

Third-order optical nonlinearities of a polymeric film doped with a novel zwitterion, DEMI-3CNQ

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ABSTRACT. We report the use of the z-scan technique with 15 ps duration pulses at 532 nm, to measure the optical nonlinearity in a polymer film containing a novel zwitterionic molecule in dispersion. The DEMI-3CNQ zwitterion was formed by a heat-induced reaction of the components of the TEA(TCNQ)₂ charge-transfer salt contained in a PMMA matrix. We have found a bleaching nonlinearity with a saturation irradiance $I_s = 1.5 \text{ GW cm}^{-2}$ and an associated nonlinear refractive index $n_2 = +7.0 \times 10^{-3} \text{ cm}^2 \text{GW}^{-1}$. The potential of this material for optical switching applications is discussed using the relevant figures of merit.

RESUMEN. En este trabajo se reporta el uso de la técnica conocida como *barrido en z* para medir la respuesta óptica no-lineal de una película polimérica que contiene un *zwitterion* novedoso en dispersión, usando para ello pulsos de 15 ps de duración a 532 nm. El *zwitterion* DEMI-3CNQ se formó mediante la reacción térmicamente inducida de los componentes de la sal TEA(TCNQ)₂, un compuesto de *transferencia de carga*, contenido en una matriz de PMMA. Encontramos que la respuesta no-lineal es de absorción saturable, con una irradiancia de saturación $I_s = 1.5 \text{ GW cm}^{-2}$ y un índice de refracción no-lineal $n_2 = +7.0 \times 10^{-3} \text{ cm}^2 \text{GW}^{-1}$. El potencial de este material para su uso en aplicaciones de conmutación óptica se discute usando los parámetros de bondad relevantes.

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1. INTRODUCTION

The study of the third-order nonlinear optical properties of organic materials for their potential application in optical information devices has been a very active field in the recent past. The required material characteristics for such an application are a large nonlinearity, a fast response time and sufficiently low linear and nonlinear absorption. In the past, the strong delocalization of π electrons in π -conjugated materials has yielded the largest $\chi^{(3)}$ known values for organic materials. Although π -conjugated materials fulfill some of the requirements, their high nonlinear absorption usually limits their practical applications. One

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recently proposed alternative [1] is to use materials with large intermolecular electronic polarizations, such as the charge-transfer (CT) complexes formed by salts of the tetracyanoquinodimethane (TCNQ) and tetracyanoethylene (TCNE) donor molecules. Indeed, the third-harmonic generation (THG) efficiency at wavelengths around $2\mu\text{m}$, has been shown to be several times larger for perylene/TCNE in crystalline form than for the conjugated material poly-[2,4-hexadiyn-1,6-diol-bis(*p*-toluenesulfonate)] (pTS), which is known as one of the most nonlinear organic materials [2]. However, the nonlinear coefficient measured by the THG technique, $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$, is not relevant for single wavelength nonlinear information processing. The degenerate four-wave mixing (DFWM) technique has also been applied to Pe/TCNE solutions in near-resonance conditions [3], and to the salts of the charge-transfer complex bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) [4,5]. The resonant $|\chi^{(3)}(-\omega; \omega, -\omega, \omega)|$ for the BEDT-TTF salts measured using DFWM were large ($\sim 2 \times 10^{-8}$ esu, or 2.8×10^{-16} m²V⁻² in SI units, with $\alpha = 3 \times 10^3$ cm⁻¹ [5]). However, the nonlinear refractive index, directly proportional to the real part of $\chi^{(3)}$, is of interest for all-optical switching applications, and it cannot be determined from DFWM results alone.

