylene) and poly(methyl methacrylate)

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We report ultrafast nonlinear optical figures of merit for a highly processible guest–host blend of poly(2-methoxy,5-(2′-(ethyl)hexyloxy)-*p*-phenylene vinylene) with poly(methyl methacrylate). Our experiments employ 120 fs pulses at 840 nm and are designed to eliminate slow thermal nonlinearity and focus exclusively on ultrafast electronic nonlinearity. We report a two-photon absorption coefficient β of 1.5 ± 0.2 cm/GW, a nonlinear refraction coefficient n_2 of $-(2.1\pm0.2)\times10^{-13}$ cm^2/W and a two-photon figure of merit T of 0.6. The blend hybridizes the desirable features of nonlinearity and processibility of its two constituents to provide (1) ultrafast response one to two orders of magnitude faster than achievable in electronic switching devices; (2) a two-photon figure of merit compatible with harnessing this nonlinearity in a practical optical device geometry; and (3) a materials system and processing methodology compatible with spin-coating and photopatterning in an ambient environment. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1420760]

Nonlinear optical materials provide a basis for optical switching, modulation, and limiting. Since photons are essentially noninteracting *in vacuo*, nonlinear materials are needed for one optical signal to influence another, providing a generalized basis for all-optical signal processing. If femtosecond ultrafast nonlinearities can be harnessed, the resulting device speeds may provide orders of magnitude improvement over what can be achieved even prospectively in the electronic domain.

Nonresonant third-order nonlinearity, wherein refractive index depends near-instantaneously on the local intensity of light, has attracted significant attention in this regard, including in π-conjugated polymers.[1–13] Such materials may exhibit promising nonresonant nonlinear coefficients and may in certain cases be highly processible. They may be deployed in organic or inorganic guest–host systems. As such they offer the opportunity to combine desirable properties processibility, speed and strength of response, extent of absorption, photopatternability, and spectral features to achieve a material designed and deployed to meet the specifications of a particular application.

Poly(*p*-phenylene vinylene) (PPV) and its derivatives have received particular attention across the field of photonics as a result of demonstrations of both efficient electroluminescence and an appreciable ultrafast optical nonlinearity.[1–6,8–11,13–15] However, PPV is insoluble. Thin films are thus typically prepared by thermal conversion of a soluble nonconjugated intermediate, or precursor, polymer. This presents a major challenge in deploying PPV in such a way to obtain optical quality, highly transparent films required for optical waveguiding. PPV semicrystalline regions formed during conversion of the precursor polymer, for example, result in appreciable scattering of light out of an intended single mode.[4,5]

One prospective way to combine the promising nonlinear properties of PPV with suitable processibility and linear properties is to prepare composites of PPV within suitably-chosen host materials.[3–5,10,11,16] We report herein results of our investigations into the guest–host polymer blend poly(2-methoxy,5-(2′-(ethyl)hexyloxy)-*p*-phenylene vinylene) (MEH-PPV) with a poly(methyl methacrylate) (PMMA) host. We selected as dopant MEH-PPV since it is a soluble derivative of PPV with lower intrinsic absorption than PPV.[6] PMMA is a good candidate for the host material since it is amorphous and has good optical transparency and is readily processible into films. In the present work, we focus on an MEH-PPV/PMMA polymer blend containing 0.2 wt % MEH-PPV. For the composite material we obtain a nonlinear Kerr coefficient $n_2=-(2.1\pm0.2)\times10^{-13}$ cm^2/W, nonlinear absorption coefficient $\beta=1.5\pm0.2$ cm/GW, and two-photon figures of merit 0.6 for ultrafast electronic non-

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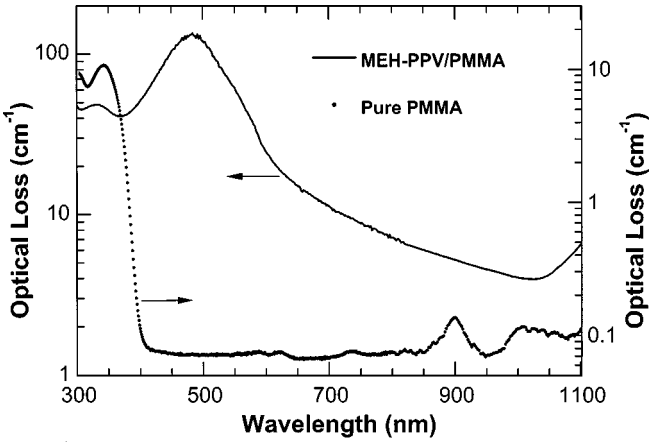

FIG. 1. Linear absorption spectra of pure PMMA (dotted) and MEH-PPV/PMMA composite (solid line).

