polymer

Synthesis, characterization and nonlinear optical properties study of polymers based on coloured monomers

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Abstract

We have synthesized coloured monomer structures characterized by the simultaneous existence of a polarizable double bond and an extended chromophore. The polymerization and copolymerization of these monomers have been tested with styrene and methyl methacrylate. The third-order nonlinear optical (NLO) properties of different samples have been studied from their solutions using chloroform as solvent. The third-order hyperpolarizability γ_{xxxx} of the better materials can reach 10^{-29} esu at 532 nm and their response time is faster than 35 ps. The corresponding third-order NLO susceptibility $\chi_{xxxx}^{(3)}$ is estimated to be 6×10^{-11} esu and the figure of merit $\chi^{(3)}/\alpha = 7.5 10^{-2}$ esu cm is larger than that of most currently known nonlinear optical polymers. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The area of nonlinear optics of organic molecules and polymers offers exciting opportunities, both for fundamental and technological development. As a result, in the last decade, there has been great interest in the synthesis of novel monomers and polymers with the intention of producing materials having large nonlinear optical (NLO) properties [1–4].

One of the most important reasons, from the application point of view for the search of third-order NLO materials, is the fact that for information technology applications, the amount of information which can be written with a light beam onto some medium for information storage increases inversely with the wavelength of the write light [5]. Thus, the decrease of the wavelength means more information written on the storage medium per unit area.

Recently, the study was focused on finding conjugated polymers with large nonlinear optical effects, fast responses and also good solubility, processability and high durability [2]. In this way, the π-conjugated polymeric structures have shown the largest values of nonresonant third-order nonlinearity, with the largest tensor component being along the chain direction. It has been shown theoretically and experimentally that the great value of the hyperpolarizability γ reflects the effective π-electron conjugation. Among these π-conjugated polymer materials, polyacetylenes and polydiacetylenes are reported to have large susceptibilities $\chi^{(3)}$ (10^{-10}–10^{-8} esu) and fast response time [6–8], but their low transparency and difficulty in processability restrict their applications. Nonetheless, third-order NLO polymers exhibiting low absorption and good processability have been reported [7].

In the present work, we have attempted to optimize the processability of polymers for NLO by introducing a new strategy of synthesis. Basically, there are two ways for obtaining NLO polymers: the first consists in linking the structure-conjugated dye (which gives the nonlinear effect) to an existing polymer. In the second method, the structure-conjugated dye is linked to the monomer and the polymerization is done afterwards. We used the second method because the dye monomer fraction can be controlled in the macromolecular structure.
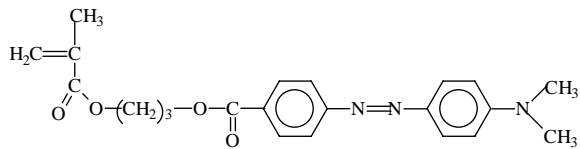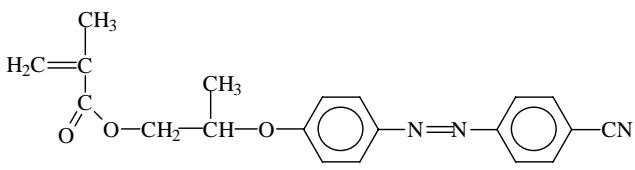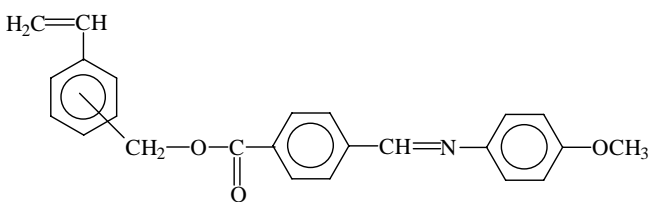
In the first part of this work, we summarize the materials

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Table 1
Structures of the synthesized dye monomers

Code	Structures
I	

1-N,N-dimethyle-azo-diphenyle, 1ʹ-carboxy-propyle-methacrylate (*red powder*)

II

1-cyano-4,1ʹ-azo-diphenyle-4ʹ-oxo-propyle-methacrylate (*orange powder*)

III

1-methoxy-4,1ʹ-azomethyne-diphe-nyle-4ʹ-carboxy-p-methyle styrene (*beige powder*)

synthesis technique and give the corresponding results. In the second part, we report the linear and nonlinear optical coefficients of the polymers that have been synthesized.