These results showed that charge-transfer compounds could in principle find potential in all-optical switching applications, but that a study of the relative contributions of the real and imaginary parts of $\chi^{(3)}$ to the nonlinearity was required to properly assess the applicability of the materials. Therefore, the present work uses the beam distortion technique known as *z*-scan [6] with picosecond pulses at 532 nm to study the nonlinear response of a poly(methyl methacrylate) (PMMA) film doped with a zwitterionic molecule formed from the components of the triethylammonium TCNQ salt, TEA(TCNQ)₂. Previous on-resonance studies of this compound [7], with a sub-picosecond laser source, tuneable around 715 nm, showed a fast nonlinearity with two decay times, 6 and 75 ps. However, the nonlinearity was dominated by $\text{Im}\chi^{(3)}$, rendering the material unsuitable for all-optical switching applications at that wavelength. By moving away from resonance, the $\text{Re}\chi^{(3)}/\text{Im}\chi^{(3)}$ ratio could, in principle, be improved, hence the use of the 532 nm wavelength in the present experiments. The *z*-scan technique was chosen to properly resolve the contribution of both the refractive and absorptive parts of the nonlinearity. The structure of this report is as follows: in Sect. 2 the sample preparation procedure is described, and a brief discussion on its resulting composition is made. Section 3 presents the *z*-scan experimental results obtained for the sample, together with the data analysis employed to extract its nonlinear coefficients. Section 3 presents an evaluation of the potential of the nonlinearities found for the material in all-optical switching applications, using for this purpose the relevant figures of merit. Finally, the conclusions of this work are presented in Sect. 5.

2. SAMPLE PREPARATION

The film was prepared from a solution of the organic conductive salt, TEA(TCNQ)₂ and PMMA in acetonitrile, by substrate withdrawal from the solution. The concentration of TEA(TCNQ)₂ was 1.5 % (weight on weight) with respect to PMMA. The resulting green film was heat-treated above the glass transition temperature of the polymer (at 150°C)

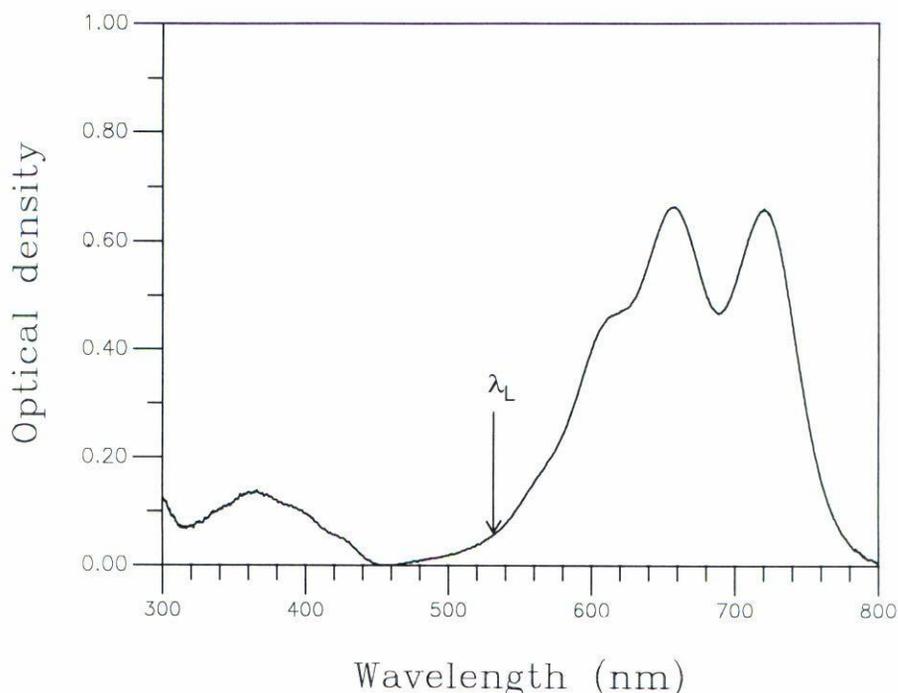


FIGURE 1. (DEMI-3CNQ)-doped PMMA film absorption spectrum.

