Two-photon Microstructure-polymerization Initiated By A Coumarin Derivative, Titanocene and N-phenylglycine System

Yang Yongyuan a, Feng Shujing a
Li Chengde b, Lao Le b, Wang Shufeng b, Huang Wentao b and Gong Qihuang b

a. Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 10000. China
b. State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing 100871. China

Two-photon polymerization initiated by a tri molecular initiating system composed of 7-diethylamino-3-(2'-benzimidazolyl)coumarin, Titanocene and N-phenylglycine was investigated. The photosensitizer has been proved to possess large two-photon absorption cross-section for 800nm femtosecond laser. The sensitizer/coinitiator system has high Photosensitivity for polymerization of photosensitive resin. This photopolymer system has been demonstrated for fabricating three-dimensional microstructure.

Keywords: Two-photon polymerization, two-photon absorption, coumarin

1. Introduction

Two-photon absorption polymerization provided a means for three-dimensional lithographic microfabrication [1-4] with much higher spatial resolution than conventional one-photon polymerization technique. However, commercially available UV photopolymer systems exhibited low photosensitivity for this purpose since the initiators have small two-photon absorption cross-sections ($\delta$) around the order of $10^{-58}$ cm$^4$ s/photon [2]. To overcome this shortcoming, bis(styryl)benzene derivatives with donor-$\pi$-donor, donor-$\pi$-acceptor-$\pi$-donor, or acceptor-$\pi$-donor-$\pi$-acceptor structure motifs have been synthesized and exhibited large $\delta$ up to 1250x$10^{-50}$ cm$^4$/s/photons[5]. These chromophores were designed on the basis that symmetric charge transfer from the ends of a conjugated system to middle or vice versa, could enhance values of $\delta$. Belfield et al. [6] realized that polar molecules undergoing large changes in dipole moment upon excitation from the ground to an excited state might have large multi-photon absorptivity. They synthesized a series of fluorene derivatives with systematic variation in molecular structure [7-9] and found some of them having two-photon absorptivity as high as $\delta=1300x10^{-50}$ cm$^4$/s/photons at wavelength of 670nm. These effective chromophores have been successfully used as photoinitiators to initiate the polymerization of acrylates for demonstration of three-dimensional optical data storage based on fluorescent bits, multi-photon fluorescent imaging, fabrication of magnetically actuated microstructure and fabrication of three-dimensional photonic band gap materials [10,11].

For free radical polymerization the rate of photopolymerization is mainly influenced by the light absorption of the photoinitiator (PI) at the wavelength of the light source, the quantum yield of radical generation, and the initiation efficiency of the generated radicals. Thus, low light absorption of a PI is not consistent with high photoinitiating efficiency. Searching after multifunctional TPA materials that incorporate functionality for high two-photon absorptivity along with molecular constructs for energy transfer, electron transport and/or morphological variation is on the way.

Coumarin dyes are well-known dyes for high fluorescent efficiency and some of them were reported having a $\delta$ around the order of $10^{-50}$ cm$^4$/s/ photon for $\lambda=750$-840nm[12]. Most ketocoumarins, especially 7-alkylamino coumarin are efficient visible light or laser sensitizers for crosslinkable polymers. The proper combinations of ketocoumarin dye with activators can give high quantum yield for initiated radical polymerization. Williams et al. [13] reported that...
N-phenylglycine, in the presence of ketocoumarin dye, shows sensitivity in the visible region up to 550nm. We used the ketocoumarin dye with titanocene compound photoinitiating system and obtained high initiating efficiency for visible light polymerization [14]. In this paper, we introduce tri molecular, e.g. ketocoumarin, titanocene, N-phenylglycine, photosensitive initiating system and investigate the possibility of employing the process of two-photon photopolymerization for the fabrication of microstructure image.

