New Third-Order Nonlinear Polymers Functionalized with Disperse Red and Disperse Orange Chromophores with Increased Stability

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Received April 29, 1997. Revised Manuscript Received July 28, 1997[⊗]

New and very stable polymers with good optical third-order nonlinearities have been prepared by condensation between a copolymer of maleic anhydride and octadecene and appropriate Disperse Red and Disperse Orange type chromophores. The nonlinear response of low concentration solutions of the polymers has been determined using a new numerical *Z*-scan technique. The polymers have been found highly stable, and their nonlinear response is very reproducible, both under intense illumination and upon several repeated experiments over months. Especially the polymer where the Disperse Orange 3 chromophore is incorporated in the main chain through imide linkages displays both the highest refractive nonlinearity and almost no two-photon absorption. Its surprisingly higher nonlinear response with respect to the parent Disperse Orange 3 is demonstrated and discussed.

Introduction

There is a still growing interest in polymers bearing nonlinear optical (NLO) chromophores,[1] due to a wide range of optical applications including signal processing,[2] photorefractivity,[3] etc. On the other hand, Disperse Red (DR) and Disperse Orange (DO) compounds make an important class, especially in the search for quadratic nonlinear effects.[4] This class of molecules is believed to also display efficient third-order nonlinearities,[5] which are required for materials with optimal Kerr effect, to meet applications such as optical modulators,[6] switches,[7a] or waveguides.[7b] For all these applications, the key point to yield good NLO materials is to combine a high off-resonant third-order susceptibility $\chi^{(3)}$ with low optical losses.

However, because of the high intensities involved in this type of application, it is also of primary importance to dispose of a highly stable support, both to ambient atmosphere and to temperature variations and intense illumination. Polymers are suitable candidates, and a convenient third-order nonlinear polymer should also possess a good ability to form thin films; its synthesis should be as easy as possible, with the highest possible chromophore content. Recently, polyimides,[3b,4c,8] or polyesters,[4b] have been prepared and shown to exhibit increased stabilities; also hybrid sol−gel polymers are promising materials.[9] All these polymers were however mainly aimed at delivering optimum and stable second-order effects.

Third-order nonlinear effects in polymers[10] have been less studied, except conjugated polymers, which have been very soon recognized as fruitful materials. Among them are especially found poly(diacetylene),[10,11a] poly(acetylene),[10,11a] poly(arylene vinylene),[11b,11c] poly-

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1997.

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S0897-4756(97)00277-9 CCC: $14.00

thiophene,[11d] and more recently polyaniline.[11e] However, such conjugated polymers are sometimes poorly processable from solutions, which limits their use in optical devices. Among them nevertheless, soluble or crystalline poly(diacetylenes) actually give the highest off-resonant $\chi^{(3)}$ values,[12] around 5×10^{-16} m^2/V^2 [12c] with low nonlinear absorption. They thus offer good opportunities for thin film or waveguide applications but turn out to be somewhat expensive materials.

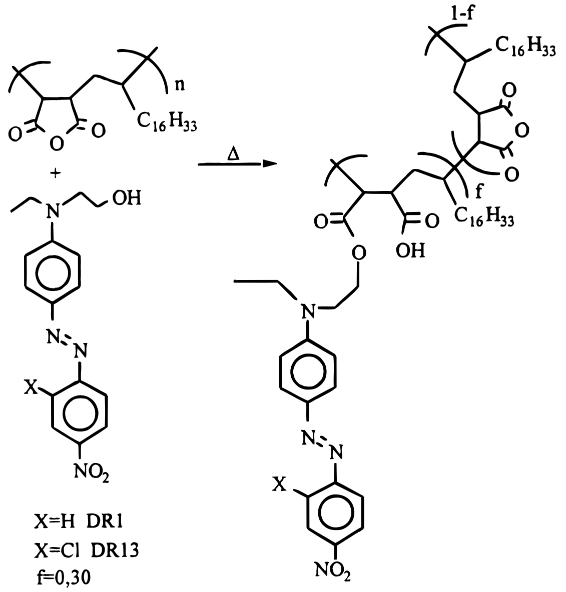
Preliminary studies performed with the classical PMMA-DR1 polymer have shown that thin films of this polymer displayed an appreciable third-order susceptibility.[7,13a] However, the situation in the case of PMMA appears relatively complicated and largely dependent on the illumination conditions. For example, according to the pulse duration and the total illumination time, the polymer exhibits at least either fast positive nonlinear index response, with poor reproducibility,[7a] or fast and slow negative responses.[7b] Besides, temperature resistance and long-term stability of this polymer often do not meet the requirements for the foreseen applications. The reasons for such behavior are not obvious, but it may be proposed that depolymerization of the metacrylate polymer may happen to a low extent, as a result of either high-intensity light or temperature elevation.[13b]