to yield a film of blue colouration whose spectrum is given in Fig. 1. The purpose of the heat treatment was to try to produce micro-crystallites of the TCNQ salt embedded in the polymer film, in order to observe quantum confinement effects on the nonlinear response of the sample. While it is not clear whether such effects will become apparent in small crystals of this organic semiconductor, there is great value in achieving micro-crystallite dispersions where Rayleigh scattering is insignificant but where the nonlinearities remain high on- or near-resonance. However, it has recently been found that heat treatment of $\text{TEA}(\text{TCNQ})_2$ in solid or liquid solution results in the formation of a highly dipolar novel molecule [8]. The heat-induced reaction between the TCNQ and TEA ions results in the formation of the zwitterionic enamine DEMI-3CNQ, shown in Fig. 2. The structure of this molecule has been unequivocally verified by X-ray crystallography, mass spectrometry and elemental analysis. Similarly to other zwitterionic donor-acceptor derivatives of TCNQ [9], DEMI-3CNQ is characterised by a very distinctive broad charge-transfer absorption band in the visible part of the spectrum. The absorption band with two maxima and a slight shoulder observed in the heat-treated film, shown in Fig. 1, correlates very well with the spectrum of DEMI-3CNQ, leading to its identification as the species found in the film.

3. EXPERIMENTAL RESULTS

The z-scan technique is based on the observation of the change in the far field pattern of a focused gaussian beam due to distortion (caused by the nonlinear response of the sample)

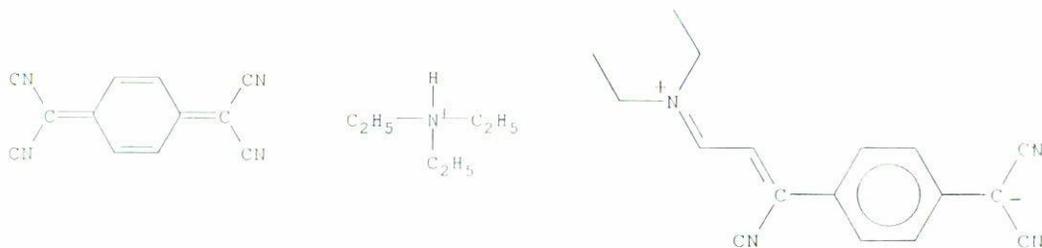


FIGURE 2. Molecular structure of 7,7,8,8-tetracyanoquinodimethane (TCNQ) (a), triethylammonium (TEA) ion (b), and the reaction product, the DEMI-3CNQ zwitterion (c).

when the sample is scanned through the focal plane, along the optical axis. A detector gathering all the transmitted light will detect changes due to the change of nonlinear absorption with position, whereas an apertured detector will detect changes in transmittance due to both the changes in nonlinear absorption and refraction. Therefore, by using this technique, we were able to determine the absorptive and refractive contributions to the nonlinearity of the sample, including their sign.

The experimental set-up for the z -scan technique is shown schematically in Fig. 3. The second harmonic of a passively mode-locked Nd:YAG laser was used to provide pulses of 15 ps (HW1/eM) duration at 532 nm with a 5 Hz repetition rate and with energies of up to 500 μ J to perform the experiments. The Gaussian beam laser output is focused at $z = 0$ to a spot size ω_0 of 35 μ m (HW1/eM), resulting in a beam with a diffraction length (Rayleigh range) $z_0 = 7$ mm. A scan of the sample position through the focal plane, along the optical axis, is made. The signal of a detector (D_2) in the far field, placed behind a finite aperture is recorded as a function of the sample position z . The use of a beam splitter makes it possible to detect the signals from the apertured and a non-apertured detector D_3 , sensitive to absorption changes only, to be recorded simultaneously, as shown in Fig. 3. Figure 4 shows the experimental open aperture z -scan results, and Fig. 5 the closed aperture results obtained for the present sample. Each point is an average taken over 15 pulses with energies contained within a 10% range around the nominal energy value. The fact that in the open aperture results, the observed sample transmittance is higher for positions near the focal plane of the beam, is indicative of a bleaching nonlinearity, *i.e.* one where the absorption is saturated. On the other hand, the closed aperture results show the signature of a positive n_2 , a prefocal transmittance minimum (valley) followed by a post-focal transmittance maximum (peak).