2. Experimental

Binder resin was synthesized by radical co-polymerization from methylmethacrylate, butylacrylate, hydroxyethylacrylate and acrylic acid in our laboratory, average molecular weight $M_w=50,000$, acid value=60mgKOH/g. Dipentaerythritol hexaacrylate was a product of SATOMER company, Titanocene, bis[r,s-2,4-cyclopentadien-1-yl]-bis-[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl] titanium was supplied by CIBA specially chemicals Limited. 7-diethylamino-3-(2'-benzimidazolyl) coumarin (DEDC), supplied by SHIKISO Institute Kankoh, Japan. N-phenylglycine (NPG) was purchased from ALDRICH chemical company. The chemical structures of photosensitive initiating system are shown in Fig.1.

Two-photon photosensitive resin was studied in dry film format by use of a typical formulation composed in Fig. 2.

| Binder resin: methyl methacrylate-butyl acrylate-hydroxyethyl acrylate-acrylic acid co-polymer |
| Monomer: hydroxyethylacrylate |
| Monomer: dipentaerythritol hexaacrylate |
| Sensitizer: 7-diethylamino-3-(2'-benzimidazolyl) Coumarin |
| Initiator: N-phenylglycine |
| Initiator: Titanocene |
| Coating solvent: diethylglycol monoethyl- Ether |

Fig.2 Formulation of the photosensitive resin for two-photo polymerization

The film of this resin were prepared by spin-coating on glass plate and followed by drying at 100°C for 2 minutes. The thickness of the film was about 4µm. A mode-locked Ti: sapphire laser(Coherent Mira 900 F) pumped by an argon laser was used for the experiments. The Ti: sapphire laser generated 120fs light pulses at the wavelength of 800nm with a repetition rate of 76MHz. In the measurement of two-photon absorption and fluorescence quenching, the solvent was trichloromethane and the concentration was 5x10^{-6}mol/l. The photopolymer films were exposed by 800nm wavelength femtosecond laser. The exposed photosensitive resin take place photomerization and reduce the solubility. The microstructure lines were obtained by dissolving away the unexposed resin in alkali solution.

3. Results and discussion

Titanocene solution in trichloromethane displays an absorption band in the 360-520 nm region[14]. The maximum absorption of DEDC in trichloromethane appears in the visible region,

$\lambda_{max}=438$nm, $\varepsilon_{max}=5.23x10^4$mol cm$^{-1}$

$\lambda_{max}=459$nm, $\varepsilon_{max}=5.13x10^4$mol cm$^{-1}$

Fig. 1 Chemical structures of photosensitive initiating system.
No absorption can be detected for a wavelength longer than 520nm. Thus, it is impossible for DEDC or DEDC/NPG/TTC to initiate one-photon polymerization of a monomer at 800nm wavelength. The examination of two-photon absorption cross-section for DEDC was followed as the procedure in the literature [13, 15] by comparison of the relative fluorescent signals produced by one- and two-photon absorption.

\[
\delta = \frac{\Phi_1 \eta_1 c F_1}{\Phi_2 \eta_2 c F_2} \quad (1)
\]

Where \( F_1 \) is fluorescence signal, \( F \) is the flux of incident photon in photons/cm\(^2\) s, \( \Phi \) is the quantum yield, \( n \) is the fluorophore number density, \( \sigma \) is the one-photon absorption cross-section in square centimeters. The subscripts 1,2 denote one photon and two-photon respectively. The measurement on the fluorescence induced by two-photon absorption was performed under laser intensity \( 4.7 \times 10^7 \text{ to } 1.4 \times 10^9 \text{ W/cm}^2 \) which correspond to the incident photon flux \( F_i \) of \( 1.9 \times 10^{26} \text{ to } 5.7 \times 10^{27} \) photon/cm\(^2\) s. Fig. 3 indicates that the fluorescence signals are fitted to the square-law dependence on photon flux (or light intensity). We adopted the second harmonic scheme for the one-photon excitation. The same optical setup and the same solution are used in both measurements. Since the final state is excited by one- and two-photon absorption, in this case it can be assumed that the quantum efficiency \( \Phi_1 \) and \( \Phi_2 \) are equal and the number densities \( n_1 \) and \( n_2 \) are also equal [13, 16]. Thus \( \delta \) for DEDC is determined as \( 29.5 \times 10^{-50} \text{ cm}^4 \text{ s/photon} \).

