

SHORT COMMUNICATIONS

Optical Third-Harmonic Generation in Polyaniline Cast Films

Masanori ANDO,[†] Hiro MATSUDA,* Shuji OKADA,^{*††}
Hachiro NAKANISHI,^{*††} Tomokazu IYODA,^{†††}
and Takeo SHIMIDZU

*Division of Molecular Engineering, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*

** National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba, Ibaraki 305, Japan*

(Received March 23, 1992)

KEY WORDS π -Conjugated Polymer / Third-Order Nonlinear Optical
Material / Polyaniline Cast Film / Third-Harmonic Generation / Emeraldine
Base / Resonance Effect /

Since large third-order nonlinear susceptibility ($\chi^{(3)}(-3\omega; \omega, \omega, \omega)$) was observed in polydiacetylene (PDA),¹ much interest has been focused on π -conjugated polymers as good candidates for third-order nonlinear optical materials.² To date, third-order nonlinear optical properties have been studied on several π -conjugated polymers. For example, $\chi^{(3)}$ measurements were reported on PDAs,^{1,2} polyacetylene (PA),³ polyarylenevinylenes (PAVs),⁴ polythiophene (PTh),⁵ poly(*p*-phenylenebenzobisthiazole) (PBT) and its derivatives.⁶ Very recently, there is also a rapidly growing attention in the nonlinear optical properties of polyaniline (PAn), an important π -conjugated polymer which has been extensively studied mainly on electrical conduction and charge-discharge properties in the last decade.⁷ PAn is theoretically predicted to have large $\chi^{(3)}$,⁸ and the resonance enhanced $\chi^{(3)}$ values of PAn in solution and in a silica gel host have been reported to be 1.6×10^{-11} esu

and 4.8×10^{-13} esu, respectively.⁹ However, there has not been reported $\chi^{(3)}$ of the PAn film which does not contain solvent or host material.

In this communication, we report $\chi^{(3)}$ measurement of polyaniline (PAn) cast films without host material by third-harmonic generation (THG). In general, processibility (solubility and fusibility) of π -conjugated polymers is poor. However, recently, it was found that emeraldine base, one of the interconvertible forms of PAn, is soluble in *N*-methyl-2-pyrrolidone (NMP) even in the case of high degree of polymerization.¹⁰ Therefore, simple fabrication of PAn films from casting solution has become possible. In our experiment, thin cast films with a range of thicknesses were prepared, and the $\chi^{(3)}$ dependence on the incident light wavelength and the film thickness was investigated. The PAn used in our experiment was prepared by chemical oxidative polymerization of aniline in

[†] Present address: *Government Industrial Research Institute of Osaka, 1-8-31 Midorigaoka, Ikeda, Osaka 563, Japan.*

^{††} Present address: *Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980, Japan.*

^{†††} Present address: *Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, U.S.A.*

1 N HCl at 0°C using ammonium peroxydisulfate as an oxidant. The molar ratio of used ammonium peroxydisulfate to aniline was 1.25. As-polymerized protonated PAN was converted into emeraldine base through deprotonation by treating with NaOH aq. followed by washing with distilled water and methanol. PAN cast films were prepared by casting the NMP solution of emeraldine base onto glass substrate (25 mm × 10 mm × 1 mm) followed by rapid heat drying. The thicknesses of the PAN cast films were estimated to be 0.08–0.14 μm by Talystep. X-ray diffraction measurement ($2\theta = 1\text{--}70^\circ$) on the films did not show evident crystalline structure.

The THG measurements were performed at pumping wavelengths ranging from 1.5 to 2.1 μm by using a tunable pulse laser system. The pulse duration was of 5 ns. The incident 1.5–2.1 μm radiation was provided by difference-frequency generation of a dye laser and the fundamental wave of a neodymium:yttrium aluminum garnet (Nd:YAG) laser. The dye laser was pumped by a frequency doubled light of the Nd:YAG fundamental wave. The angle between the normal of the film plane and the incident light was varied from -45° to $+45^\circ$ while the rotating axis was defined parallel to the fundamental beam polarization direction, and the TH intensity was recorded as a function of the incident angle.

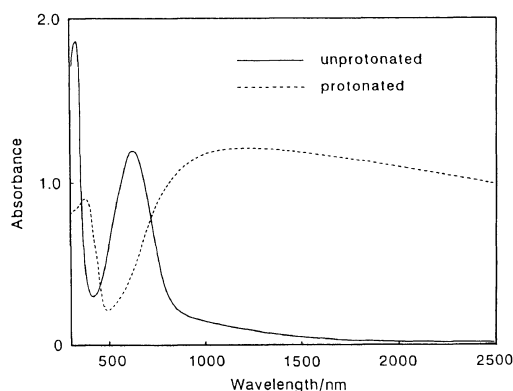


Figure 1. Visible-near IR absorption spectra of unprotonated PAN cast film and protonated PAN cast film.