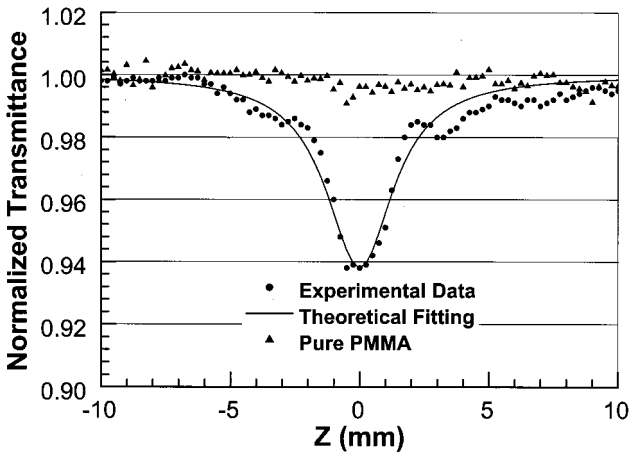

FIG. 2. Normalized open-aperture *Z*-scan transmittances of MEH-PPV/PMMA (circles) and pure PMMA (triangles) film samples using 120 fs pulses at $\lambda = 840$ nm. The solid line is a theoretical fitting.

linearity probed using 120 fs pulses centered at 840 nm.

PMMA and MEH-PPV were separately dissolved in pyridine. These two solutions were then combined and stirred for 20 min. The homogeneous pink solution was evaporated to remove most of the solvent and the concentrated solution was then poured into a mold with a Teflon™ substrate. The sample was dried at room temperature overnight and subsequently in an oven at 70 °C for 10 h to remove the pyridine. The sample was then passed into films at 140 °C and slowly cooled to room temperature to avoid the shrinkage of the films. The weight ratio of MEH-PPV to PMMA was 0.2% throughout the present work. The thickness of the composite film was 0.2 mm.

The MEH-PPV/PMMA composites were characterized for linear optical loss using a Cary 500 UV-VIS-NIR spectrophotometer. The nonlinear properties of the films were measured using amplified pulses from a Coherent MIRA 900 femtosecond Ti:Sapphire laser at 840 nm. Autocorrelation results indicated a pulse width of 120 fs. In order to ensure that fast electronic nonlinear optical effects were observed rather than slow thermo-effects, a MEDOX Pockels cell was used to provide an output pulse repetition rate of 5 kHz. The laser beam was focused onto the sample using a lens of focal length $f = 100$ mm. The beam profiles at the sample surface were measured to have $1/e^2$ diameter of 39–49 μm. An aperture with linear beam transmittance $S = 0.1$ was used for all closed-aperture measurements.

The linear optical losses, including both absorption and scattering, are shown in Fig. 1 for both MEH-PPV/PMMA composites and pure PMMA. For the composite, a peak is evident near 485 nm with peak absorption value 135 cm^{-1}. Above 600 nm, the optical loss gradually decreases to a minimum near 1050 nm. For the purposes of the present work, the pertinent wavelength for loss measurements is 840 nm, the wavelength at which nonlinear experiments were carried out and linear loss was found to be 6.2 cm^{-1}. In contrast, pure PMMA is essentially transparent from 380 to 1100 nm. A small peak around 900 nm results from C–H overtones.[17] The absorption spectrum of MEH-PPV/PMMA exhibits similar features to those of pure MEH-PPV.[6,18]

Figure 2 shows the result of a single-beam open-aperture *Z*-scan measurement at 840 nm for MEH-PPV/PMMA composites and pure PMMA. The laser intensity at the focal point is calculated to be 6.12 GW/cm^2. The calculation is made using the expressions of Sheikh-Bahae *et al.*[19] Multiphoton absorption from pure PMMA is not observed in Fig. 2. As seen in Fig. 1, PMMA is transparent down to 380 nm, so only weak three-photon absorption could contribute to nonlinear processes at 840 nm. The normalized transmittance from MEH-PPV/PMMA composites exhibits an almost symmetric valley with respect to the focus ($Z = 0$), which is the character of the nonlinear absorption from multiphoton absorption.[19]

For the pure MEH-PPV material, thee is an absorption peak around 500 nm. The observed nonlinear absorption is thus from the two-photon absorption due to MEH-PPV and not from PMMA. For a small third-order nonlinear loss and for a Gaussian temporal shape pulse, the normalized transmittance can be described by[20]

$$T(Z) = 1 - \frac{\beta I_0 L_{\text{eff}}}{2\sqrt{2}} \frac{1}{1 + Z^2/Z_0^2},$$

where β is the two-photon absorption coefficient, $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, with L the sample thickness, α the linear absorption coefficient, and $Z_0 = \pi u_0^2/\lambda$ with u_0 the beam radius at focal point. At 840 nm, $L_{\text{eff}} = 0.19$ mm. A theoretical fitting to the experimental data is shown in Fig. 2. From the fitting we obtain $\beta = 1.5 \pm 0.2$ cm/GW and $w_0 = 21$ μm. w_0 is in agreement with beam profiler measurements.

