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Non linear optical properties of novel amphiphilic azo-polymers bearing well defined oligo (ethylene glycol) spacers

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Non linear optical (NLO) properties of a new series of **pnPEGMAN** polymers: **p2PEGMAN** or Poly[(E)-2-(2-(methyl(4-((4-nitrophenyl) diazenyl)phenyl) amino)ethoxy)ethyl methacrylate], **p3PEGMAN** or Poly[(E)-2-(2-(2-(methyl(4-((4-nitrophenyl)diazenyl)phenyl) amino) ethoxy)ethoxy)ethyl methacrylate], **p4PEGMAN** or Poly[(E)-2-(4-((4-nitrophenyl)diazenyl)phenyl)-5,8,11-trioxa-2-azatridecan-13-yl methacrylate] and **p6PEGMAN** or Poly[(E)-2-(4-((4-nitrophenyl) diazenyl) phenyl) -5,8,11,14,17-pentaoxa -2- azanonadecan -19-yl methacrylate] were studied by the Z-Scan technique. These azo-polymers exhibited high $\chi^{(3)}$ NLO-responses with excitation below the resonance absorption region of the polymers and the evaluated n_2-values are in the order of 10^{-4} to 10^{-5} esu, with negative sign for all the studied materials.

Keywords: Polymers; azobenzene; poly(ethylene glycol); optical properties.

Las propiedades ópticas no lineales (ONL) de una nueva serie de polímeros **pnPEGMAN**: **p2PEGMAN** o poli[(E)-2-(2-(metil(4-((4-nitrofenil)diazenil)fenil) amino)etoxi)etilmetacrilato], **p3PEGMAN** o poli[(E)-2-(2-(2-(metil(4-((4-nitrofenil)diazenil)fenil)amino) etoxi) etoxi)etilmetacrilato], **p4PEGMAN** o poli[(E)-2-(4-((4-nitrofenil)diazenil)fenil)-5,8,11-trioxa-2-azatridecan-13-il metacrilato] y **p6 PEGMAN** o poly[(E)-2-(4-((4-nitrofenil) diazenil)fenil)-5,8,11,14,17-pentaoxa-2- azanonadecan -19-il metacrilato] fueron estudiadas mediante la técnica de Z-Scan. Estos azo-polímeros mostraron una alta respuesta de ONL del tipo $\chi^{(3)}$ a una excitación por debajo de la zona de absorción de los polímeros y sus valores de n_2 fueron evaluados en el orden de 10^{-4} a 10^{-5} esu, con signo negativo para todos los materiales estudiados.

Descriptores: Polímeros; azobenceno; poly(ethylene glycol); propiedades ópticas.

PACS: 78.30.Jw; 78.20.-e; 74.25.Gz

1. Introduction

Azopolymers are considered as highly versatile materials due to the photoinduced motions which occur on them when they are irradiated with polarized laser light [1]. Several reviews covering most of the implications of azobenzene in polymer structures have been published [1-4]. In the last years, various azo-polymers bearing amino-nitro substituted azobenzene units, such as those of the **pnMAN** series, have been synthesized and characterized [5]. In general, they exhibit maxima absorption wavelength close to those reported for similar push-pull azo-compounds [6,7]. In these materials, both J and H-type aggregation have been observed in casted films [5].

In previous work, we have reported the synthesis, characterization and optical properties of a series of novel amphiphilic amino-nitro substituted azobenzenes bearing end-capped oligo(ethylene glycol) side chains (**RED-PEGM-n** series) [8-10]. Azobenzene and poly(ethylene glycol) have been incorporated into various sophisticated systems such as copolymers [11-12], nanomaterials [13-14], cellulose derivatives [15-16] and cyclodextrin polymers [17-18], in some cases forming supramolecular complexes with interesting properties [19]. Poly(ethylene glycol) moieties provide flexibility and water solubility to the systems to whom they are incorporated. Furthermore, we published the synthesis and characterization of four novel azo-dyes bearing terminal hydroxyl groups (**RED-PEG-n** series) [20]. These dyes were incorporated into a low density polyethylene (**LDPE**) matrix, using acryloyl chloride as grafting agent and gamma radiation, in order to obtain a series of grafted azo-polymer films containing oligo(ethylene glycol) segments (**AC-g-PE-RED-PEG-n** series). The obtained materials showed to be very sensitive to moisture, giving rise to solvatochromic effects after exposure to steam, which make them good prospects for the elaboration of humidity sensors [20].