Therefore we describe here the preparation of new kinds of DR and DO type chromophore functionalized polymers exhibiting a stable off-resonant positive fast nonlinear index n_2. The proposed compounds are easy to synthesize and relatively cheap. They are based on a copolymer of maleic anhydride and octadecene (COPA). This copolymer could fix a wide range of chromophores by reaction with the anhydride, and the side chain increases both the solubility and the ability to deposit thin films of the functionalized polymers. Besides, it has recently been shown that $\chi^{(3)}$ effects should be optimized in case of an adequate contribution of the neutral and the zwitterionic form in the ground state of the chromophore.[14] Such a property has been interestingly developed in this work in the case of the functionalization of COPADO3. Indeed, we give evidence of the modification of DO3 chromophore by reducing the donor power of the amine nitrogen, changing it to an amide or even to an imide function, as shown below. This happens by reaction of the polyanhydride with DO3 chromophore, in the course of the functionalization. However, we have also introduced the classical DR1 and DR13 chromophores in this polymer.

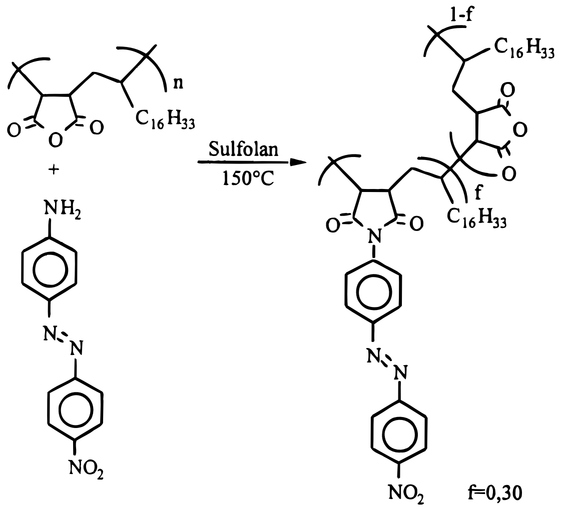
Experimental Section

The poly(maleic anhydride-*co*-octadecene) was purchased from Aldrich; since this polymer was not characterized, the M_W was determined by standard SEC (polystyrene standard) and was found to be 10 500 with a polydispersity of 2.9. DR1, DO3, and DR13 were Aldrich products and were used without further purification.

Scheme 1. Synthesis of COPADR1 and COPADR13



Scheme 2. Synthesis of COPADO3



Functionalization of Poly(maleic anhydride-*co*-octadecene). Two methods were used.

Functionalization with DR1 or DR13 (COPADR1 or COPADR13) (see Scheme 1). Poly(maleic anhydride-*co*-octadecene) and the required amount of DR1 or DR13 were introduced into a flask flushed with nitrogen. The flask was maintained at a temperature of 150 °C (for DR1) or 110 °C (for DR13) for 2 h. The resulting solid was taken into dichloromethane and precipitated by slow addition in methanol–water at 0 °C. The precipitate still contained a small amount of DR1 (from TLC analysis), and the operation was repeated as many times as required (usually three times) in order to get the pure polymer, until no DR1 was detectable in the solution (by TLC). IR spectra showed the presence of the ester (1725 cm^{-1}) and the acid groups (1710 cm^{-1}) in the polymer.

Functionalization with DO3 (COPADO3) (See Scheme 2). In a flask were introduced 20 mL of sulfolane, 1 g of poly(maleic anhydride-*co*-octadecene) and the required amount of DO3. The mixture was heated at 150 °C for 2 h. Dichloromethane (20 mL) was added, and the polymer was precipitated two times in methanol–water at 0 °C, as described before.

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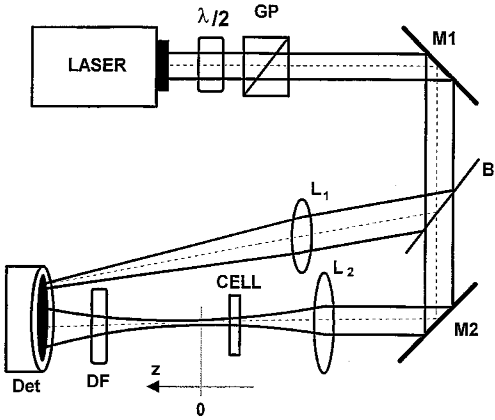

Figure 1. Schematic diagram of the experimental setup: pulsed Nd:YAG laser (LASER), mirrors (M_i), half-wave plate ($\lambda/2$), Glan polarizer (GP), beam splitter (BS), cell (CELL), converging lenses (L_j), neutral-density filter (DF), CCD-camera (Det).

