Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 6851–6855

polymer

www.elsevier.com/locate/polymer

Linear and tri-branched copolymers for two-photon absorption and two-photon fluorescent materials

Fanshun Meng[a], Jun Mi[b], Shixiong Qian[b], Kongchang Chen[a], He Tian[a,*]

[a]*Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, People's Republic of China*
[b]*Department of Physics, Fudan University, Shanghai 200433, People's Republic of China*

Received 23 April 2003; received in revised form 30 July 2003; accepted 22 August 2003

Abstract

The one- and two-photon properties of linear (M2) and tri-branched (M3) copolymers with triphenylamine and cyano groups in the main chain were experimentally investigated. Open-aperture z-scan experiments were performed with 1 kHz, 120 fs, and 800 nm Ti:sapphire laser pulses to measure the two-photon absorption cross sections. The two-photon cross sections of M2 and M3 were determined to be 0.304 and 1.441×10^{-20} cm^4/Gw per repeating unit, respectively. In a $CHCl_3$ solution, M2 and M3 emit strong frequency up-converted fluorescence under the excitation of 120 fs pulses at 800 nm with the peaks located at 561 and 542 nm.

Keywords: Two-photon absorption materials; Two-photon induced fluorescence; Copolymers

1. Introduction

Two-photon absorption (TPA) and two-photon fluorescence (TPF) materials have been receiving considerable attention due to their potential usage in two-photon laser scanning fluorescence microscopy, three-dimensional optical data storage, frequency upconverted lasing, and optical power limiting [1–4]. Some of these applications are further based on the fluorescence properties of two-photon excited molecules. The full utility of two-photon materials depends on the development of highly efficient materials with large TPA cross section. Several design strategies have successfully been used to improve the TPA cross section [5–14]. One strategy is to introduce donor and acceptor symmetrically or unsymmetrically to the end groups of the π-conjugated bridge [5–9]. The electron-donating or electron-accepting strength and the conjugation length of the molecules have great effect on TPA cross section. Another strategy is to design and synthesize multi-branched molecules to increase the chromophore number intensity without causing any aggregation [10–12]. Besides, dendrimers functionalized with TPA chromphores have been synthesized to further increase TPA cross section [13,14].

Although a lot of molecules with large TPA cross section have been synthesized, they have to be incorporated into polymer to form thin films for many practical applications [2]. In this case the disperse concentration of TPA materials in the matrix is limited and the phase segregation would easily happen under a strong laser irradiation. So it is of great interest to develop polymers with large TPA cross section. A few polymers have been synthesized as two-photon materials, but their TPA cross section is relatively small compared to the molecular materials [15–17]. In this paper, the TPA and fluorescence properties of linear and tri-branched copolymers (Fig. 1) with triphenylamine and cyano groups in the main chains are described. Triphenylamine is used as electron donor and cyano groups as electron acceptor and they form D–π–A conjugation along the extended polyvinylene π-bridge systems. The bulkiness of triphenylamine inhibits aggregation of polymer chains and therefore effectively decreases possible inter-chain quenching. This structural feature restricts the close packing of the polymer chains, resulting in a more highly soluble amorphous polymer. Therefore the TPA cross sections of these polymers were improved.

---

* Corresponding author. Tel.: +86-21-64252756; fax: +86-21-64252288.

E-mail address: tianhe@ecust.edu.cn (H. Tian).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.08.030

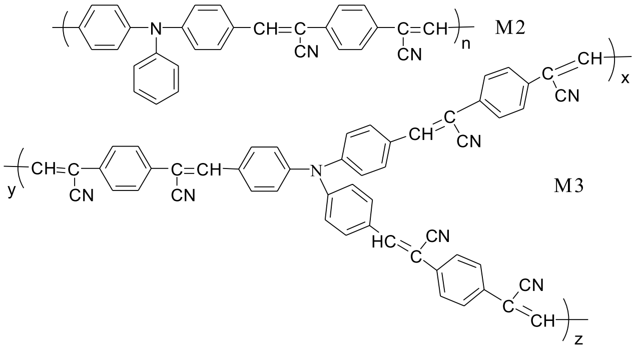

Fig. 1. Chemical structure of the copolymers.

