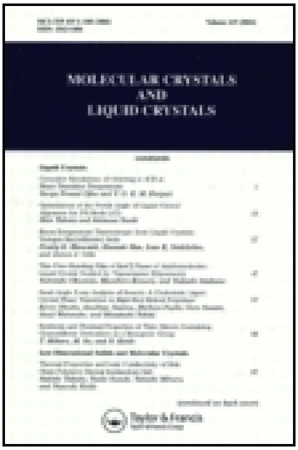

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# Competitive Optical Nonlinearities and Photoinduced Transformation of Epoxy Polymer Based on Diglicidyl Ether of Bisphenol A

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We have studied competitive optical nonlinearities – excited state absorption (ESA), absorption saturation (SA) and two-photon absorption (TPA) – of epoxy polymer based on diglicidyl ether of bisphenol A with picosecond Z-scan technique at 532 nm. The complexity of the analysis was dealt with problem of the selection of the part of Z-scan curve which corresponds to the dominant contribution of the proper nonlinear mechanism on the background of competitive others. The TPA coefficient is $\beta$=4.0±0.5 cm/GW for the polymer. At high laser intensities (>7 GW/cm$^2$) photoinduced transformation into some new configuration is taken place that is more absorbent at 532 nm ($\beta$=16.7±3 cm/GW for the photoproduct). Up to a pumping irradiance of 20 GW/cm$^2$ no optical damage of the polymer was observed.

*Keywords:* nonlinear absorption; nonlinear refraction; Z-scan; epoxy polymer; photoinduced transformation

**One of the promising approaches to optical processing and limiting applications is the design of solid guest-host systems and polymeric materials with attached chromophores showing the nonlinear optical properties[1-3]. The most typical solid host is transparent polymer such as polymethyl methacrylate (PMMA) or an epoxy compound. The epoxy based polymers have shown high optical damage[4] threshold and are very perspective media for the novel highly efficient nonlinear optical (NLO) materials design.**

Our group has experience and traditional interest in the epoxy based polymers produced from diglicidyl ether of bisphenol A monomer due to the thermal polymerization with different organic dyes or metalorganic complexes as polymerizing agents. The efficient nonlinearity $\chi^{(3)} = 5\ 10^{-8}$ esu ($\lambda$=532 nm) was obtained[3] for the 4-aminoazobenzene NLO chromophore covalently attached to the linear polymer chain. This highly efficient materials have multiple nonlinear mechanisms with wide range of temporal response. Our first attempts to decode the Z-scan data for the materials failed due to the complex behavior of the polymers NLO properties under high excitation level.

In order to simplify experimental data treatment we have started with the epoxy material with the simplest and transparent polymerizing agent. This study has both a fundamental aspect and very important application for the further NLO chromophore concentration dependencies research, including absolute data calibration.

The epoxy polymer was produced from diglicidyl ether of bisphenol A monomer (M=400) due to the thermal polymerization with aminophenol as polymerizing agent. The polymerization was performed at 100$^0$ C with 10 % aminophenol concentration in monomer solution. The chemical structure of the epoxy polymer is illustrated in Fig. 1.

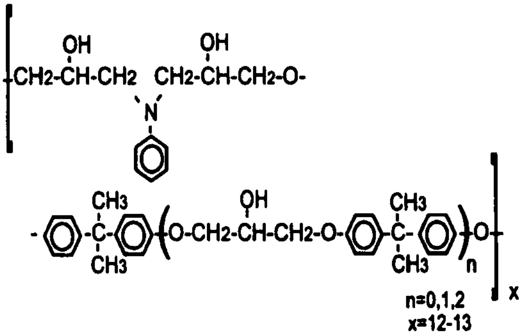

FIGURE 1 Chemical structure of the epoxy polymer.

The obtained polymer ($M_n$=2000) is transparent in the visible range and is highly resistant to the optical and radioactive-induced damage. The polymeric samples used in this study represent triplexes in which epoxy polymeric film (thickness 0.1 - 0.5 mm) is placed between two glass plates with strong adhesion between their surfaces and the polymer layer.

The Z-scan technique[5-6] is a comprehensive method for measuring optical nonlinearities using a single laser beam. The advantage of the Z-scan is that it immediately indicates the sign and type of nonlinearity (refractive or/and absorptive). In the Z-scan technique (Fig.2) a sample is scanned along the optic axis (the z-direction) through the focus of a laser beam, while the total energy transmittance (sensitive to nonlinear absorption) and on-axis energy transmittance in the far field (sensitive to nonlinear refraction) are recorded as functions of a sample position Z relative to the focal position of Gaussian laser beam.