Recently, we reported the synthesis and characterization of a new series of polymethacrylate based azo-polymers bearing well-defined oligo(ethylene glycol) spacers, named here **pnPEGMAN:** According to this nomenclature, **p** means polymer, **n** indicates the number of ethylene glycol units in

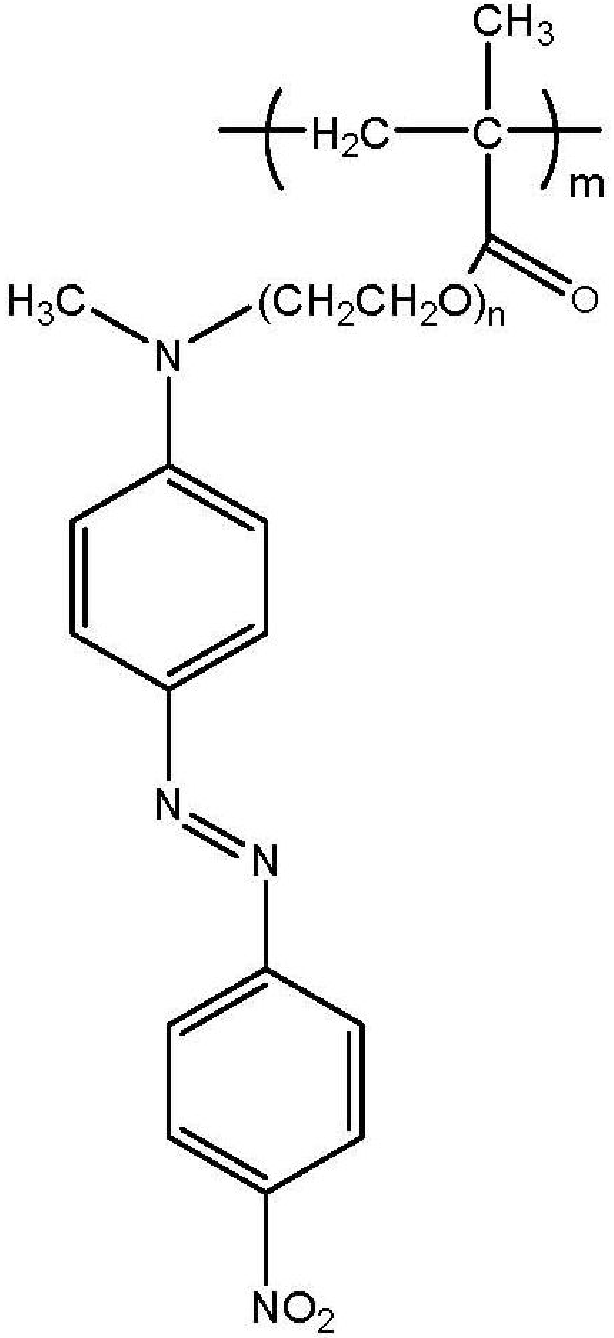

FIGURE 1. Synthesis of the **pnPEGMAN** polymers.

the spacer, **PEG** indicates the presence of a short poly(ethylene glycol) segment, **M** means methacrylate and **AN** indicates the presence of an amino-nitro substituted azobenzene unit. The structures of the **pnPEGMAN** polymers are shown in Fig. 1.

