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Efficient initiators for two-photon induced polymerization in the visible range

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Abstract

We present two derivatives of biphenyl or fluorene symmetrically substituted, which could initiate the two-photon absorption (TPA) photopolymerization of acrylates in the visible range. Both compounds show broadband TPA between 500 and 650 nm with cross sections of respectively 30 and 80 × 10^{-50} cm^4 s $photon^{-1}$ at 532 nm, the photoinitiation wavelength. Threshold energies and dynamic ranges for polymerization were measured in both cases. As expected, the fluorene derivative was slightly more efficient than the biphenyl one. Our initiators appeared to be orders of magnitude more sensitive than the commercial UV ones, commonly used for TPA photopolymerization. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, two-photon absorption (TPA) processes in organic materials were intensively studied in view of applications for optical limiting [1], three-dimensional optical data storage [2], fluorescence imaging [3] and microfabrication [4]. These three latter techniques take advantage of the high spatial resolution of two-photon excitation. As far as concerned 3D microfabrication, the TPA initiated polymerization technique, which appears to be complementary to the well known layer-by-layer fabrication [5], led to 3D micro-objects in a single step with a very high resolution [6,7]. Recent works on TPA photopolymerization use mainly femtosecond lasers in the near IR. Two types of photoinitiators are described : (i) commercial UV-visible photoinitiators [8,9], (ii) electron-rich molecules optimized for TPA in this wavelength range [10,11]. Larger values of TPA cross section obtained for the second class of systems allow lower powers and shorter times of exposure, which could lead to a cheaper technology. A wide variety of laser sources are available at shorter wavelengths in the visible range (Ar-ion laser or frequency doubled Nd-YAG laser) which could lead to a better polymerization resolution and smaller 3D

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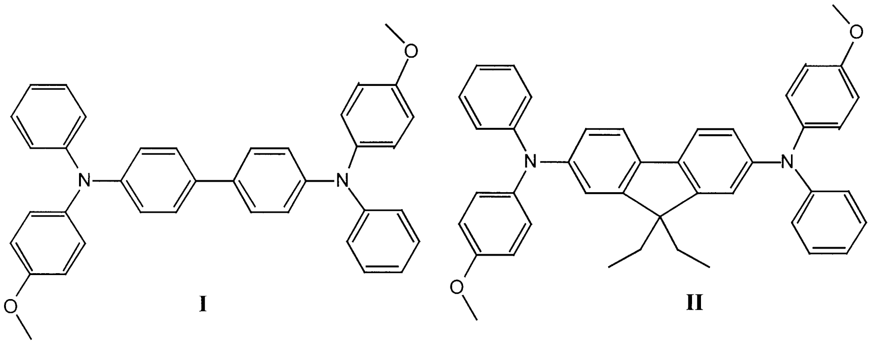

Fig. 1. Molecular structures of compounds I and II.

structures. The engineering on TPA initiators in this wavelength range is just emerging [12].

In this paper, we present two molecules, which are efficient TPA initiators for the polymerization of triacrylates in the visible range. These photoinitiators are two symmet N,N'-bis-(4-methoxyphenyl)-N,N'-diphenyldiamino derivatives (Fig. 1). They were previously described for TPA optical limiting applications in the visible range [13,14]. Their D-Π-D structure (where D is a donor and Π the conjugated bridge) is known to be well-adapted for photopolymerization [4]. The moderate conjugation in our systems (biphenyl or fluorene derivatives) shifts TPA properties in the visible range. In this work, we have characterized their TPA cross-sections, ground-state oxidation potentials and their threshold energies for the polymerization of triacrylate monomers. The initiation efficiencies of these two compounds are compared and discussed relatively to their physical properties.