2. Material and samples

In Table 1 we present the structure of the dye monomers that are synthesized. The starting materials used for the syntheses by the ester and ether monomers were: methacrylic acid, bromo or chloro-propanol (Aldrich), 4-carboxybenzaldehyde (ACROS Organics) and 4-Methyl Red sodium salt 99.9% (Fluka). The preparation of the azoic monomers I and II involves an intermediary reaction succession. For the synthesis of the ester monomer I a first

step is necessary: the preparation of the hydroxypropil-methacrylate [8,9]. For the preparation of the ether azoic monomer II, the first step is to obtain the dizonium salt [10]. Both types of monomers are obtained by the phase transfer catalyse reaction [11]. We used the tetrabutyl ammonium hydrogen sulphate (TBAH) as a transfer agent and a mixture of *N,N*-dimethyl sulphoxide (DMSO) and tetrahydrofuran (THF) as a reaction medium. The reaction temperature was 60°C and the ratio was (THF:DMSO) 6:1 in volume. The synthesis efficiencies were of 60–80% after 72 h of reaction. The most difficult part of the synthesis is the purification. The purification method was the preparative chromatography using silica A60 (from FLUKA), ether petroleum and of mixtures ether petroleum/methyl chloride.

Table 2
The characteristics of the synthesized monomers

Monomers	λ_1[a] (nm)	ϵ_1[b] (l/mol cm)	λ_2[a] (nm)	ϵ_2[b] (l/mol cm)	T_m[c] (°C)
I	250	24 657	409	22 222	44
II	260	2956	361	4807	–
III	256	47 740	356	22 250	109.4

[a] The wavelengths of the first and the second absorption peaks.
[b] The molar extinction coefficients.
[c] The melting temperature.

Table 3
Synthesis characteristics of the polymers

Copolymer	x^a	C (%)	$10^4 M_n$	X^b	T_G (°C)	Initiator type
MMA-I	0.76	35	3.4	0.70	89	PB
S-II	0.50	60	4.0	0.47	85	PB
MMA-III	0.20	6.64	4.7	0.12	103	AIBN

[a] Molar fraction of the dye monomer in the substrate.
[b] Molar fraction of the dye monomer in the copolymer.

The azomethynic monomer (III) was synthesized by a series of condensation processes using benzene as reaction medium and azeotropic agent [12,13]. The starting materials are an isomeric mixture *m-p*-chloromethyl styrene (6/4); *p*-anysidine; 2,6-di-*t*-butyl-4-methyphenol as inhibitor for the vinyl group and *p*-toluene sufonic acid as catalyst. The reaction takes place at the reflux of the benzene during 15–17 h. The obtained reaction compound was purified by a series of successive recrystallizations using absolute ethanol. The global efficiency is approximately 68%.

The main characteristics of the obtained monomers are presented in Table 2. The IR spectral analysis shows the characteristic bands of the synthesized monomers structures that are confirmed by ^{1}H NMR spectra. The melting temperatures were measured by differential scanning calorimetry.

The copolymers have been synthesized using the tube polymerization technique in nitrogen atmosphere by the solution procedure. The global molar concentration of the monomers in substrate was 1 mole/l and we varied the dye monomer fraction (see Table 3). The solvent was chlorobenzene and the initiators were benzoyle peroxide (PB) and 2,2′-azo-izo-buthyrodinitryl (AIBN) at the concentration of 3×10^{-3} mol/l. The temperature of polymerization was 80°C. The copolymers have been separated in methanol. In Table 3 are presented the main characteristics of the process and the obtained polymers.

3. Experimental set-up and results

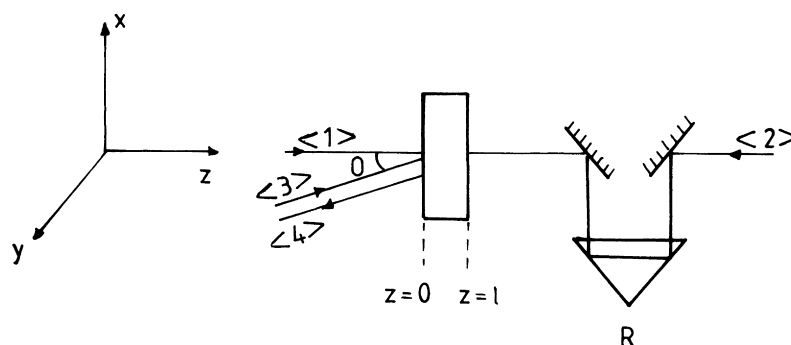A typical absorption spectrum of the synthesized polymers dissolved in chloroform solution is shown in Fig. 1; the peak of absorption is at 410 and 532 nm is a near-resonance wavelength. The optical losses of the different polymers studied at 532 nm are given in Table 4.