2. Experimental

The preparation of the linear (M2) and tri-branched (M3) copolymers as well as their structural data has been reported elsewhere [18]. UV–Vis spectra were recorded on Varian Cary 500. Photoluminescent spectra were recorded on Varian Cary Eclipse.

TPA cross section of polymer M2 and M3 were measured by open-aperture z-scan technique [19]. The incident laser pulses with pulse energy of 8 μJ were generated by a regenerator amplifier (Spitfire, Spectra Physics). The repetition rate of the pulse is 1 kHz, the duration is 120 fs and the wavelength is 800 nm. After passing through an attenuator (with transmission rate 0.0012), the incident laser beam was focused by a 10 cm lens, transmitted through a 1 mm thick quartz sample cell, collimated and detected by a photodiode. The differential transmission was recorded as the function of sample position when the sample was moved along the propagation direction (z-axis) of the focused beam. The beam's radius at the focus is ca. 13 μm, and the intensity is 151 Gw/cm^2.

The normalized transmission (i.e. $I(z)/I(\infty)$, with $I(\infty)$ being the linearly transmitted intensity far from the focal position) of open-aperture z-scan signal is fitted by the following equation:[19]

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z,0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z,0)\exp(-\tau^2)]\mathrm{d}\tau$$

where $q_0(z,0) = \beta I_0 L_{\mathrm{eff}}/(1 + z^2/z_0^2)$, β is the TPA coefficient, I_0 is the intensity at the focus, and L_{eff} is effective sample length. L_{eff} is defined by $L_{\mathrm{eff}} = (1 - \exp(-aL))/a$, where a is linear absorption coefficient, L is sample length. Since there is no linear absorption at 800 nm, $L_{\mathrm{eff}} = L$.

TPA cross section is calculated by the following equation [20]:

$$\sigma_2 = \beta/(N_{\mathrm{A}} d \times 10^{-3}) \ \ (\text{in cm}^4/\text{Gw})$$

where β (in cm/Gw) is the TPA coefficient, N_{A} is the Avogadro constant (6.02×10^{23}), and d is the concentration of the polymer (in mol/l).

TPF of M2 and M3 was excited by laser pulses at 800 nm. TPF emitted from a 1 mm thick quartz cell was collected at the direction perpendicular to the excitation beam by 500-Pi spectrometer with CCD detector. The excitation with various intensities was employed to measure the dependence of TPF intensity on the excitation intensity.

For both open-aperture z-scan and TPF measurement, the molecular concentration of M2 and M3 are 5.46 mmol/l (23 mg/10 ml) and 2.19 mmol/l (17 mg/10 ml) in repeating unit, respectively. The solvent is chloroform.

3. Results and discussion

The number-average (M_{n}) and weight-average (M_{w}) molecular weights of the copolymers were determined by gel permeation chromatography (GPC) using polystyrene as the standard and the data including the one- and two-photon properties are shown in Table 1. Figs. 2 and 3 show the linear absorption and fluorescence of M2 and M3 in chloroform. The one photon absorption peaks corresponding to π-conjugated structure are at 467 nm for M2 and 436 nm for M3. No absorption was observed at longer wavelengths (>550 nm). The maximum absorption wavelength of M2 is red shifted 31 nm from that of M3. The reason may be that M2 is a linear structure and has more coplanarity therefore has longer conjugation length than M3. Polymers M2 and M3 emit yellowish green fluorescence with peaks at 542 and 535 nm, respectively. The Stokes shifts are 75 and 99 nm for M2 and M3, respectively. From Figs. 2 and 3, we can see that the polymer M2 and M3 emit strong orange–red fluorescence in the solid state and no excimer/aggregate emission can be observed, which indicating that these polymers have low tendency to aggregate in the solid state and the formation of excimers is efficiently suppressed.