The nonlinear refractive index n_2 was obtained from closed-aperture *Z*-scan measurements. To obtain the refractive nonlinearity in the presence of two-photon absorption, the closed-aperture scan was first divided by the open-aperture scan. The result is shown in Fig. 3. The experimental data were fitted to the expression given by Sheik-Bahae *et al.*,[19] which relates the normalized transmittance $T(Z, \Delta\phi_0)$ directly to phase change $\Delta\phi_0$,

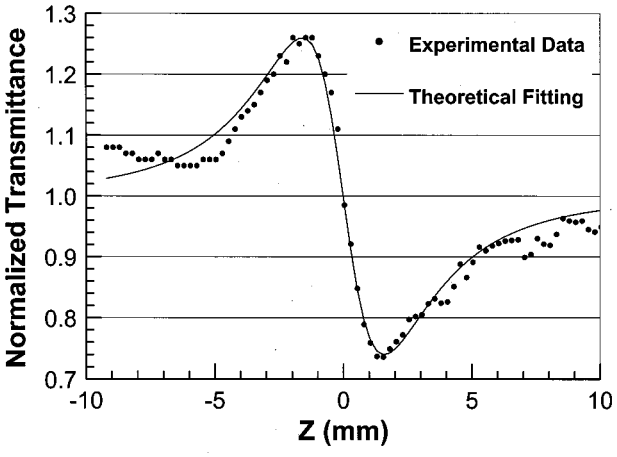

FIG. 3. Normalized closed-aperture ($S=0.1$) Z-scan transmittance of 0.2 mm thick MEH-PPV/PMMA film sample using femtosecond pulses at $\lambda=840$ nm with $I_0=6$ GW/cm^2. The open-aperture scan was subtracted. The solid line is a theoretical fitting.

$$T(Z,\Delta\phi_0)\approx 1+\frac{4\Delta\phi_0 x}{(1+x^2)(9+x^2)},$$

where $x=Z/Z_0$. Nonlinear least-squares fitting with $\Delta\phi_0$ and Z_0 as parameters yielded $\Delta\phi_0=-1.28$ and $Z_0=0.001\,84$. From the relation $\Delta\phi_0=2\pi\Delta n L_{\text{eff}}/\lambda$, we obtain refractive index change at the focal point of $\Delta n=-9.02\times10^{-4}$ and Kerr coefficient $n_2=-(2.1\pm0.2)\times10^{-13}$ cm^2/W. From Z_0, the beam size at the focus point is calculated to be 44 μm in good agreement with the beam profiler measurement. More rigorous calculation including the correction from the aperture size $S=0.1$ gives the same n_2 value to within 5% uncertainty.[19] The negative sign in n_2 indicates that the material has a defocusing nonlinearity. This is consistent with the fact that the laser wavelength sits between the one- and two-photon absorption edges of MEH-PPV.

For a third-order nonlinear material to provide a useful phase change before it is substantially absorbed, it is essential that the two-photon figure of merit $T=\beta\lambda/n_2$ be less than 1. The results reported above indicate that the 0.2% MEH-PPV/PMMA composite has figure of merit of 0.6 at 840 nm for 120 fs pulses.

The one-photon figure of merit, W, is defined as $W=\Delta n/\alpha\lambda$, where α is the absorption coefficient. For $\Delta n=9.02\times10^{-4}$, $\alpha=6.2$ cm^{-1}, and $\lambda=840$ nm, the figure of merit $W=1.7$. The value of W is promising but marginal. We note that the absorption measured includes all sources of loss, both intrinsic and extrinsic, and that it may be possible to reduce extrinsic loss (e.g., scattering due to sample inhomogeneities). Thus, unlike the more fundamental figure of merit T, which for the material presented herein is good for nonlinear device performance, the figure of merit W has a substantial technological component susceptible to further optimization.

It is worthwhile to compare these results with those obtained for pure MEH-PPV and PPV materials. Samoc *et al.*[1] have obtained $n_2\geqslant10^{-11}$ cm^2/W and a nonlinear absorption coefficient β of 80 cm/GW at 800 nm, yielding $T\leqslant0.6$, measured by degenerate four-wave mixing for the pure PPV materials (sign of n_2 has not been determined). The same group[2] also reported Z-scan measurements at 800 nm on MEH-PPV in solution. The value of n_2 has been determined from the slope of the n_2-versus-concentration dependence, as the authors have mentioned, which in principle is substantially different from the value of n_2 for the pure material in the solid phase. They obtained $n_2=-2.1\times10^{-12}$ cm^2/W, $T=4.7$ for MEH-PPV measured in THF and $n_2=-3.4\times10^{-12}$ cm^2/W, $T=4.2$ for MEH-PPV measured in $CHCl_3$.

In summary, a guest–host MEH-PPV/PMMA polymer blend was synthesized and its linear and nonlinear optical properties were investigated with a goal of controlling its optical properties for a practical application. Third-order nonlinear optical properties were measured by the single-beam Z-scan technique at 840 nm using 120 fs pulses in the ultrafast electronic nonlinear regime.

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