DO3 was incorporated in the same proportions (from elemental analysis) as DR1 in poly(maleic anhydride-*co*-octadecene) to give pale-orange COPADO3. IR spectra showed the presence of the imide (1779 and 1719 cm^{-1}) in the polymer. (See characterization further for both polymers.)

Optical Measurements. For measuring the third-order nonlinear coefficients of the three chromophores and their respective functionalized polymers in the picosecond pulsed regime, we have utilized the recently proposed numerical open *Z*-scan method.[15] This technique is a versatile and more sensitive[15c] extension of the well-known single-beam Z-scan first proposed by Sheik-Bahae *et al.*[16] In the numerical *Z*-scan, the whole far-field profile nonlinear distortion is recorded using a two-dimensional CCD camera. By image processing, the distorted beam for a given z position of the sample is compared with the undistorted beam (i.e., in the absence of nonlinearity).

The total area of integration on the CCD sensor is numerically sampled with 30 concentric circles centered on the far-field pattern. Any of these circles can be chosen appropriately for defining a circular diaphragm or a block disk, so that it is simple to perform "classical" apertured or open *Z*-scan measurements for the same single pulse with the same detection scheme. After sampling, the developed software calculates the energy of each circular or ring area independently of one another. By monitoring the total energy recorded by the largest circle for each z position, this numerical treatment permits also the determination of the nonlinear absorption coefficient β of the materials. By normalizing and dividing the apertured *Z*-scan curve by the latter one, it is therefore easy to determine the nonlinear refractive index coefficient n_2 of the materials.[16]

The experimental scheme is depicted in Figure 1. The experiments were performed with a linearly polarized TEM_{00} pulsed mode-locked Nd:YAG laser, operating at $\lambda = 1064$ nm. An electrooptic shutter ensures the selection of a single nearly Gaussian pulse of $t = 50$ ps duration at a repetition rate of 10 Hz. The laser beam energy is adjusted by means of a half-wave plate and a Glan polarizer. Then the beam is focused by the lens L_2 whose focal distance f is 400 mm. The waist radius at the focal plane ($z = 0$) is ω_0, corresponding to a Rayleigh range $Z_0 = \pi\omega_0^2/\lambda$ (values of Z_0, 5.3 mm for DR1 and DR13 and 4.12 mm for DO3 and CS2, respectively). The sample cell is 1 or 2 mm thick, approximately one-third or one-fourth of the Rayleigh range. The incident (respectively, transmitted) energy is measured right before (respectively, after) the cell by a calibrated energy meter. The CCD camera, located at a distance D away from the linear beam waist, operates in single-shot mode for detecting the far-field pattern.

For each z position of the sample cell, the detection setup gives therefore one measurement for a single pulse issued from the laser. Besides, a small part of the incident beam is directed by means of the beam splitter through lens L_1 toward the camera without interfering with the previous far-field pattern. As shown below, this energy reference allows the correction of the rough experimental data by accounting for the pulse-to-pulse energy fluctuations.[15a]

All measurements on the polymers were calibrated relative to the experimental *Z*-scan curves in CS_2 obtained in the same experimental conditions. This liquid is well-known to exhibit a nearly pure nonlinear refraction (only real third-order susceptibility) with a commonly adopted value of $n_2 = 3.5 \times 10^{-18}$ m^2/W.[15a,16] For achieving the measurements, the chromophores and the polymers were dissolved in dichloromethane. Indeed, this solvent exhibits a very good transparency at the utilized wavelength. The concentrations were rather low, in the 10^{-2} $mol \cdot L^{-1}$ (of chromophore) range, because solubilization of dry polymer was not achievable at higher concentrations. Preliminary *Z*-scan measurements on the pure solvent allowed us to check that the nonlinear response of the solvent remained under the noise level in our experimental conditions, whatever the incident energy.