In this work, we studied the third order NLO properties of the **pnPEGMAN** polymers as well as those of a model polymer containing Disperse Red-1 units (**pMDR-1**) [21] by the Z-Scan technique. Nowadays, nonlinear optics and photonics are important disciplines for the development of high-technology applications in many research fields and industries; therefore, the study and development of new optical materials have attracted the interest of several research groups. Nonlinear optical processes, resulting from the interaction of matter with laser beams, are particularly important since they offer not only the possibility of novel applications, but also the opportunity of understanding physical processes at a fundamental level. In this context, the Z-Scan technique is a relatively simple method usually implemented to analyze cubic NLO properties of matter, such as variations of both the intensity dependent nonlinear refractive index (IDRI or n_2: $\mathrm{Re}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]$) and reverse saturable nonlinear absorption (β or RSA). For these reasons, a preliminary study of the cubic $\chi^{(3)}$ IDRI-nonlinearities of the sensitized **pnPEGMAN** polymers was carried out in this work, in accordance to the Z-Scan technique [22-24].

2. Experimental Work

All the reagents used in the synthesis were purchased from Aldrich and used as received. **RED-PEG-2**, **RED-PEG-3**, **RED-PEG-4** and **RED-PEG-6** have been synthesized according to the method previously reported by us [20]. The preparation of the **nPEGMAN** monomers and the **pnPEGMAN** polymers has been previously reported by us [25].

2.1. Non linear optical properties

Saturated THF solutions of the **pnPEGMAN** polymers (n=2,3,4,6) and the reference polymer **pMDR1** were employed to prepare film samples, according to the spin-coating technique, suitable for Z-Scan characterization. For this purpose, 8 mg of each polymer were dissolved in only 6 mL of THF. Homogeneous samples were obtained with this method and further deposited on Pyrex glass substrates, with a film thickness in the order of 10 μm.

For the experimental Z-Scan set-up, we implemented an S-polarized laser beam from a 5 mW He-Ne laser system, working at 633 nm (Melles Griot); this energy was maintained constant during Z-Scan measurements. The spatial mode of the laser was close to Gaussian TEM_{00}. The laser beam was focused on the selected sample by means of a positive lens (f=5 cm). The sample was attached to a translation stage (25 mm in steps of 2 μm) in order to perform Z-Scan experiments. Large area Si-photo-detectors (EOT ET-2040) were used for signal and reference purposes; the signal detector was located at 0.96 m from the focusing lens, after a 2 mm diameter diaphragm-aperture. All signals captured from photo-detectors were measured with a digital oscilloscope (Tektronix TDS 744A). Finally, all motion systems and the administration of the set-up were automated via a LabView control program.

In this experimental system, variations of the sample transmission are monitored using the photodiode through an aperture, while varying the sample position (along the longitudinal Z-axis) in the vicinity of the focal point of a fast focusing optical system. An iris is placed in front of the

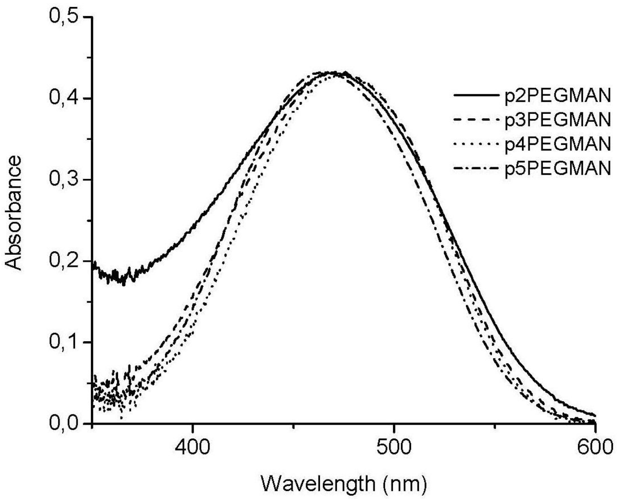

FIGURE 2. Absorption spectra of the **pnPEGMAN** azo-polymers in THF solutions.