For the measurement of the nonlinear coefficients of the samples, we used the retroreflection degenerated four wave mixing (DFWM) method [14,15]. The basic geometry is illustrated in Fig. 2. The excitation is provided by 35 ps light pulses at 532 nm. The pulses are generated by an amplified, mode-locked Quantel Nd^{3+}:Yag laser that operates at 1 Hz repetition rate. These pulses are nearly Fourier transform limited. The angle θ between beams ⟨1⟩ and ⟨3⟩ in air is 13° and the thickness of the cell containing the sample is 1 mm. The conjugated signals were detected by a photomultiplier and a BOXCAR interfaced to a microcomputer. Carbon disulphide (CS$_2$) was used to calibrate the result, and the reflectivity R of the sample (in DFWM geometry) was calculated by the relation:

$$R = \left(\frac{48^3}{\lambda C n^2} \|\chi^{\langle 3 \rangle}\| (Il) \right)^2 \kappa(\alpha) \tag{1}$$

where $\kappa(\alpha)$ is a parameter of material which describes the linear absorption at the operating wavelength (i.e. 532 nm here) and it is defined by the relation:

$$\kappa(\alpha) = \frac{T_l}{(\alpha l)^2 [\coth(\alpha l/2) + 1]^2} \tag{2}$$

In these relations, l is the cell length, **n**, the refractive index, T_1 and α, the linear transmission and absorption coefficients, respectively; I the pump beam intensity. For a given pump intensity I and a given cell length l, the third-order susceptibility $\chi^{\langle 3 \rangle}(-\omega, \omega, \omega, -\omega)$ of the sample can be calculated by the equation below (in the low reflectivity regime):

$$\chi^{\langle 3 \rangle} = \left[\left(\frac{n}{n_r} \right)^2 \sqrt{\frac{R}{R_r}} \sigma(\alpha) \right] \chi_r^{\langle 3 \rangle} \tag{3}$$

where every subscript "*r*" denotes the reference CS$_2$ ($\chi_r^{\langle 3 \rangle}$ for CS$_2$ is $\chi_{xxxx}^{\langle 3 \rangle} = 6.8 \times 10^{-13}$ esu) and $\sigma(\alpha) = 1/\sqrt{\kappa(\alpha)}$. The molecular third-order hyperpolarizability y is connected to

Fig. 1. Four-wave mixing set-up: ⟨1⟩ and ⟨2⟩, counter-propagating pumps; ⟨3⟩, probe beam; ⟨4⟩, conjugate beam (or signal); R, delay line.

Table 4
Characteristics of the samples at 532 nm. α: linear absorption, $\chi_{xxxx}^{\langle 3 \rangle}$: third-order susceptibility, $\langle \gamma_{xxxx} \rangle$: molecular hyperpolarizability of the monomer $F = \chi^{\langle 3 \rangle}/\alpha$: figure of merit of the material. All these parameters are related to the optimal concentration, i.e. the value of C that gives the best DFWM reflectivity

Code	C_{opt} (mg cm^{-3})	α (cm^{-1}) at 532 nm	$10^{11}\chi_{xxxx}^{\langle 3 \rangle}$ (esu)	$10^{12}F$ (esu cm)	$10^{28}\gamma_{xxxx}$ (esu)
MMA-I	5.00	8.2	6.13	7.5	2.0
S-II	6.25	11.4	0.45	0.4	0.5
MMA-III	2.30	4.0	0.40	4.0	1.0

$\chi^{\langle 3 \rangle}$ by:

$$\chi^{\langle 3 \rangle} = F^4(C_{solute}\gamma_{solute}) + \chi^{\langle 3 \rangle}_{solvent} \qquad (4)$$

Here $F = [(n^2 + 2)/3]$ is the local field correction factor.

As in many organic materials, the DFWM reflectivity R of the studied samples depends on the concentration of solution [14,15]. The value of the concentration which gives the best DFWM reflectivity R is usually called the optimal concentration and is c_{opt}. Fig. 3 shows the dependence of $\chi^{\langle 3 \rangle}$ of MMA-I (see Table 3 for the code significance) on the concentration of the polymer in chloroform.

The other two materials (S-II and MMA-III) showed the same kind of dependence. This curve is obtained by using the experimental results and relationship (3). As it is seen in this figure, $\chi^{\langle 3 \rangle}$ is proportional to the concentration for values of C up to 5 mg/cm³. The open circles indicate the experimental points and the line is the linear regression. According to the experimental set-up, the error of the measurement comes mainly from the fluctuation of the laser pulse that causes the fluctuation of the detected signal by a photomultiplier tube. From the parameters of regression using formula (4) and experimental data, we have estimated the hyperpolarizability γ_{xxxx} of the studied materials. These values are listed in Table 4.