Figure 1 shows the absorption spectra of PAN cast films. The unprotonated PAN (emeraldine base) film is transparent in the 1.5–2.1 μm wavelength region, while the film has a large absorption band in the 500–700 nm wavelength region, corresponding to the frequency tripled light wavelength. Therefore, $\chi^{(3)}$ of the unprotonated PAN film in the resonant wavelength region can be estimated by THG. On the other hand, the protonated PAN film prepared by exposure of the emeraldine base cast film to HCl vapor, has large absorption in the 1.5–2.1 μm region. Therefore, THG measurement on the protonated PAN film was impossible because of the damage of the film by the incident light.

TH intensities were measured for glass substrate, fused silica glass as a standard and the PAN cast films on glass substrate. The TH intensity from the glass substrate showed the so-called Maker fringe pattern, corresponding to the consecutive optical path-length variations. On the other hand, in the PAN cast films, monotonous variation of the TH intensity was observed, because the large TH signal from the PAN layer predominates over the substrate signal. $\chi^{(3)}$ of the PAN cast film was calculated using the following equation:

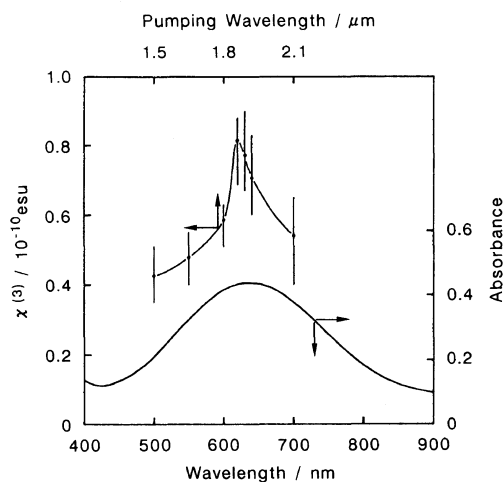


Figure 2. $\chi^{(3)}$ and absorption spectrum of unprotonated PAN cast film.

Table I. $\chi^{(3)}$ values of unprotonated PAN cast films

Thickness/ μm	$\chi^{(3)} \times 10^{11}/\text{esu}$						
	Pumping wavelength/ μm						
	1.5	1.65	1.8	1.86	1.89	1.92	2.1
0.08	5.1	5.5	6.3	8.8	9.0	8.3	6.5
0.09	4.4	4.8	6.0	8.1	8.2	7.1	6.1
0.11	4.1	4.9	6.0	8.8	7.0	6.9	5.0
0.14	3.5	4.0	5.1	6.9	6.7	6.0	4.0

$$\chi^{(3)} = \frac{2}{\pi} \chi_Q^{(3)} \sqrt{\left(\frac{P - P_{\text{sub}}}{P_Q}\right) \left(\frac{\alpha t/2}{1 - e^{-\alpha t/2}}\right)^2} \frac{l_{c,Q}}{t} \quad (1)$$

where $\chi_Q^{(3)}$ is the $\chi^{(3)}$ of the fused silica,¹¹ P , P_{sub} , and P_Q are the measured TH intensity of the thin film on the glass substrate extrapolated to 0° of the incident angle, that of the glass substrate and that of the fused silica, respectively. α is the absorption coefficient of the sample, $l_{c,Q}$ is the coherence length of the fused silica and t is the sample thickness assumed to be much less than the coherence length of the sample. Equation 1 was derived from the generally used equation for thin film samples¹² by the approximation neglecting the difference of the refractive indices between the PAN film and the fused silica glass and by the correction considering the absorption of the PAN film.

Figure 2 shows the wavelength dependence of $\chi^{(3)}$ of the PAN cast film and its absorption spectrum. At a wavelength of $1.86 \mu\text{m}$, $\chi^{(3)}$ reached to the maximum value of 9.0×10^{-11} esu. This $1.86 \mu\text{m}$ incident light wavelength corresponds to 620 nm of the TH wavelength, which is nearly identical to the absorption peak wavelength (634 nm). This tendency indicates the resonance effect. For the more accurate estimation of $\chi^{(3)}$ in the resonant region, it is better to multiply the $\chi^{(3)}$ obtained from eq 1 by a coefficient of $|1/[n(\omega)^2 - n(3\omega)^2]|$ according to the Kajzar's method,¹³ where $n(\omega)$ and $n(3\omega)$ are refractive indices of PAN film at the incident light wavelength and at the TH wavelength. For example, the $\chi^{(3)}$ value at

650 nm was about 2.5 times enhanced by taking account of $n(\omega)$ and $n(3\omega)$ preliminarily measured by ellipsometry (Mizojiri Optical Co., Ltd.). This means that the true $\chi^{(3)}$ of the PAN film is larger than 1.7×10^{-10} esu. As the PAN backbone is considered to be randomly oriented in the present cast films, we can expect $\chi^{(3)}$ value larger than 1.7×10^{-10} esu in the oriented PAN film.