Figs. 4 and 5 show the open-aperture z-scan data of M2 and M3 and TPA coefficient β got by data fitting. The valleys of the experimental data in Figs. 4 and 5 are a little bit wider than those of theoretic fitted data, which can be attributed to the linear absorption of two-photon excited states. The respective values of TPA cross section for M2 and M3 (Table 1) are 0.304 and 1.441×10^{-20} cm^4/Gw per repeating unit. These values are much larger than those

Table 1
The properties of the copolymers

	M_{n}	M_{w}	$\lambda_{\max}$ (abs) (nm)$^{\mathrm{a}}$	$\lambda_{\max}$ (fl) (nm)$^{\mathrm{b}}$	T_{g} (°C)	σ (10^{-20} cm^4/GW)$^{\mathrm{c}}$	$\lambda_{\max}$ (TPF)$^{\mathrm{d}}$
M2	4596	13,240	467	542	193	0.304	561
M3	3748	5089	436	535	176	1.441	542

[a] The maximum one photon absorption in chloroform.

[b] The maximum one photon fluorescence in chloroform excited at the one photon absorption maximum.

[c] Two-photon absorption (TPA) cross section (σ per repeating unit) excited at 800 nm (120 fs).

[d] The maximum two-photon fluorescence (TPF) excited at 800 nm.

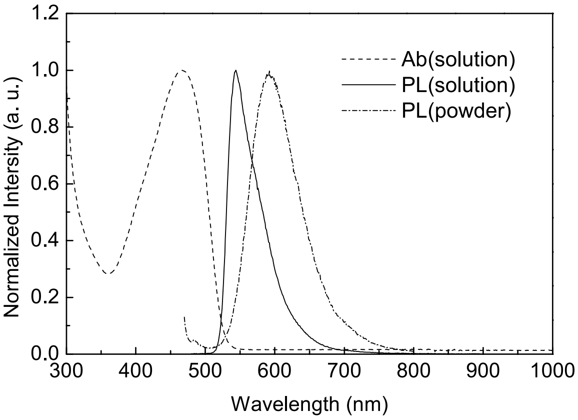

Fig. 2. The one-photon absorption and fluorescence spectra of M2 in $CHCl_3$ and solid state.

previously reported for polymers [15–17]. Alternating electron donors (triphenylamine) and electron acceptors (cyano groups) form D–π–A conjugation along the extended polyvinylene π-bridge systems and the effective conjugated units repeat themselves in the whole polymer chain. When simultaneously absorbing two photons, the charge transferred from the donors to acceptors and redistributed in the whole polymer. The bulkiness of triphenylamine inhibits aggregation of polymer chains and therefore effectively decreases possible inter-chain quenching. These structural characteristics lead to polymers with exceptional thermal stability (high T_g as shown in Table 1) and the ability to make good optical-quality thin films [21].

The TPA cross section of these polymer is comparable with previously reported materials [5,10,16]. The TPA cross section of M3 is nearly four times larger than that of M2, due to M3's unique multi-branched structure. The triphenylamine in polymer M3 connects the conjugated moieties via a tri-branched network, which serves as a spacer and a conjugated interrupt, thus effectively controlling the conjugation length of polymer M3. This structural feature restricts the close packing of the polymer chains, resulting in a highly soluble amorphous polymer, in which the tendency to form aggregate/excimers would be suppressed. In particularly, the octopus-like or octupolar molecular structure of M3 results in a very large TPA cross section, which was suggested theoretically by Cho et al. [17,22] as a promising direction for further development of novel TPA materials.