The saturation of absorption observed can be accounted for using the simple phenomenological model for the irradiance-dependent absorption coefficient $\alpha(I)$ given by [10]

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_s}, \quad (1)$$

where α_0 is the linear absorption coefficient, and I_s is the saturation irradiance of the sample. When the sample is located at a distance z from the focal plane of the beam, the output irradiance $I(z' = L; z, r, t)$ at the exit plane of the film is obtained by integrating the evolution equation for the irradiance, $dI/dz' = -\alpha(I)I$, where z' is a coordinate along

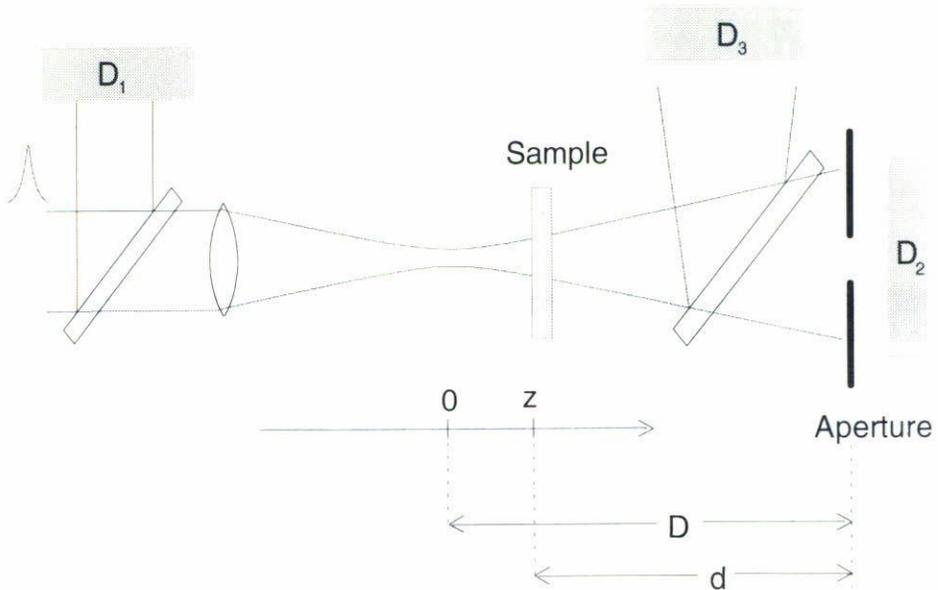


FIGURE 3. Experimental set-up for the z-scan measurements. Detector D_1 is used to discriminate pulses within the desired energy range, detector D_2 is sensitive to nonlinear absorption and refraction changes, and detector D_3 is sensitive to nonlinear absorption changes only.

the sample, over the sample length L . The result of this integration is given by

$$\ln \frac{I(L; z, r, t)}{I(0; z, r, t)} = -\alpha_0 L - \frac{I(L; z, r, t) - I(0; z, r, t)}{I_s}, \quad (2)$$

where $I(0; z, r, t)$ is the input irradiance, which is assumed to be a Gaussian in the traverse direction r . The open aperture z-scan is obtained by solving Eq. (2) numerically and integrating over r and t to obtain the normalized transmittance $T(z)$ for each z position. Figure 4 shows the best fit to the experimental open aperture z-scan data, obtained using Eq. (2) with $I_s = 1.5 \text{ GWcm}^{-2}$ and where the value of the linear absorption coefficient $\alpha_0 = 360 \text{ cm}^{-1}$ was used.