detector, adjusted with a narrow or a wide aperture (for closed or open aperture Z-Scan measurements, respectively). In the first case, only the laser beam passes through the aperture so that the signal intensity is affected by both the NLO-absorption and the NLO-refraction. In the latter case, it is possible to investigate the effect of the NLO-absorption alone (not reported here). By comparing open and closed aperture Z-Scan data, it is possible to single-out the NLO-changes of the refractive index. Such changes can be due to local mechanisms, such as reversible alterations in the molecular structure, and non-local mechanisms, where the absorbed energy can be diffused as heat producing a thermal lens effect or a molecular thermal agitation, and consequently a density change via the thermoelastic coupling or the electrostrictive effect. Z-Scan is a sensible characterization instrument which helps in the design of new materials that exhibit third order non-linearities. Depending on the behaviour of the obtained transmittance curve and the optical parameters, it allows the determination of the n_2 value, its sign and the associated phase shift produced by the investigated material.

3. Results and discussion

The **pnPEGMAN** have been previously prepared by us, according to the methods previously reported in the literature [20,25]. Molecular weights of the polymers were determined by Gel Permeation Chromatography in THF against a polystyrene standard, and they exhibit low molecular weights in the range of M_w = 4,200-5,800 g/mol; similar M_w and M_n values were reported for the **pnMAN** series by Natansohn *et al.* Polymerization of methacrylates bearing azobenzene groups usually gives middle to low molecular weights [5].

3.1. Optical properties of the polymers

Optical properties of the **pnPEGMAN** polymers and **pMDR1** were studied by UV-vis spectroscopy in solution and in the solid state (thin films). The optical properties of the polymers are summarized in Table I, and their absorption spectra in THF solution are shown in Fig. 2.

All azo-polymers exhibit maximum absorption wavelength bands in the range between λ_{max}=468-477 nm due to the $\pi - \pi^*$ and n-π^* transitions of the azobenzene chromophores [1]. Precursor **RED-PEG-n** dyes show also maximum absorption bands at about λ_{max} = 471-480 nm due to the same transitions [20] as other similar push-pull aromatic systems [7]. In this case, since both **RED-PEG-n** compounds and **pnPEGMAN** polymers contain amino-nitro substituted azobenzene moieties in their structure, they exhibit a total overlap of the $\pi - \pi$ and n-π^* bands in their absorption spectra, so that only one absorption band can be observed. This behaviour is typical for donor-acceptor substituted azobenzenes, belonging to the “pseudoestilbenes” category (high dipole moment amino-nitro substituted azobenzenes), according to Rau’s classification [6].

On the other hand, it is worth pointing out that the precursor **RED-PEG-n** dyes in THF solution

$$(\lambda_{\text{max}} = 471 - 480 \text{ nm})$$

exhibit red-shifted maximum absorption bands with respect to those of the corresponding **pnPEGMAN** polymers

$$(\lambda_{\text{max}} = 468 - 477 \text{ nm}).$$

This indicates that **RED-PEG-n** compounds are more polar and possess higher charge transfer character than their corresponding azo-polymers. In contrast, **p2PEGMAN** and **p3PEGMAN** in THF solution show a very discrete red-shifted shoulder, which reveals the presence of traces of J-aggregates (head-tail) in these polymers [20,26]. The presence of aggregates in diluted solutions is a proof that intramolecular interactions between neighbour azobenzene chromophores take place due to a coiling of the polymer backbone. The aggregation phenomenon is more evident in the solid state and can occur either in intramolecular or intermolecular way. Highly polar amino-nitro substituted azobenzenes have a natural tendency to form pairs (primly H-aggregates) in order to reach certain electronic stability. In most of the cases, the amino group (donor) of one azobenzene unit interacts in a “face to face” manner with the nitro group (acceptor) of a similar chromophore; this behaviour was also observed for polymers of the **pnMAN** series [27].

TABLE I. Optical properties of **pMDR1** and the **pnPEGMAN** polymers in THF solutions and thin films.