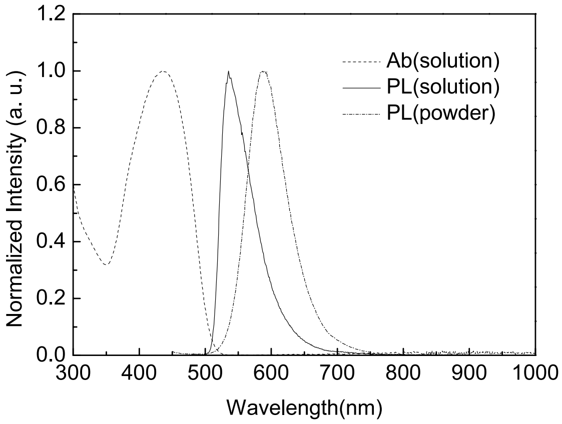

Fig. 3. The one-photon absorption and fluorescence spectra of M3 in $CHCl_3$ and solid state.

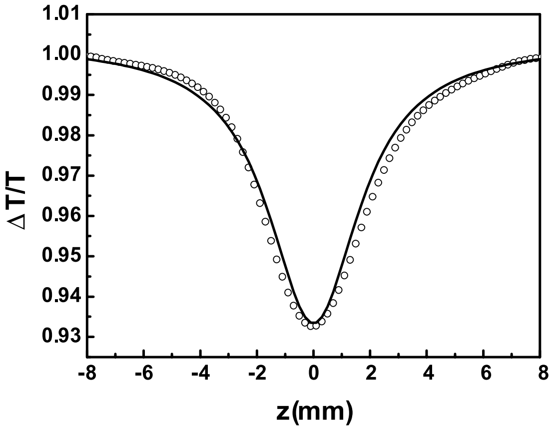

Fig. 4. Open-aperture z-scan trace of M2: scattered circle represents the experimental data, while the solid line is the theoretically fitted result. $\beta = 0.01$ cm/Gw, $\sigma_2 = 0.304$ cm^4/Gw.

Under the excitation of 120 fs, 800 nm pulses, M2 and M3 in $CHCl_3$ solution emit strong frequency up-converted fluorescence. The yellow–green fluorescence can be observed under excitation of unfocused pulses with energy of several μJ. TPF spectra of M2 and M3 with various excitation intensities are shown in Figs. 6 and 7. The insets in Figs. 6 and 7 show the relation of the TPF intensity at the peak of TPF spectra with the excitation intensity. Linear dependence of fluorescence intensity on square of the excitation intensity confirms that TPA is the main excitation mechanism of the intense fluorescence emission. Strong TPF was even observed at the excitation intensity of 2.65 Gw/cm^2 for polymer M3 and M2, indicating that two polymers have large TPA cross section and high fluorescence quantum yields. This is an important prerequisite

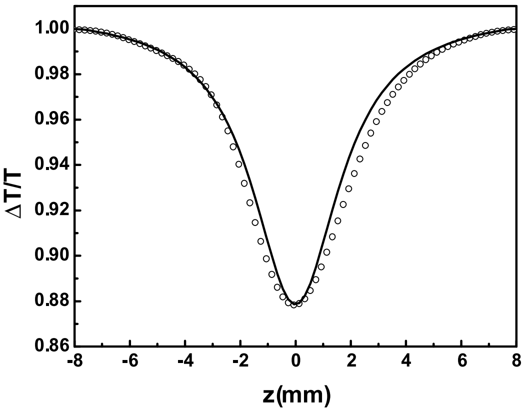

Fig. 5. Open-aperture z-scan trace of M3: scattered circle represents the experimental data, while the solid line is the theoretically fitted result. $\beta = 0.019$ cm/Gw, $\sigma_2 = 1.441$ cm^4/Gw.