In our experiments the beam was focused to the waist of radius 22μm (half width at $1/e^2$ maximum in irradiance). The range of input energies was 0.3 - 6 μJ and the range of fluencies - 3.2 $10^{-3}$ - 6.4 J/cm$^2$ (corresponding intensities were 10 MW/cm$^2$ - 20 GW/cm$^2$). The experiments were performed with the second harmonic of a mode-locked Nd:YAG laser ($\lambda$=532 nm) that produced single pulses of 30 ps (FWHM) duration and with a repetition rate 5 Hz.

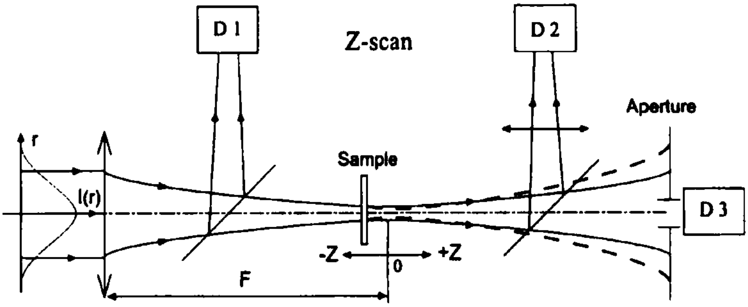

FIGURE 2 The Z-scan experimental setup in which the ratios D2/D1 and D3/D1 are recorded as functions (open and finite aperture Z-scans) of the sample position Z, D1-D3 – detectors; the solid line - the Gaussian beam radius versus propagation coordinate Z without sample, the dashed line – after external self-focusing in the sample.

We varied the input intensity (fluence) and thickness of the samples in order to expand the range of the nonlinear coupling which is proportional to the applied field and interaction length. Thus we have obtained signatures of the different competitive nonlinear mechanisms in the Z-scan curves. The complexity of the analysis was dealt with problem of the selection of the part of Z-scan curve which corresponds to the dominant contribution of the proper nonlinear mechanism on the background of competitive others.

In the excited state absorption process, weak absorption from the ground state results in population of excited states having a larger absorption cross-section and hence an overall decrease in transmittance [1]. Within picosecond excitation range most organic dyes and polymers are well described by a singlet three-level subsystem[2] (for longer pulses a five-level system including triplet states is usually more appropriate).

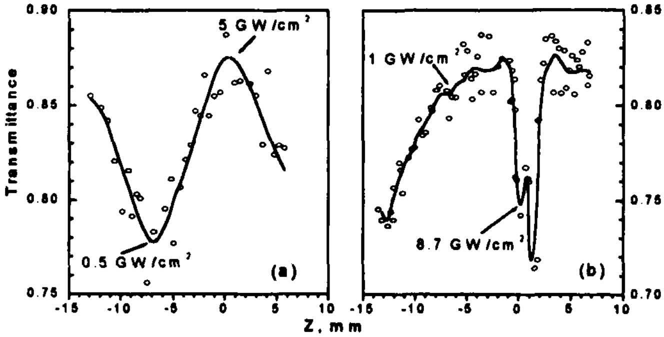

FIGURE 3 Measured open aperture Z-scan of 100 µm (a) and 200 µm (b) polymer samples with pulse energies 1.7µJ (a) 3 µJ (b): circles –experiment, the solid lines – smoothed data.

The linear absorption at 532 nm is initially low ($\alpha$=0.65cm$^{-1}$) since laser radiation is exciting carriers high in the vibrational manifold of singlet state $S_1$. The fast relaxation to the bottom of this electronic state makes the exciting state absorption resonant with the laser light. ESA (Fig. 3 a) is accompanied with slight self-focusing of the laser radiation in the sample. For the higher intensity ESA changes to SA, which gains the maximum at the waist (100µm sample). For a thicker sample 200µm and higher pulse energy (3 µJ) we observed only the final part of the ESA effect which turns to SA (Fig. 3 b). The most thick sample 500 µm with pulse energy 4.1 µJ exhibits only SA beyond the waist (Fig 5a).

The further increasing of the laser intensity leads to the absorption saturation with typical saturation intensity $I_s$=1GW/cm$^2$ (Fig. 4 a). This bleaching of the sample is owing to a fast reabsorption process from $S_1$ to $S_2$ with saturation of the ESA. For the input intensity $I < Is$ we observed self-defocusing of the beam in the sample which turns to self-focusing for $I > Is$ (Fig. 4 b). Such behavior is typical for the saturation mechanism of optical nonlinearities.