We found that in order to model the closed-aperture z-scan results obtained, we needed to take into account the saturation of the induced refractive index change Δn . This is done by considering [11]

$$\Delta n(I) = n_2 \frac{I}{1 + I/I_s}, \quad (3)$$

which in the limit $I/I_s \rightarrow 0$ reduces to $\Delta n \simeq n_2 I$, with n_2 the usual third-order nonlinear refractive index. The nonlinear phase change $\Delta\phi_{\text{NL}}(z'; z, r, t)$ as a function of z' position within the sample is given by [12]

$$\frac{d\Delta\phi_{\text{NL}}}{dz'} = \frac{2\pi}{\lambda} \Delta n(I), \quad (4)$$

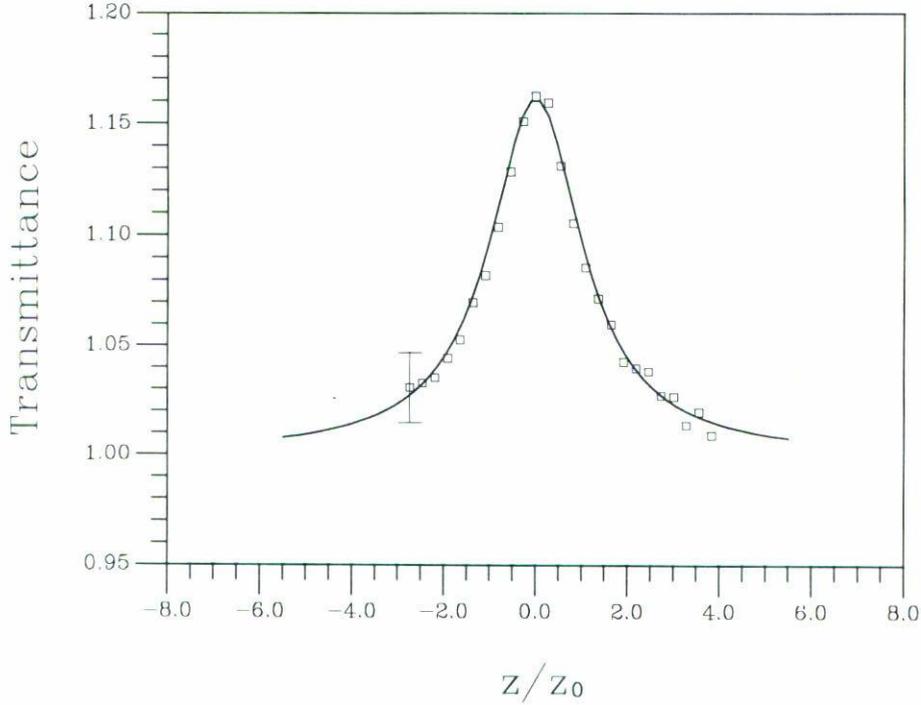


FIGURE 4. Open aperture z-scan results for the (DEMI-3CNQ)-doped PMMA film, z_0 is the Rayleigh range of the focused beam. The data was taken for a pulse energy of $1.5 \mu\text{J}$. The transmittance is normalized to the linear transmittance of the sample. The solid line shows the fitting made using Eq. (2) with $I_s = 1.5 \text{ GWcm}^{-2}$.

with $\Delta n(I)$ given by Eq. (3). The total nonlinear phase change $\Delta\phi_{\text{NL}}(L; z, r, t)$, in the external self-focusing approximation, *i.e.*, when the effect of induced phase changes on beam propagation inside the sample is negligible [12], will be obtained by integrating Eq. (4) over the sample length L :

$$\Delta\phi_{\text{NL}}(L; z, r, t) = \frac{2\pi}{\lambda} n_2 \int_0^L \frac{I(z')}{1 + I(z')/I_s} dz', \quad (5)$$

where $I(z')$ is given by Eq. (2) evaluated at z' , instead of L . The electric field at the apertured detector plane, situated a distance D from the focal plane, $E_{\text{ap}}(z + d, r, t)$ is calculated using the Huygens-Fresnel formalism [12]