Compound	λ_{max} (nm) THF solution	Cut off (nm) THF solution	λ_{max} (nm) film
pMDR1	473	618	478
p2PEGMAN	470	626	489
p3PEGMAN	473	586	475
p4PEGMAN	473	603	476
p6PEGMAN	468	604	478

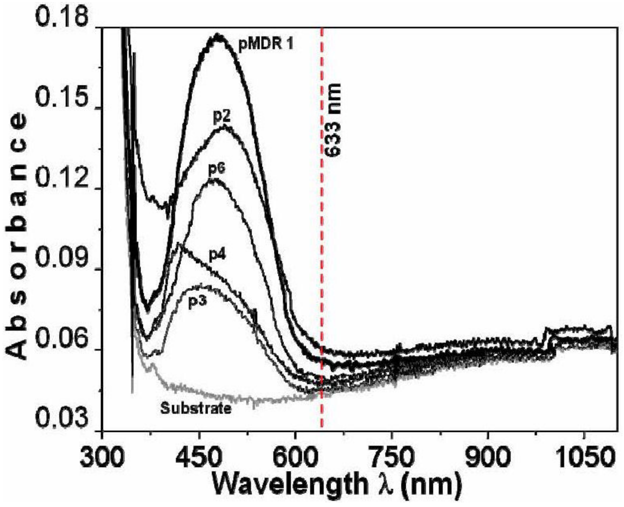

FIGURE 3. Absorption spectra of **pnPEGMAN** and **pMDR1** azo-polymers in spin-coated films.

3.2. NLO properties of the polymers

Although these polymers were synthesized for quadratic NLO-applications, the low T_g values obtained for these molecular systems did not allow suitable conditions for second harmonic generation (SHG) measurements in electrically poled film samples. In such experiments a pulsed Nd:YAG laser systems is typically implemented to provide the fundamental wave at λ_ω=1064 nm. This powerful beam is capable of destroying any existing molecular alignment induced by electrical poling, thereby producing vanishing or unstable SHG-signals, as verified in preliminary studies with these kind of polymeric compounds. Instead, a cubic NLO-characterization was performed via the Z-Scan technique, where a continuous low energy He-Ne laser system (λ=532 nm) was implemented. In general, the molecular structure of compounds synthesized for quadratic applications can also show a good performance for cubic NLO-effects, in this case, however, no material symmetry restrictions are required and amorphous film samples can be straightforwardly characterized. As shown in this section, the evaluation of the nonlinear refractive index of the reference **pMDR1** and **pnPEGMAN** polymers was directly performed according to the Z-Scan technique, regardless of their inconvenient thermodynamic properties for optical applications.

Figure 3 shows the absorption spectra of the **pnPEGMAN** polymers and **pMDR1** (reference polymer) in spin-coated films (see parameters in Table I). As we can see, the azo-polymers show absorption bands at: **pMDR1** (λ_{max}=478 nm), **p2PEGMAN** (λ_{max}=489 nm), **p3PEGMAN** (λ_{max}=475 nm), **p4PEGMAN** (λ=419 nm, λ_{max}=476 nm), and **p6PEGMAN** (λ_{max}=478 nm). All **pnPEGMAN** polymers exhibit red-shifted λ_{max} values, compared to those observed in THF solution, followed by the presence of red-shifted discrete shoulders due to the presence of traces of J-aggregates [26]. Particularly, the absorption spectrum of **p4PEGMAN** shows an additional intense blue-shifted band at λ=419 nm, which clearly indicates the presence of H-aggregates in this polymer film [26]. A similar behaviour was also reported for some polymers of the **pnMAN** series [27]. On the other hand, **pMDR1** exhibits a symmetric absorption band at λ_{max}=478 nm in the same environment and no aggregation is observed. In this Figure, the excitation line of the laser beam used for Z-Scan experiments (λ_{exc}=633 nm) is also exposed in order to exhibit the low absorption and non-resonant experimental conditions applied in such studies with the available cw laser source.