Results

Characterization of the Polymers. The maximum chromophore inclusion in poly(maleic anhydride-*co*-octadecene) is 30% relatively to the initial anhydride content, as determined by elemental analysis from the nitrogen content (because nitrogen is present only in the chromophores (see Table 1)) and NMR ^1H and ^{13}C spectra. This contrasts with a previous work on related polymers that relates that only 6%–10% of chromophores could be substituted to the polymer.[17] The presence of long alkyl chains in our polymers is expected to enhance the solubility and the reactivity of the precursor polymer toward the functionalization. In addition, the use of sulfolane as solvant greatly enhances the efficiency of the functionalization reaction in the case of COPADO3. However, high nonlinearities are achievable at this incorporation level. The steric hindrance of the hexadecyl chains is probably responsible for this limit. The precursor copolymer presents rigorously alternate maleic anhydride and hexadecyl groups. However, the chromophores are randomly incorporated during the functionalization reaction. The glass transition temperatures T_g (Table 1) have been determined for all polymers. They are very close together whatever the nature of the chromophore, therefore showing that the glass temperature is, as expected, controlled by the alkyl side chains dynamics. The polymers are soluble in common organic solvents and display good filmogen properties due to the presence of the long alkyl chains that help both the solubilization of the polymer and its film-forming ability. Since the functionalization reaction does not affect the main backbone, the chain length is the same as that in the precursor polyanhydride, with the same polydispersity of 2.9.

The UV–visible absorption spectra of the polymers have been registered (Figure 2). For all polymers, a bathochromic effect is encountered, the absorption wavelength of the molecular chromophore alone being

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Table 1.

products	COPADR1	COPADR13	COPADO3
formula	$C_{82}H_{132}N_4O_{12}$	$C_{82}H_{131}N_4O_{12}Cl$	$C_{78}H_{122}N_4O_{10}$
anal. calcd	C, 72.08%; H, 9.76%; N, 4.10%	C, 70.31%; H, 9.45%; N, 4.00%	C, 73.41%; H, 9.66%; N, 4.39%
found	C, 72.18%; H, 9.79%; N, 3.85%	C, 70.44%; H, 9.49%; N, 3.94%	C, 73.50%; H, 9.74%; N, 4.31%
T_g (°C)	91	89	93
λ_{max} (nm)	483	498	415
$\Delta\lambda$ bathochromic, (nm)	19	5	28
yield (%)	74	73	60

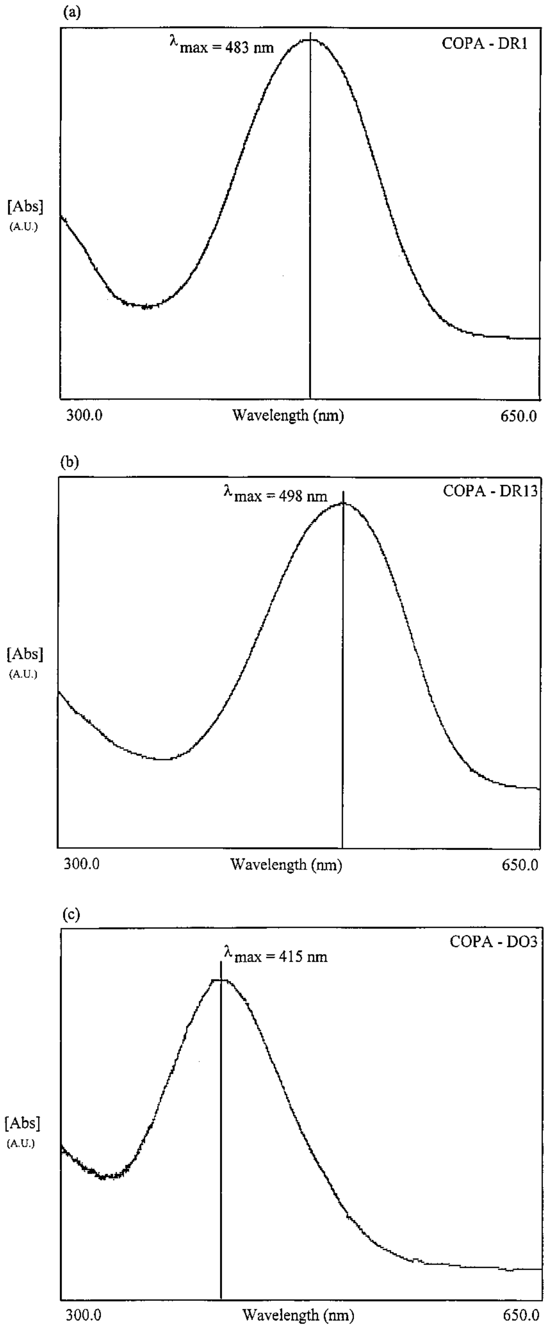

Figure 2. Absorption UV–visible spectra; (a) COPADR1, (b) COPADR13, (c) COPADO3.

higher than when it is incorporated into the polymer (see Table 1 and discussion below).