2. Experimental section

Details about the synthesis of molecules I and II ($N^4,N^{4'}$-bis-(4-methoxyphenyl)-$N^4,N^{4'}$-diphenyl-4, 4′-diaminobiphenyl and $N^4,N^{4'}$-bis-(4-methoxyphenyl)-$N^4,N^{4'}$-diphenyl-2,7-diamino-9,9-diethylfluorene respectively) are given in the Appendix A.

TPA spectra were obtained by up-conversion fluorescence measurements using a Nd-YAG laser pumped optical parametric oscillator supplying 2.6 ns pulses in the 450–650 nm spectral range with 10 Hz repetition rate. The pulse energy was kept low enough to ensure a quadratic dependence of the fluorescence signal on input energy. The TPA cross-section was determined using 1,4-bis(2-methylstyryl)benzene as reference [15,16].[1]

The ground oxidation potential of both compounds was measured by cyclic voltammetry versus Ag/Ag$^+$ in acetonitrile/0.1 M $(\mathrm{Bu_4N^+})(\mathrm{BF_4^-})$.

The resins consisted in 3% photoinitiator (I or II), 70% monomer (tris(2-hydroxyethyl) isocyanurate triacrylate with a radical inhibitor level of 100 ppm.) and 27% polymer binder (poly(styrene-co-acrylonitrile)(75/25)). Films with a thickness of about 50 μm were obtained by solvent evaporation from a chloroform solution.

All TPA induced photopolymerization experiments were performed using a frequency doubled Nd-YAG microlaser Nanolase from JDS Uniphase ($\lambda = 532$ nm, pulse duration 0.5 ns, maximum pulse energy 4 μJ, repetition rate 6.5 kHz) focused through a ×5 objective lens. Films were placed on a 3-axis piezoelectric stage allowing their translation relative to the laser focal point.

3. Results and discussion

3.1. Physical properties of I and II

3.1.1. Optical properties

These molecules present linear absorption maxima at $\lambda_{\max} = 349$ nm and $\lambda_{\max} = 374$ nm re-

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[1] $\sigma_{\mathrm{TPA}} = 62 \times 10^{-50}$ cm^4 s photon^{-1} at 600 nm; the value of the TPA cross-section has been corrected for a typographical error.

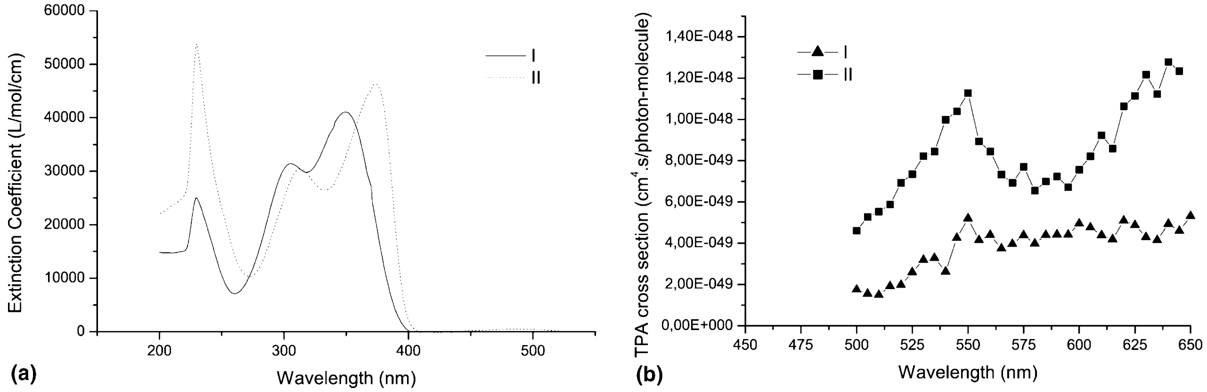

Fig. 2. Optical properties of compounds I and II: (a) UV-visible absorption spectra in dichloromethane; (b) TPA spectra in *N*,*N*-dimethylformamide.

spectively for I and II (Fig. 2), leading to transparent molecules for wavelengths above 400 nm.