Z-Scan transmittance curves measured with linearly S-polarized light and the evaluated $n_2$nonlinear refractive indexes obtained for the **pnPEGMAN** based films are shown in Fig. 4. Implementing our Z-Scan device, the cubic nonlinear refractive response of the **pnMDR1** and **pnPEGMAN** polymers was characterized. It is observed from Figs. 4(a-e) that the nonlinear response of all the polymers unambiguously exhibits negative nonlinear refraction, confirmed in all curves by the peak-valley signal typically detected for $n_2 < 0$. Negative n_2 values obtained below the resonance region, such as the observed ones, are consistent with a two-level absorption model, which predicts a positive n_2 value above resonance crossing through zero at exact resonance and becomes negative below resonance [28]. The observed nonlinear mechanism is therefore closely related to the $S_0 \rightarrow S_1$ transition, and the subsequent reversible *trans-cis* transformation of the implemented polymers.

For each Z-Scan curve, the well known relation used to determine the nonlinear refractive index was employed [22-24]; $\gamma = \lambda\Delta\Phi/2\pi I_0 L_{eff}$ where λ is the wavelength, $\Delta\Phi_0$ the associated phase shift, I_0 is the input beam intensity (at z=0 or focal point) and L_{eff} is the effective thickness of the sample. Hence, according to original work developed by Sheik-Bahae *et al.*, the nonlinear refractive index γ of the samples was evaluated according to the following formula [22-23]:

$$\Delta T_{P-V} = 0.406\,[1-S]^{0.25}\,|\Delta\Phi_0|\,, \tag{1}$$

where ΔT_{P-V} is the distance between the peak and the valley of the transmission curves, S represents the allowed fraction of the total incident energy transmitted through the diaphragm aperture (0< S <1). The numbers 0.406 and 0.25 are empirical constants obtained as the calibration of the classical Z-Scan technique was performed [22-23]. Traditional calculations permitted the evaluation of the sign and magnitude of the NLO-refractive indexes of our polymers (Fig. 4).

The evaluated n_2-values are in the order of 10^{-4} to 10^{-5} esu, with negative sign for all the studied materials. In fact, based on recent literature reports and according to the Z-Scan measurements performed by J.C. Liang and Q. Zhou [29], an experimental n_2-value of -3.2×10^{-9} cm^{2}W^{-1} (or -1.2×10^{-6} esu, using the conversion factor: $n_2^{esu}=(cn_0/40\pi)\,n_2^{MKS}$ [30]) has been already reported for the **DR1**-dye. This is a considerably lower value compared to those reported in Figs. 4(a-e) and particularly

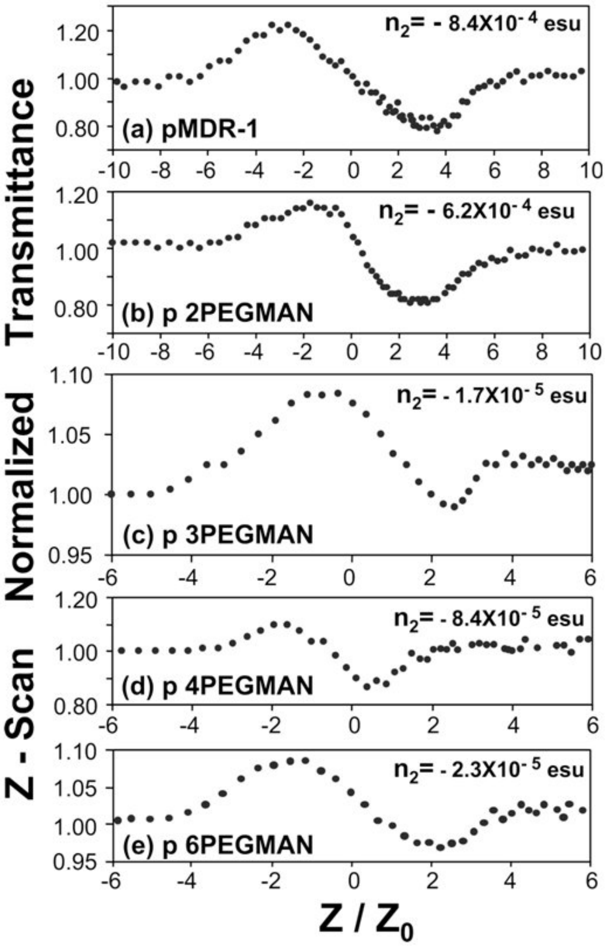

FIGURE 4. Z-Scan transmittance curves and calculated nonlinear refractive index (n_2), obtained from the studied film samples with linearly S-polarized light: a) **pMDR1**, b) **p2PEGMAN**, c) **p3PEGMAN**, d) **p4PEGMAN**, and e) **p6PEGMAN**.