Z-scan Measurements. Figure 3 presents normalized apertured *Z*-scan curves obtained from COPADR13 (a, b, c) and COPADO3 (d) in solution. The incident energies were $E = 233$ (a, b, c) and 182 (d) μJ, respectively, and the chosen numerical diaphragms corresponded to linear transmittance factors[16] S of 0.33 and 0.02, respectively. The uncorrected curve (a) exhibits the so-called valley-peak shape representative of a positive (Kerr-like) nonlinear refraction. For two reasons, however, this curve differs from the typical *Z*-scan symmetrical curve characterizing a purely refractive (real) nonlinearity. First, Figure 3a displays the energy fluctuations of the Nd:YAG laser; second, the observed asymmetry clearly indicates the presence of two-photon absorption (2PA). We performed measurements with $S = 1$ (no aperture) in order to estimate the 2PA coefficient. Figure 3b shows the corresponding normalized experimental data obtained during the same *Z*-scan as for Figure 3a but with the largest numerical diaphragm gathering the entire far-field pattern. Also plotted in Figure 3b is the theoretical fitting using the Gaussian decomposition method (GDM),[18] well described in ref 16. After correcting for the energy fluctuations, we then divided curve 3a by curve 3b in order to get the corrected–normalized apertured *Z*-scan curve of Figure 3c. This gives with a very good approximation the transmittance due to only the refractive part n_2 of the nonlinear response.

For COPADO3, the uncorrected *Z*-scan curve was already found to be symmetrical, indicating that 2PA was negligible in our experimental conditions. The corresponding normalized curve has only been corrected for the energy fluctuations.

Since the utilized wavelength $\lambda = 1064$ nm lies far from the resonant one-photon transition band of the three chromophores and their relative functionalized polymers (see Figure 2 and Table 1), calibrations of the transmitted energy allowed us to verify that, in our operating energy range, the effective lengths L_{eff} of the solutions were close to the lengths L of the sample cells, within less than 5% error.

In all cases, the n_2 values (in m^2/W) and the 2PA coefficients β (in m/W) were measured by both theoretical fitting and direct determination from the experimental datas, using the procedure of ref 16, which gives (for $|\Delta\phi_0| \le \pi$ and assuming a Gaussian pulse intensity distribution both in time and space):