Both molecules exhibit broadband TPA properties in the visible range between 500 and 650 nm due to a moderate conjugated charge transfer system as mentioned above. The compound II is more efficient than I in terms of TPA properties, in good agreement with an increase of the charge transfer process within II due to the planarity of the fluorene core. At the experimental photopolymerization wavelength (532 nm), the TPA cross-sections of I and II are respectively 30 and 80×10^{-50} cm^4 s $photon^{-1}$. Although such values are comparable or sligthly weaker than those published for synthetic initiators for TPA polymerization in the near IR [4,17], they are several orders of magnitude larger than the TPA cross-sections of a commercially available resin that have been used for TPA stereo-lithography [18].

3.1.2. Electrochemical properties

The ground-state oxidation potential is a relevant parameter for the characterization of the photopolymerization process since in the initiation step of acrylates radical photopolymerization, a monoelectronic transfer from the photoinitiator to the monomer is required [4]. This potential, relative to Ag/Ag^+, was found to be respectively 380 mV for I and 320 mV for II. These low values show the ability for both molecules to give an electron from the donor group (*N*-(4-methoxyphenyl)-*N*-phenyl-amino) of the photoinitiator to the carbonyl acceptor group of the monomer, with slightly more efficient electronic transfer properties in II.

3.2. Initiation properties of I and II

Both chromophores are efficient TPA initiators for acrylates polymerization under 532 nm laser excitation. The threshold energy of polymerization is a relevant feature to characterize the initiation

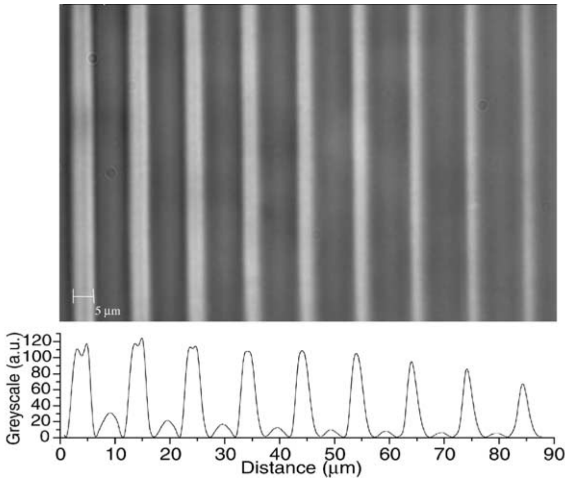

Fig. 3. Polymer lines fabricated from initiator II using a 1.26 mW average power laser and a 1.8 µm waist beam with speeds increasing from 90 to 300 µm/s; the corresponding greyscale profiles are displayed on the bottom.

properties. It was evaluated by analyzing lines of polymer produced by translating the resin across laser beam at increasing speeds. The average laser power, beam waist, and scan speeds were 1.26 mW, 1.8 μm and 30–500 μm/s, respectively. A transmission microscope image of lines written at increasing speeds is shown on Fig. 3. The contrast between the polymerized material and the original resin could be due to a significant increase of the refractive index upon polymerization as already observed for other monomers [19]; brighter parts correspond to high refractive index regions trapping light. The linewidth decreases when the scan speed increases. This a due to the narrowing of the exposure dose area that is above threshold. We used the greyscale profile shown on the bottom part of Fig. 3 to estimate linewidth values. However, this profile does not reproduce directly the physical shape of the solidified structures and should be considered with care, since it depends critically on how such phase objects are imaged through an optical microscope. Assuming a Gaussian beam profile, the incident energy E (in J/m^2) at a distance d from the middle of the line can be expressed following the relationship (1), in which P is the average power of the beam, ω_0 its half width at $1/e^2$ of the intensity maximum and s the scan speed.