Fig. 4 shows the fluorescence spectra of DEDC and DEDC+NPG+TTC in trichloromethane with concentration of \( 5 \times 10^{-4} \text{ mol/l} \) under the irradiation of the 76 MHz, 800nm, 120fs laser pulses.

It indicates obviously that NPG+TTC has strong quenching effect on DEDC. The decrease of fluorescence signal with the concentration \( [Q] \) of the NPG+TTC can be described by Stern-Volmer equation [17]

\[
\frac{I_0}{I_q} = 1 + k_q [Q] \quad (2)
\]

Where \( I_0, I_q \) are the fluorescence intensities of DEDC solution and the solution quenched by NPG+TTC, \( K_q \) is the bimolecular quenching rate constant, \( \tau_s \) is the singlet state lifetime of DEDC and it is estimated by [18].

\[
\frac{1}{\tau_s} \approx 10^4 \epsilon_{\text{max}} \quad (3)
\]

where \( \epsilon_{\text{max}} \) is the maximum excitation coefficient. From Fig.4, we deduced the \( K_q = 2.6 \times 10^{16}/\text{mol/s} \) using Eqs. (2) and (3). To investigate more details about the two-photon photosensitivity of the photopolymer, singlet-line exposures were performed by focusing the laser beam into the photopolymer plate with a lens (f=75mm). The
focus size was determined to be 54.6µm by knife edge method. The scan speed of the laser spot was 400µm/s. We found that the polymerization did not occur as the incident laser power was lower than 30 mw. So the threshold exposure does in mJ per square centimeter for two-photon polymerization in the resin film at 800nm is \( E_d = 1.7 \times 10^5 \text{mJ/cm}^2 \).

Fig.5 shows a cured line written by the 800nm femtosecond laser beam with a 0.65 NA microscope objective at a scanning speed of 40µm/s on glass plate.

Fig.6 Two-layered log stack structure with a period of 4.3µm fabricated with femtosecond laser direct writing by two-photon absorption photopolymerization.

In our experiments the absorption spectrum of ketocoumarin dye (DEDC) in trichloromethane does not exhibit any change on irradiation, indicating that, by itself, DEDC dye is photochemically stable in the solution. When NGP+TTC was added to the solution, the spectrum of DEDC dye showed a remarkable change due to irradiation with 800nm wavelength laser. This result indicates that the photo induced reaction between DEDC and NPG/TTC occurred.

We consider that the photopolymerization mechanism is proposed as follows: firstly DEDC dye absorbs two near IR photons at the same time and excited to singlet state which transfer firstly to triplet state, the excited triplet state of DEDC with NPG undergo electron transfer reaction to produce the ionic radical of NPG which through decarboxylation reaction generates

\[
\begin{align*}
\text{NH} - \text{CH}_2^* \\
\end{align*}
\]

radical. This radical initiates efficiently the photopolymerization of monomer and oligomer [19]. In the same time the excited triplet state of DEDC can intereacts with Ti tanocene through electron transfer reaction to generate organic Ti:radical which initiates the photopolymerization of monomer and oligomer [20].

**Conclusion**

We have investigated the two-photon polymerization of the photopolymer resin initiated by a trimolecular type initiators composed of 7-diethylaino-3- (2'-benzimidazolyl) coumarin, Titanocene and N-phenylglycine under the 800nm wavelength irradiation of a Ti: sapphire femtosecond laser. The excellent photosensitivity of the trimolecular initiating system has been demonstrated. A microstruture line was fabricated under low laser intensity.
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References