$$\Delta T_{pv} \approx 0.406(1-S)^{0.25} \cdot |\Delta\phi_0|$$

with

$$n_2 = \frac{\lambda\Delta\phi_0}{2\pi I_0 L}$$

and

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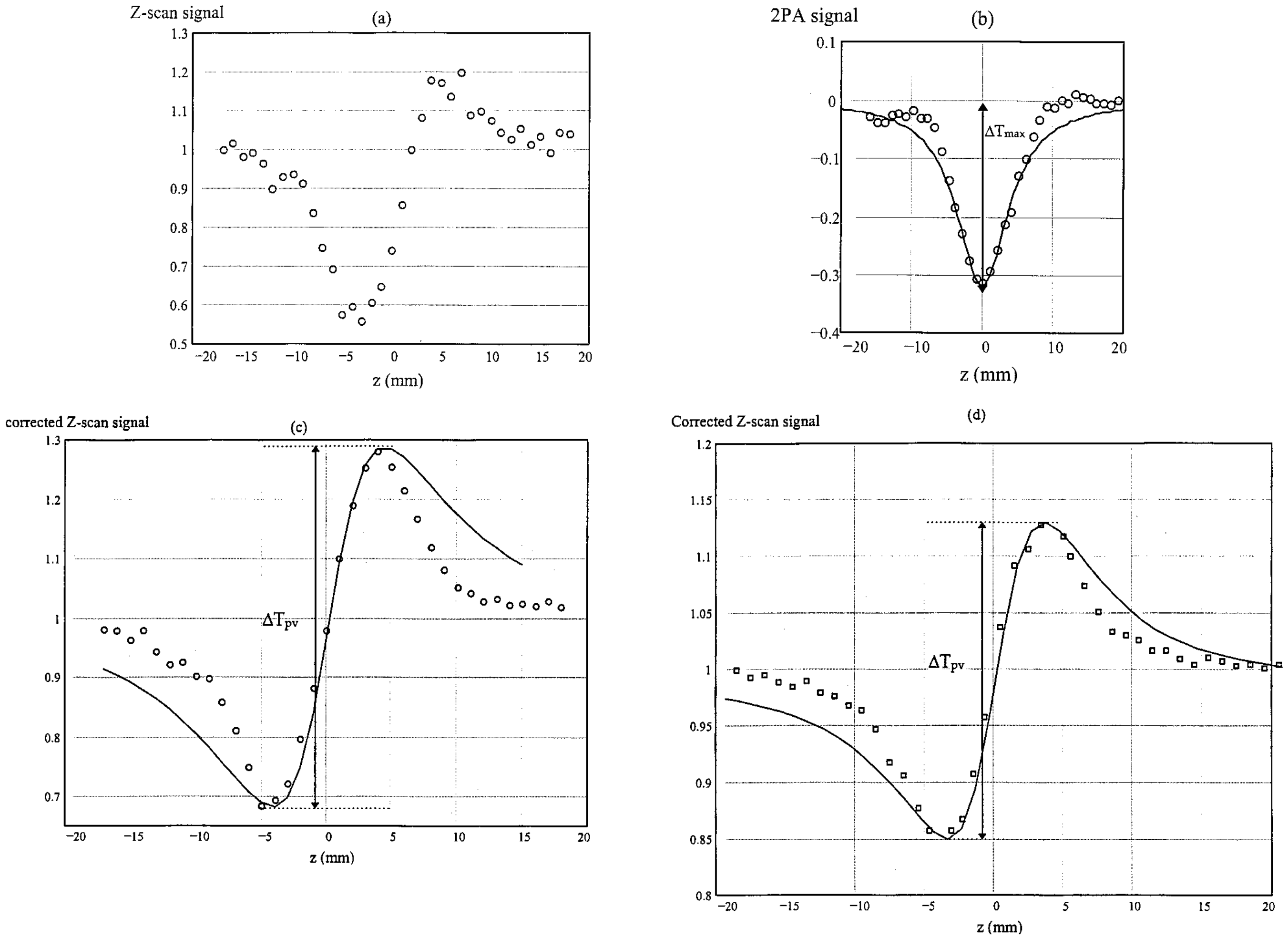


Figure 3. Normalized *Z*-scan curves: COPADR13: $L = 2$ mm, $D = 115$ mm, $E = 233\ \mu$J. COPADO3: $L = 1$ mm, $D = 162$ mm, $E = 182\ \mu$J. ○, experimental data; solid curves, theorical fitting. (a) COPADR13, uncorrected apertured *Z*-scan with $S = 0.33$; (b) COPADR13, nonapertured *Z*-scan ($S = 1$) featuring the 2PA; (c) COPADR13, corrected apertured *Z*-scan with $S = 0.33$; (d) COPADO3, corrected apertured *Z*-scan with $S = 0.03$.

$$\beta \approx -\frac{2\sqrt{2}\Delta T_{\max}}{I_0 \cdot L_{\mathrm{eff}}}, \quad \text{with} \quad L_{\mathrm{eff}} \approx L$$

ΔT_{pv} is the difference between the normalized peak and valley transmittances of the apertured *Z*-scan, as indicated in Figure 3c,d $\Delta\phi_0$ is the maximum on-axis nonlinear induced phase shift at focus ($z = 0$), I_0 is the pulse peak intensity at focus, and $\Delta T_{\max}$ is the difference between the normalized energy transmittances at $z = 0$ (maximum 2PA) and $z \rightarrow \infty$ (negligible 2PA) of the nonapertured *Z*-scan, as indicated in Figure 3b, while the third-order susceptibility $\chi^{(3)}$ (in m^2/V^2) is linked to n_2 through

$$\chi^{(3)}(-\omega;\omega,-\omega,\omega) = \frac{4\epsilon_0 c n_0^2}{3} \cdot n_2$$

c being the light speed in vacuum, ω the optical pulsation, and n_0 the linear refractive index of the medium, which we approximate here to the n_0 (=1.424 for CH_2Cl_2) value of the solvent.

Table 2 summarizes the measurements performed with the highest polymer concentration reachable in dichloromethane (lowest experimental error), as well as the comparison with their parent chromophores and with the pure CS_2 values. Clearly, the very diluted solution responses of our polymers are in the range of the CS_2 response. Therefore, from the results of Table 2, the susceptibilities of the polymers are all much higher than the CS_2 one. A straightforward extrapolation from the values obtained in dilute solutions would show that the susceptibility of pure polymers is about 150 times the CS_2 value in the case of COPADR1 and COPADR13 and about 3000 times in the case of COPADO3 ($\chi^{(3)}$ values of about 9×10^{-18} and 7×10^{-17} m^2/V^2, respectively). Of course, extrapolation to pure polymers assumes a few requirements, for example that we could continue to neglect the dipole−dipole interaction. The $\chi^{(3)}$ values of polymer solutions have also been performed at lower concentrations (Figure 4) and show that n_2 increases linearly with the concentration.