Despite the strong SA absorption the probability of the TPA process is high in the intense fields because of the two-photon transition to the final real resonant state (linear absorption peak at 270 nm). In the vicinity of the beam waist with high intensity levels the TPA process starts. The part of the Z-scan curve with comparable contributions of the sample bleaching (SA) and the TPA is very complicate for the analysis due to interplay of this competitive mechanisms and a large variance of the experimental data.

The 200μm sample has shown photodarkening right after the waist (Fig. 3 b) at intensities ~ 7 GW/cm$^2$. This effect rises at higher laser pulse repetition rates. It is important to note that after the waist the nonlinear transmission of the sample is about the same as before the waist.

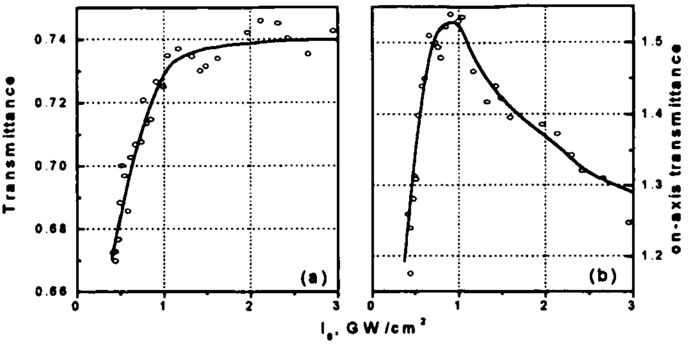

FIGURE 4 Open aperture (total) transmittance (a) and finite aperture transmittance (b) versus peak laser beam intensity for the epoxy polymer 200 μm sample: circles – experiment, the solid line – smoothed data. The sample placed before the waist: self-focusing in the sample corresponds to the beam focusing at the registration plane.

In the 500μm sample with higher energy pulses we observed the transmittance deep broadening at the waist due to the laser field heterogeneity along the sample (Fig. 5 a). The open aperture Z-scan is nonsymmetrical in respect to the waist position. After the intensive exposure at the waist region ($z>0$) the low-intensity transmittance decreases in 20%. The estimated TPA coefficient is $\beta=4.0\pm0.5$ cm/GW before and $\beta=16.7\pm3$ cm/GW after the waist.

Thus we interpret the observed nonlinear absorption enhancement at high level excitation ( $I > 7$ GW/cm$^2$) appears to be connected to a photochemical reaction of the excited state of the polymer, leading to the formation and accumulation of a new product.

According to the contemporary experience the exposure of different materials with intense laser fields of a visible spectral range causes the same optical damage effects as exposure with UV and radioactive emission (due to the multiphoton processes, continuum generation etc.) . A script of the radioactive-induced transformations[4] is known for the epoxy polymer: creation of the supramolecules and a growth of the structure ordering, which are accompanied with the transparency decrease and coloration of the polymer. This product absorbs at longer wavelength owing to creation of carbonyl chromophore groups which can be conjugated with benzene rings ($\beta=16.7\pm3$ cm/GW for the photoproduct). Up to a pumping intensity of 20 GW/cm$^2$ no optical damage of the polymer was observed.

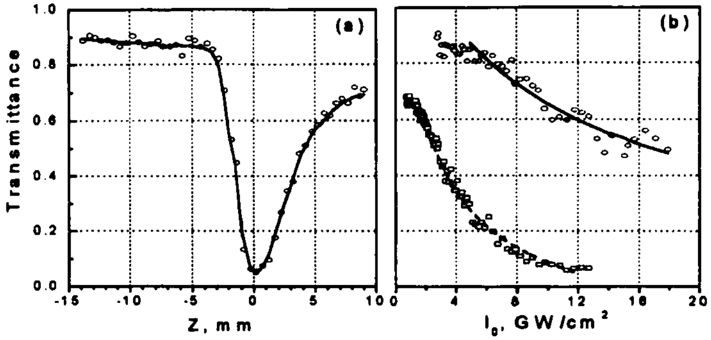

FIGURE 5 (a) Measured open aperture Z-scan of the 500 μm sample with pulse energy 4.1 μJ. (b) The transmittance versus peak laser intensity: circles – experimental data before the beam waist, squares – after the waist. The solid line is the calculated result with the TPA coefficient β=4 cm/GW, the dashed line – β=16.7 cm/GW.

In this paper we have shown how to interpret single Z-scan experimental data for the highly efficient NLO materials with multiple nonlinear responses. The complexity of the analysis was dealt with the nonlinearities signatures recognition problem and selection of the measured Z-scan curve part which corresponds to the dominant contribution of the proper nonlinear mechanism on the background of competitive others.

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