The transmission T of the samples when they are submitted to high pump intensity is also studied and shows that T remains constant (for intensity up to 2 GW/cm²). This result enables us to conclude that there is no
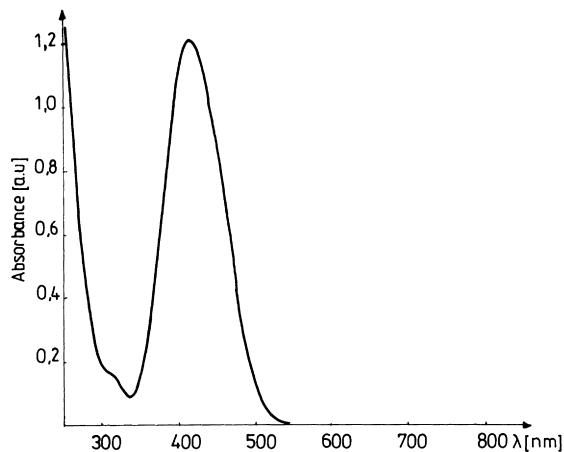
nonlinear absorption and thus the values of $\chi^{\langle 3 \rangle}$ are real numbers at 532 nm. The functional dependence of the phase conjugated signal on the incident pump (or probe) delay is measured [15] and shows that the response times of the materials are faster than the pulse duration (i.e. 35 ps). The experimental result is summarized in Table 4 and indicates the values of the linear absorption coefficient α of the materials at the concentrations used at 532 nm. These coefficients α are obtained from the absorbency measurement with the experimental set-up of Fig. 2. From the values of α and $\chi^{\langle 3 \rangle}$ we have calculated the figure of merit $F = \chi^{\langle 3 \rangle}/\alpha$ of the different studied samples. These values of F listed in Table 4, are larger than that of most currently known nonlinear optical polymers.

4. Conclusions

We have synthesized coloured monomer structures characterized by the simultaneous existence of a polarizable double bond and an extended chromophore. The polymerization and copolymerization of these monomers have been tested with styrene and methyl methacrylate. Although the method is rather time-consuming, the efficiency of the reactions is high.

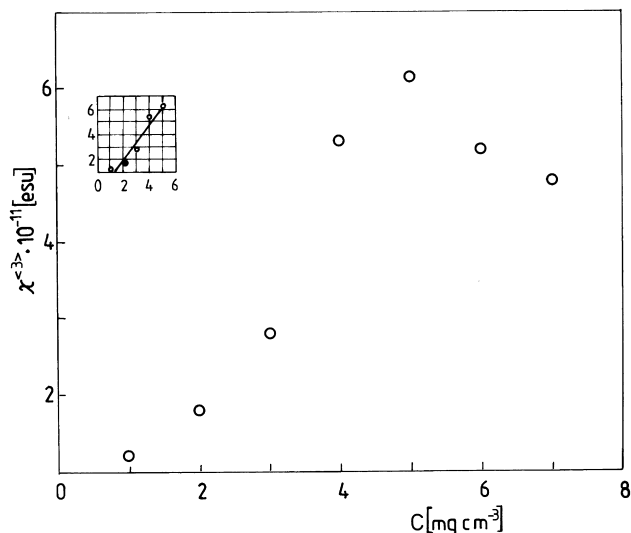By the copolymerization of these dye monomers with the

Fig. 2. Absorption spectra of MMA-I.

Fig. 3. Dependence of $\chi^{\langle 3 \rangle}$ coefficient and concentration of MMA-I.

styrene or the methyl methacrylate, we obtained macromolecular structures ($M_n > 10^4$).

Using the elementary analyse of the copolymers and the ^{1}H NMR spectra we estimated the molar fraction values of the dye monomers included in copolymers. The experimental results show the preservation of the molar fraction values from the initial substrate, thus suggesting an ideal statistic copolymerization.

The structural dye units in the copolymer preserve the optical properties characteristic for the azoic or azomethynic monomers.

The third-order nonlinear properties of the obtained polymers have been measured by the degenerated four wave mixing method at 532 nm with good results. Thus, these polymers are potentially suited for optical signal processing applications. Because the wavelengths used in telecommunications are bigger, and the third-order NLO answer of the obtained polymers is expected to be lower at these wavelengths, they can be used in schemes together with other devices, halving or trebling the wavelength.

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