smaller than that measured for the reference **pMDR1** and related homologues **pnPEGMAN** (n=2,3). Although π-conjugation along the azobenzene molecules will give rise to a third-order nonlinearity, this is probably not enough to explain the large nonlinearity measured in our samples. This could be only possible considering the collective molecular behavior and molecular photoisomerization and photoalignment effects which usually occurs in azo-compounds, since photoalignement can lead to a much larger change of the refractive index in azobenzene derivatives than Kerr nonlinearity can [31-32]. In fact, it has been demonstrated that a huge difference in the measurements of n_2 arises as the photoisomerization mechanism is activated [29], since the refractive index change and absorption properties associated with photoalignement are extremely strong. Last point can be very possible for usual long Z-Scan experimental procedures [29], even for implemented low laser powers of lasers working at low energy wavelengths and below the resonance range. Thus, two different effects should be separately considered: the first one is associated to the third order nonlinear refractive index itself, whereas the second one (photoalignement) is not, because photoalignement is not related to the cubic nonlinear processes. In addition, it has been proven that linearly polarized light in Z-Scan measurements induce stronger linear optical refractive changes (Δn) in photoisomerizable compounds, such as azobenzene derivatives, than the use of unpolarized light [29]; this effect occurs even if the wavelength of the light is not in the center of the absorption band of the sample. The long irradiation time is then enough to induce *trans-cis* photoisomerization with photoalignement via the Z-Scan procedure, leading to a more ordered phase. Since the photoinduced reversible *trans-cis* isomerization has been shown to happen in a subpicosecond timescale [28], it certainly may permanently take place under the *cw*-polarized laser irradiation conditions used in the present experiments.

Since the n_2-value of SiO_2 glassy materials are in the order of 10^{-13} to 10^{-14} esu [33-34], it is clear that the NLO effects induced by the glass substrate are negligible and do not interfere with the magnitude of the measured nonlinear refractive indexes of the organic compounds (Z-Scan transmittance curves of the substrates alone, are not shown here for simplicity). From Fig. 3, it is observed that maximal absorption occurs for the pMDR1 and p2PEGMAN based films, followed by the pnPEGMAN (n=3,4,6) polymers containing more oligo (ethylene glycol) spacers. Accordingly, Z-Scan measurements exhibit larger n_2-values for compounds containing shorter PEG-segments. These facts imply an interesting dependence of n_2 on the number of PEG-units which provide outstanding molecular flexibility and suggest a complex ordering of the constituting azo-compounds within the polymethacrylate based polymers. This unambiguous and clear dependence of the n_2-values on the number of poly-ethylene-glycol units can be better understood when comparing our experimental results with other; where monomeric azo-dyes, without PEG-segments, have been employed [35-36]. Although nonlinearity is notably improved in comparison to monomeric azo-compounds (which represents a plus point in our research), a comparative analysis of our obtained data suggests that the addition of excessive PEG-segments deteriorates the NLO-response of these polymers. In fact, the **pMDR1**-reference polymer, not containing PEG-segments, exhibit the largest n_2-value, followed by the **pnPEGMAN** homologues (for n=2, 3 and n= 6 and 4, respectively). The trade off observed in the n_2-values for the n=6 and 4 samples may be due to the bad film quality obtained for these two compounds, in comparison to those obtained from the shorter PEG-based polymeric compounds (n=2, 3). In fact, **pnPEGMAN**-based THF-solutions with larger PEG-segments are more viscous and therefore more difficult to deposit via Spin-Coating. The n_2-values are, in any case, larger than those reported in the literature for monomeric compounds [35]. Thus, it is concluded that the higher nonlinearity mainly arise from the enhanced optical properties of our polymerized compounds and from the induced trans-cis photoisomerization process (due to long cw-polarized laser irradiation below resonance conditions); this process drastically affects the overall nonlinear optical response of the material and is usually observed in azo-based compounds (both polymeric and monomeric systems). This fact has been widely accepted in the literature, although no definitive and full explanation for this interesting phenomenon has been yet given [28,35-36].