$$E_{\text{ap}}(z + d, r, t) = \frac{2\pi}{\lambda} \exp\left(\frac{i\pi r^2}{\lambda d}\right) \int_0^\infty r' dr' E_{\text{out}}(z, r', t) \exp\left(-\frac{i\pi r r'^2}{\lambda d}\right) J_0\left(\frac{2\pi r r'}{\lambda d}\right), \quad (6)$$

where $E_{\text{out}}(z, r, t) \propto \sqrt{I(L, z, r, t)} \exp(i\Delta\phi_{\text{NL}}(L; z, r, t))$ is the electric field at the sample exit face, and J_0 is the zeroth-order Bessel function. Finally, the apertured detector transmittance $T(z)$ is obtained by integrating $I_{\text{ap}} \propto |E_{\text{ap}}(z, r, t)|^2$ up to the aperture radius r_{ap}

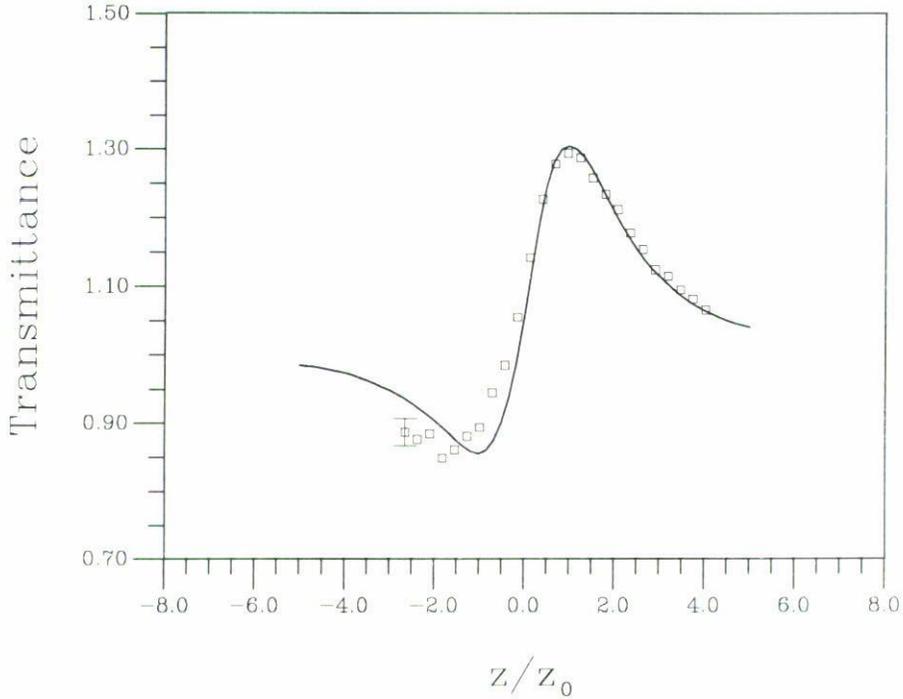


FIGURE 5. Closed aperture z -scan results for the (DEMI-3CNQ)-doped PMMA film. The aperture linear transmittance was $S = 0.19$. The transmittance is normalized to the linear transmittance of the sample. The solid line shows the fitting made using Eq. (6) with $n_2 = +7.0 \times 10^{-3} \text{ cm}^2\text{GW}^{-1}$.

given through $S = 1 - \exp(-2r_{\text{ap}}^2/\omega^2(D))$, where S is the linear aperture transmittance and $\omega(D)$ is the beam spot-size in the aperture plane in the absence of the sample. Figure 5 shows the theoretical fitting to the closed-aperture data using the I_s value obtained from the open aperture data analysis and $n_2 = +7.0 \times 10^{-3} \text{ cm}^2\text{GW}^{-1}$.