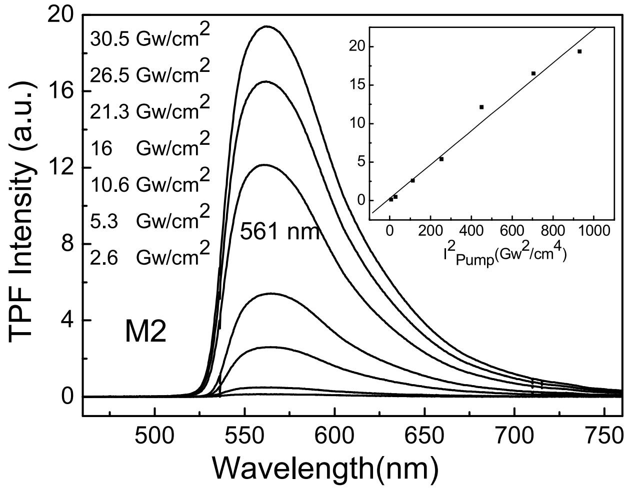

Fig. 6. Two-photon fluorescence spectra of M2 in $CHCl_3$.

for TPA-based applications such as fluorescence microscopy and upconverted lasing. The maximum wavelengths of two-photon induced fluorescence for M2 and M3 are 561 and 542 nm. Compared with the one photon fluorescence, the peaks of TPF are red shifted 19 and 7 nm for M2 and M3, respectively. The red shift of TPF spectrum can be explained by reabsorption effect. Since the absorption and the emission spectra of M2 and M3 are overlapped, part of the light emitted from the solution will be reabsorbed by the solution again. The one-photon excitation beam has much shorter penetrating length in the sample than that of two-photon excitation laser beam due to the strong linear absorption of one-photon excitation beam. Thus, one-photon induced fluorescence emits from the surface of the sample and the reabsorption affects the fluorescence spectra slightly. While the two-photon excitation laser beam at 800 nm can penetrate the sample deeply. So the reabsorption effect of two-photon induced fluorescence is greater that of one photon excited fluorescence. The small shift of M3 might be M3 has smaller overlap between the absorption and emission spectra than that of M2; therefore the reabsorption effect is smaller.

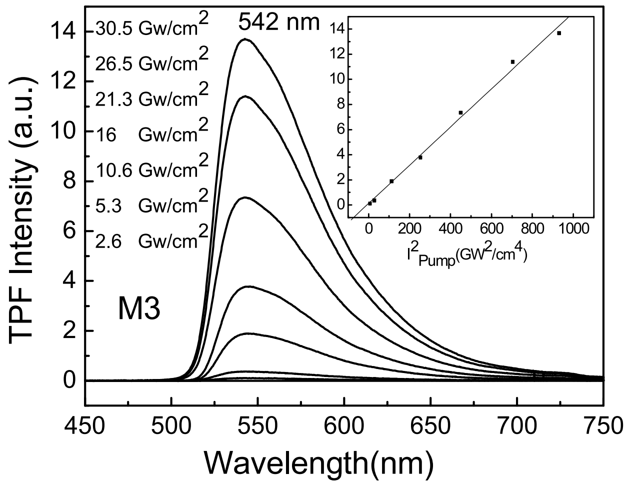

Fig. 7. Two-photon fluorescence spectra of M3 in $CHCl_3$.

It should be pointed out that the TPA measurements of these copolymers had been carried out at the non-optimized wavelength, which was chosen because it is the optimum wavelength as imaging tool for non-destructive evaluation of aircraft paint. Generally, at the wavelength that is twice of that for one-photon absorption peak, TPA effect might be expected, but not all the materials can possess large TPA cross section. A significant enhancement of TPA cross section values is expected at optimized wavelength, the experiments with varying excitation wavelength are being carried out. In addition, for z-scan experiment, the used chopping frequency is certainly different from the laser pulse repetition rate. Though the chopping blade would change the spatial profile of the pulse, long time constant (300 ms used in the experiment) and the lock-in amplifier would have an average effect on the signal. We changed the chopping frequency from 500 to 1000 Hz in femtosecond pump-probe experiment and z-scan experiment, and we did not observe obvious influence on the results. In that case, the difference between the laser repetition rate and the chopping frequency would not cause the big effect on the open-aperture data and hence the TPA cross section.

4. Conclusions

TPA and fluorescence properties of linear and tri-branched copolymers with triphenylamine and cyano groups in main chain were studied by femtosecond z-scan technique. The octopus-like or octupolar molecular structure of M3 results in a TPA cross section as large as 1.44×10^{-20} cm^4/Gw per repeat unit. These copolymers exhibit strong two-photon induced frequency up-converted fluorescence under the excitation of 120 fs pulses at 800 nm.