On the other hand, as general and related information, we have recently reported the quadratic NLO-SHG properties of monomeric azo-dyes containing PEG-units (**RED-PEG-n** series, n = 2, 3, 4, 6) in sol-gel environment [37-38]. These azo-compounds, embedded in a sol-gel matrix, are closely related to the polymeric **pnPEGMAN** compounds reported in the present paper. This is indeed due to the incorporation of the same PEG-units attached to the monomeric azo-dyes in a similar way as in the polymerized **pnPEGMAN** series. Similarly to the **pnPEGMAN** compounds, the **RED-PEG-n** ones (in sol-gel) also show a dependence on the NLO-properties with the number of PEG-segments (in this case quadratic SHG). Here, the highest SHG-response was obtained from the **RED-PEG-2**, followed by the n=3 and n=4 based sonogel hybrid films, indicative of better induced monomeric alignment and NLO-response for the shorter PEG-based molecules. This fact suggests possible molecular steric-effects for the long PEG-based compounds which limit long-range chromophore mobility for optimal electrical alignment, which is particularly important for quadratic NLO-effects. However, more important and relevant for the NLO-effects is the fact that in such PEG-based systems a clear withdraw of the electronic conjugation is evidenced as the SHG-signals decrease for longer PEG-segments; thus decreasing both the intra-molecular charge transfer of the compound and the overall NLO-properties. Indeed, this effect has more pronounced consequences in the purely electronic-dependent cubic NLO-effects, as is the case in the present work. Last but not least, it was realized that the polymerized **pnPEGMAN** compounds containing longer PEG-units exhibit lower T_g-values; this fact makes such polymeric systems more susceptible to thermal orientational molecular processes induced by laser irradiation, leading to a drastic decrease on the overall NLO-properties. However, a clear theoretical interpretation taking into account local and/or non-local mechanisms and the accurate influence of the *trans-cis* photoisomerization and photoalignment processes, to strictly and correctly predict the behavior of the NLO-refractive index of these kind of samples, should be performed in order to best fit the obtained experimental data; such interpretations are presently under way and will be presented in future work.

4. Conclusions

The optical and NLO properties of a novel series of azo-polymers (**pnPEGMAN**) containing amino-nitro substituted azobenzenes were studied by absorption spectroscopy and the Z-Scan technique, respectively. Absorption spectra of the polymers exhibit absorption bands about $\lambda_{\max}$ = 468 - 470 nm in solution, and in the range of $\lambda_{\max}$ = 476 - 489 nm in solid state films. The absorption spectrum of **p4PEGMAN** in film shows the presence of H-aggregates, whereas the rest of the polymers only exhibit traces of J-aggregates in the solid state. Finally, NLO properties of the **pnPEGMAN** polymers were studied by the Z-Scan technique (nonlinear refraction). The evaluated n_2-values are in the order of 10^{-4} to 10^{-5} esu, with negative sign for all the studied materials. From the Z-Scan data, it can be inferred that the polymerization of the azo-chromophores and the induced trans-cis photoisomerization process play major roles in the occurrence of strong cubic nonlinearities. As a matter of fact, the incorporation of PEG-units to the pendant azo-chromophores has weakened the NLO-response of our polymers. Hence, the observed “giant” n_2-values are definitely more related to an adequate architecture/functionalization and polymeric properties of these particular chromophores; and not to the addition of PEG-moieties (which play additional roles: amphiphilic properties, etc.). Furthermore, the addition of PEG-units also induces a decrease on the T_g-values of the **pnPEGMAN**-polymers, which in consequence, decreases the NLO-activity up to one order of magnitude.

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