4. DISCUSSION OF RESULTS

There are two potential regimes for optical switching. In the off-resonance (transparency) regime the nonlinearity is due to weak, virtual-transition processes and switching may be prevented if two-photon absorption is significant or if insufficient refractive index changes are achievable. In the near-resonance regime considerably higher nonlinearities are expected, due to real excitation, but either the high linear absorption or any induced absorption may prevent switching. Here we investigated the near-resonance regime, on the short-wavelength tail of the dominant 715 nm absorption band. The nonlinear absorption proves to be a bleaching one, which is not detrimental to switching and the linear absorption is an order of magnitude below the peak value $\alpha_0\lambda \sim 0.02$.

In order to assess the usefulness of a material in all-optical switching applications, a series of figures of merit have been defined [13, 14]. For a saturable refractive index change,

the relevant figure of merit is W defined through

$$W = \frac{\Delta n_{\text{sat}}}{\lambda \alpha_0} = \frac{n_2 I_s}{\lambda \alpha_0}. \quad (7)$$

Depending on the actual switching geometry intended, the W value has to exceed a given value for a material to be of practical use, for example, a half beat-length nonlinear directional coupler requires $W > 1$ [13], while a nonlinear Fabry-Perot resonator only requires $W > \sqrt{3}/2\pi$ [15]. From the present measurements, we found $W = 0.51$, marginally smaller than the required minimum value for a nonlinear directional coupler, but large enough for the material to be used in a nonlinear Fabry-Perot. Another figure of merit frequently used to compare different materials is F given by $F = n_2/(\alpha_0\tau)$, where τ is the response time of the nonlinear medium. There is no required minimum F value, but its magnitude is inversely proportional to the energy density required to achieve switching in a Fabry-Perot configuration [15]. Therefore, a larger F value implies a lower switching energy density is required. As it was mentioned before, previously reported [7] DFWM studies carried on the same sample with subpicosecond pulses at 712 nm, showed a nonlinear response composed of two lifetimes, $\tau_1 = 7$ ps, and $\tau_2 = 75$ ps.

For the DEMI-3CNQ-doped film $F = 2.6 \times 10^{-4} \text{ cm}^3/\text{J}$, where we have used $\alpha_0 = 360 \text{ cm}^{-1}$ and the longest lifetime of 75 ps was also used. For comparison, near-resonance measurements on the pTS polydiacetylene, which is one of the best π -conjugated materials known, give $F = 2 \times 10^{-2} \text{ cm}^3/\text{J}$ [2], and recent results for another polydiacetylene, 9-BCMU report $F = 0.19 \text{ cm}^3/\text{J}$ at $\lambda = 642 \text{ nm}$ [16]. Although the F value for pTS is two orders of magnitude larger than that of our sample, its linear absorption is considerably higher ($\alpha \sim 10^4 \text{ cm}^{-1}$) than that of the DEMI-3CNQ-doped sample, and it also presents a strong induced absorption ($\text{Im } \chi^{(3)} = 5 \times 10^{-8} \text{ esu}$), that can limit its applicability. The 9-BCMU results were taken in a wavelength region where induced absorption effects are negligible, and where linear absorption is moderately high. It follows that the small F value obtained for the present sample would imply a switching energy considerably larger than that required for pTS or 9BCMU, but in a regime of relatively low linear absorption and in the absence of increased nonlinear absorption.

5. CONCLUSIONS

We have used the z-scan technique to study the near-resonance nonlinear optical properties of a PMMA film doped with a novel zwitterionic compound, DEMI-3CNQ. We found a bleaching nonlinearity and measured the associated saturation irradiance and nonlinear refraction, including its sign. We observed that the nonlinear refraction saturates as well, and estimated the maximum refractive index change achievable. The measured index change was large enough to allow switching in a Fabry-Perot configuration without being limited by linear absorption, as expressed in the figure of merit W . However, when the figure of merit F is compared with that for other materials, it is clear that a relatively high switching energy would be needed, limiting the potential of this material for practical all-optical switching applications. Both figures of merit can in principle be increased by using

a wavelength closer to the absorption maxima, just before $\text{Im } \chi^{(3)}$ becomes the dominant contribution, as it happens at exact resonance. To clarify this point, a systematic study of the nonlinearity with a tunable laser source is needed.

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