Acknowledgements

This work was supported by National Science Foundation of China and Education Committee of Shanghai.

References

[1] Denk W, Strickler JH, Webb WW. Science 1990;248:73.
[2] Belfield KD, Schafer KJ. Chem Mater 2002;14:3656.
[3] Abbotto A, Beverina L, Bozio R, Bradamante S, Ferrante C, Pagani GA, Signorini R. Adv Mater 2000;12:1963.
[4] Ehrlich JE, Wu XL, Lee IYS, Hu ZY, Röckel H, Marder SR, Perry JW. Opt Lett 1997;22:1843.
[5] Albota M, Beljonne D, Brédas JL, Ehrlich JE, Fu JY, Heikal AA, Hess SE, Kogej T, Levin MD, Marder SR, McCord-Moughon D, Perry JW, Röckel H, Rumi M, Subramaniam G, Webb WW, Wu XL, Xu C. Science 1998;281:1653.
[6] Rumi M, Ehrlich JE, Heikal AA, Perry JW, Barlow S, Hu ZY,

McCord-Maughon D, Parker TC, Röckel H, Thayumanavan S, Marder SR, Beljonne D, Brédas JL. J Am Chem Soc 2000;122:9500.
[7] Liu ZQ, Fang Q, Wang D, Xue G, Yu WT, Shao ZS, Jiang MH. Chem Commun 2002;2900.
[8] Abbotto A, Beverina L, Bozio R, Facchetti A, Ferrante C, Pagani GA, Pedron D, Signorini R. Org Lett 2002;4:1495.
[9] Kannan R, He GS, Yuan L, Xu F, Prasad PN, Dombroskie AG, Reinhardt BA, Baur JW, Vaia RA, Tan LS. Chem Mater 2001;13:1896.
[10] Chung SJ, Kim KS, Lin TC, He GS, Swiatkiewicz J, Prasad PN. J Phys Chem B 1999;103:10741.
[11] He GS, Swiatkiewicz J, Jiang Y, Prasad PN, Reinhardt BA, Tan LS, Kannan R. J Phys Chem A 2000;104:4805.
[12] Chung SJ, Lin TC, Kim KS, He GS, Swiatkiewicz J, Prasad PN, Baker GA, Bright FV. Chem Mater 2001;13:4071.
[13] Adronov A, Fréchet JMJ, He GS, Kim KS, Chung SJ, Swiatkiewicz J, Prasad PN. Chem Mater 2000;12:2838.
[14] Drobizhev M, Karotki A, Rebane A, Spangler CW. Opt Lett 2001;26:1081.
[15] Hohenau A, Cagran C, Kranzelbinder G, Scherf U, Leising G. Adv Mater 2001;13:1303.
[16] Chung SJ, Maciel GS, Pudavar HE, Lin TC, He GS, Swiatkiewiez J, Prasad PN, Lee DW, Jin JI. J Phys Chem A 2002;106:7512.
[17] Cho BR, Piao MJ, Son KH, Lee SH, Yoon SJ, Jeon SJ, Cho M. Chem Eur J 2002;8:3907.
[18] Meng FS, Liu CZ, Hua JL, Cao Y, Chen KC, Tian H. Eur Polym J 2003;39(7):1325.
[19] Bahae MS, Said AA, Wei TH, Hagan DJ, Van Stryland EW. IEEE J Quantum Electron 1990;26:760.
[20] He SG, Xu GC, Prasad PN, Reinhardt BA, Bhatt JC, Dillard AG. Opt Lett 1995;20:435.
[21] Shirota Y. J Mater Chem 2000;10:1.
[22] Cho BR, Son KH, Lee SH, Song YS, Lee YK, Jeon SJ, Choi JH, Lee H, Cho M. J Am Chem Soc 2001;123:10039.