Discussion

According to our experiments on COPADO3, the third-order susceptibility of this polymer is about 25 times higher (after correction from dilution variations) than that of DR1 or DR13 functionalized polymers (related to the weight amount of polymer in solution, which is quite correlated to the chromophore content). This shows the very promising features of this polymer. In addition, this polymer is used completely off-resonance and was found to display negligible two-photon absorption (as well as one-photon absorption) at the considered wavelength. This is attested by the

Table 2

compounds	concn (10^{-2} mol·L^{-1})	exptl nonlinear refractive index: n_2 (10^{-18} m^2/W) fitting	exptl nonlinear refractive index: n_2 (10^{-18} m^2/W) direct	relative nonlinear refractive index: n_2/n_{2CS2} fitting	relative nonlinear refractive index: n_2/n_{2CS2} direct	nonlinear absorption coefficient: β(10^{-14} m/W) fitting	nonlinear absorption coefficient: β(10^{-14} m/W) direct	nonlinear susceptibility $\chi^{(3)}$ (10^{-21} m^2/V^2)
CS_2	1666	3.53	3.57	1	1	negligible		74.9 ± 0.2
DR1	2	0.85	0.79	0.24	0.23	4.0	4.1	13.2 ± 0.2
COPADR1	2	0.67	0.64	0.19	0.18	1.1	1.3	10.5 ± 0.2
DR13	2	0.78	0.74	0.22	0.21	4.4	4.5	12.2 ± 0.2
COPADR13	2	0.64	0.61	0.18	0.17	4	3.6	10.0 ± 0.2
DO3	0.05	0.11	0.09	0.03	0.03	negligible		1.7 ± 0.2
COPADO3	0.05	0.28	0.28	0.08	0.08	negligible		4.4 ± 0.2

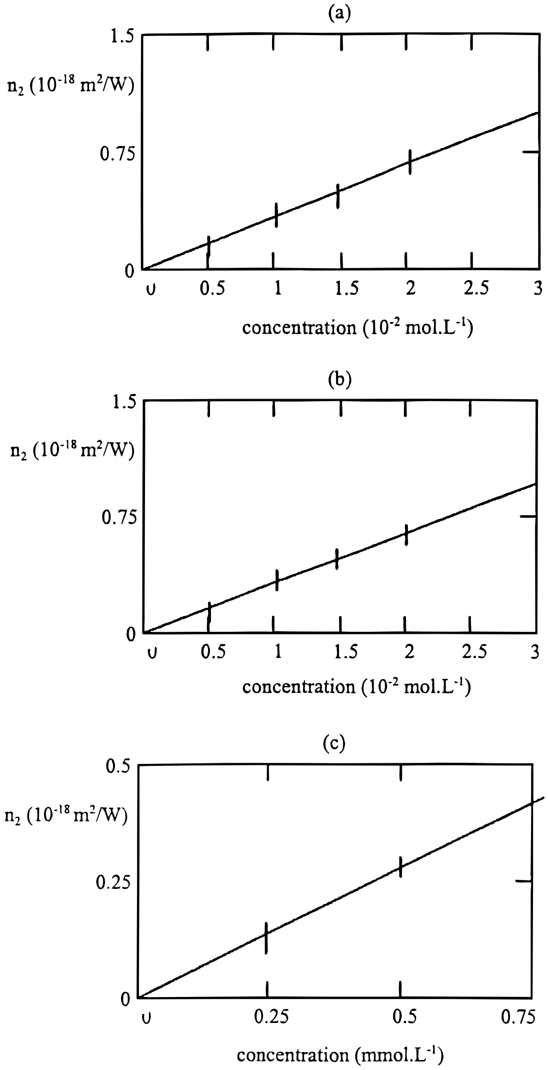


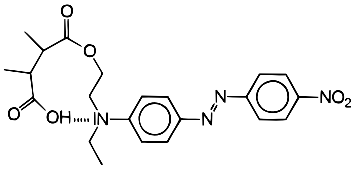
Figure 4. n_2 coefficient versus concentration: (a) COPADR1, (b) COPADR13, (c) COPADO3.

completely symmetrical character of the apertured *Z*-scan plot (Figure 3d), while the DR13 (and DR1, not represented) polymers exhibit non symmetrical plots (Figure 3a), typical of two-photon absorption.