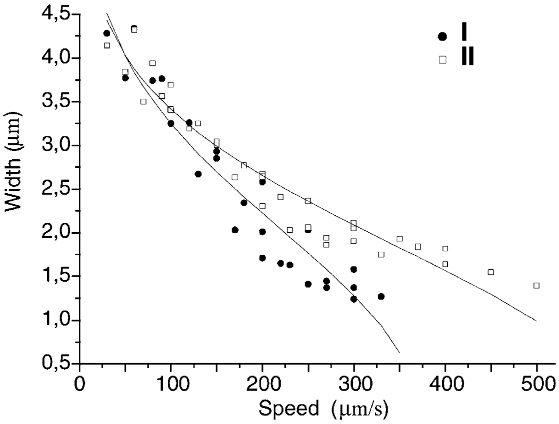

Fig. 4. Width of lines as a function of scan speed using a 1.26 mW average laser power and compounds I and II as photoinitiators. The data points are fitted according to model described in text.

$$E = \sqrt{\frac{2}{\pi}} \frac{P}{\omega_0 s} e^{-2d^2/\omega_0^2} \tag{1}$$

This expression leads to the relation (2) between the linewidth W and the scan speed, where $E_{\max}$ is the incident energy at the waist ($d = 0$; $E_{\max} = \sqrt{\frac{2}{\pi}} \frac{P}{\omega_0 s}$) and E_{th} the polymerization threshold energy.

$$W = \omega_0 \sqrt{2 \ln \frac{E_{\max}}{E_{\text{th}}}} \tag{2}$$

Fig. 4 displays the changes in the line width as a function of the scan speed. The solid line corresponds to the data analysis using Eq. (2). From this model the threshold energies for I and II are 136 J/cm^2 and 95 J/cm^2, respectively. This is in agreement with the higher TPA efficiency of initiator II. For both compounds, the threshold energy is seven orders magnitude lower than for UV radical generators used as TPA initiators [8].

A further relevant parameter for the effective fabrication process is the dynamic range of a resin, defined as the ratio $E_{\text{damage}}/E_{\text{th}}$, in which E_{damage} is the damage energy. This damage energy is approximatively 2500 J/cm^2 for I and II, leading to a dynamic range of 18 for I and 26 for II. These values are an order of magnitude higher than those obtained with commercial UV-photoinitiators [20]. This enlarges significantly the intensity window available for fabrication.

4. Conclusion

Two TPA photoinitiators optimized for the visible range have been synthesized and characterized. These molecules present an efficient TPA in the 500–650 nm spectral range. They have been successfully used for acrylates photopolymerization without any coinitiator. The polymerization thresholds were determined by the analysis of polymer lines produced at variable exposure dose. The fluorene derivative leads to a lower polymerization threshold than the biphenyl one in agreement with its larger TPA cross-section. For both compounds, these features are seven orders of magnitude lower than those of commercial UV initiators. In addition, our compounds provide a large intensity dynamic range before damage. The recent work reported in Ref. [12] and our results confirm the importance of a molecular engineering approach to optimize TPA photoinitiators. They open a path towards an improved reliability for TPA fabrication and make possible the use of inexpensive laser sources. TPA 3D microfabrication at 532 nm using microlasers is in progress in our group.

Appendix A. Chemical synthesis of molecules I and II

The synthesis of I and **II** using the Cu-mediated Ullmann condensation will be described elsewhere [21]. The molecule I was obtained in one step from *N*,*N*-diphenylbenzidine and 3-iodoanisole (yield: 72%). MP: 158 °C. (Litt.: 158–159 °C [22]).

The molecule II was prepared from *N*-(4-methoxyphenyl)-*N*′-phenylamine and 2,7-diiodo-9,9-diethylfluorene (yield: 61%). All the spectroscopic data are in full agreement with the proposed structure. $C_{43}H_{40}N_2O_2$ (616.80): C, 83.73; H, 6.54; N, 4.54; O, 5.19. Found: C, 83.50; H, 6.52; N, 4.51. MP: 151 °C.

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