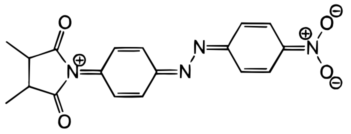
This large $\chi^{(3)}$ value is somewhat surprising, considering the classical expression for $\chi^{(3)}$ proportionnal to $\psi(-\omega,\omega,-\omega,\omega) \propto -\mu_{01}^4/(\omega_{01}^2 - \omega^2)^3 + \Delta\mu^4/\{(\omega_{01}^2 - \omega^2)^2(\omega_{01}^2 - 4\omega^2)\}$.[19] The second positive term of the expression is the most important in our case since ω is not far from $\omega_{01}/2$ (two-photon resonance), thus leading to large positive $\chi^{(3)}$.

In the case of the DO3 family of chromophores the two-photon resonance is more distant from the pulsation used in the experiments; therefore, the $(\omega_{01}^2 - 4\omega^2)$ should be higher than in the case of the DR family; an overall decrease of $\chi^{(3)}$ should be expected. This explains for example, that the $\chi^{(3)}$ of the DO3 molecule is lower than those of DR1 and DR13 (Table 2).

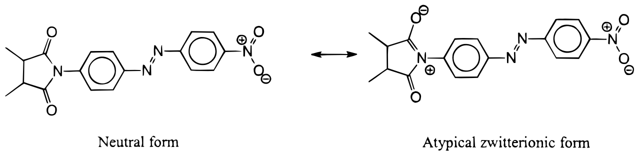
Scheme 3. Illustration of the Possibly Existing Hydrogen Bonding in COPADR1



Scheme 4. Classical Limiting Resonance Formula for the Chromophore in COPADO3



Scheme 5. Both Resonance Formulas That Are Supposed To Be Involved in the "Neutral" Form of COPADO3



The $\chi^{(3)}$ value in the DR functionalized polymers is slightly lower than those with their molecular equivalents DR1 and DR13. This probably stems similarly from the bathochromic shift of the maximum absorption wavelength. It should be noted that in these cases the chromophore electronic structure undergoes only a very small influence when entering the polymer. We suggest that the slight modification in the absorption is related to the proximity of the carboxylic group, which should create a hydrogen bond with the chromophore nitrogen, slightly decreasing its donating power (Scheme 3).

However, the chemical and electronic chromophore structure is strongly modified between DO3 and COPADO3. While the main zwitterionic form of the chromophore in COPADO3 remains certainly the classical one (Scheme 4), the opposed "neutral" structure may be seen as a mixture between the totally neutral form and another opposite atypic zwitterionic form where the nitrogen electrons are delocalized this time on the oxygen atoms of the imide groups (Scheme 5). Therefore the dipolar moment of the classical zwitterionic form μ_Z keeps more or less the same value, while on the contrary the dipolar moment μ_N of the "neutral"

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[19] Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1.

form should be strongly decreased by the intervention of the opposite zwitterionic form.

According to Barzoukas et al.,[14] the $\Delta\mu$ value is directly proportional to $\mu_Z - \mu_N$. Therefore $\Delta\mu$ should be expected to be strongly enhanced when compared to the unmodified DO3 chromophore. Since $\Delta\mu$ comes at the fourth power in the expression of γ, the large enhancement of $\chi^{(3)}$ could therefore be explained.

Last, let us emphasize the fact that the reproducibility of the nonlinear response of the three functionalized polymers is actually very good. In the course of a set of experiments, unlike PMMA DR1,[13b,7] the illumination time of the polymers has absolutely no appreciable influence on their observed fast positive Kerr-like index response, nor the power of the source, which can be chosen as high as desired. Indeed, the same measurements frequently repeated on these three products during a whole year did not reveal any appreciable change of their response, either on a short or long-term scale.

It is possible that the polymer backbone of theses polymers is more resistant than that of poly(acrylates) to powerful illumination conditions. In particular, it is clear that the imide links in COPADO3 are very strong and rigid bonds when compared with most of the previously described functionalized polymers in view of optical applications. The nonlinear optical properties of spin-coated films are currently under investigation.

Acknowledgment. The authors thank B. Fahys (Lab. d'Electrochimie du Solide, University de Franche Comté) for his help in the characterization of the polymers and M. Blanchard-Desce (Lab. de Chimie, Ecole Normale Supérieure, Paris) for fruitful discussions.

CM9702777