The measured $\chi^{(3)}$ data of PAN films with different thicknesses are listed in Table I. The data were obtained by eq 1. At every wavelength, the thinnest film has the highest $\chi^{(3)}$ value. Such tendency has been sometimes reported for thin film samples.¹⁴ Our speculation on the reason for this tendency is that the deviation of the calculated $\chi^{(3)}$ from the true $\chi^{(3)}$ may become larger with increasing film thickness due to the approximated absorption correction.

As described above, it has been proved that the third-order nonlinear susceptibility as large as 10^{-10} esu was shown in the unprotonated PAN cast film without evident crystalline structure. This value is larger than that of the PAN-silica gel composite film⁹ by two orders of magnitude. Also, the value of the PAN cast film is larger than that of the PBT spin-coated film⁶ by one order of magnitude and in the same order of magnitude as those of the PAV cast films and spin-coated films.⁴ Since PAN has interconvertible forms with different electronic structures and the fabrication of PAN into various aggregation states at the molecular level is possible, the present study on the

third-order nonlinear optical property of PAN induces much interests for the development of organic nonlinear optical functional systems.

REFERENCES

1. C. Sauteret, J. P. Hermann, R. Frey, F. Pradere, J. Ducing, R. H. Baughman, and R. R. Chance, *Phys. Rev. Lett.*, **36**, 956 (1976).
2. H. Nakanishi, H. Matsuda, S. Okada, and M. Kato, *Polym. Adv. Technol.*, **1**, 75 (1990).
3. A. J. Heeger, D. Moses, and M. Sinclair, *Synth. Met.*, **17**, 343 (1987); M. R. Drury, *Solid State Commun.*, **68**, 417 (1988).
4. T. Kaino, K. Kubodera, H. Kobayashi, T. Kurihara, S. Saito, T. Tsutsui, S. Tokito, and H. Murata, *Appl. Phys. Lett.*, **53**, 2002 (1988); K. Kamiyama, M. Era, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, **29**, L840 (1990).
5. P. N. Prasad, J. Swiatkiewicz, and J. Pflieger, *Mol. Cryst. & Liq. Cryst.*, **160**, 53 (1988).
6. D. N. Rao, J. Swiatkiewicz, P. Chopra, S. K. Ghoshal, and P. N. Prasad, *Appl. Phys. Lett.*, **48**, 1187 (1986); S. A. Jenekhe, W. -C. Chen, S. Lo, and S. R. Flom, *Appl. Phys. Lett.*, **57**, 126 (1990).
7. W. Huang, B. D. Humphrey, and A. G. MacDiarmid, *J. Chem. Soc., Faraday Trans. 1*, **82**, 2385 (1986).
8. J. M. Ginder, A. J. Epstein, and A. G. MacDiarmid, *Synth. Met.*, **29**, E395 (1989); M. C. dos Santos and J. L. Bredas, *Phys. Rev. Lett.*, **62**, 2499 (1989).
9. B. R. Mattes, E. T. Knobbe, P. D. Fuqua, F. Nishida, E. -W. Chang, B. M. Pierce, B. Dunn, and R. B. Kaner, *Synth. Met.*, **41**, 3183 (1991).
10. M. Angelopoulos, A. Ray, and A. G. MacDiarmid, *Synth. Met.*, **21**, 21 (1987); M. Abe, A. Ohtani, Y. Umemoto, S. Akizuki, M. Ezoe, H. Higuchi, K. Nakamoto, A. Okuno, and Y. Noda, *J. Chem. Soc., Chem. Commun.*, **1989**, 1736.
11. G. R. Meredith, B. Buchalter, and C. Hanzlik, *J. Chem. Phys.*, **78**, 1533 (1983).
12. S. Tomaru, K. Kubodera, S. Zembutsu, K. Takeda, and M. Hasegawa, *Electron. Lett.*, **23**, 595 (1987); K. Kubodera and H. Kobayashi, *Butsuri (Japan)*, **46**, 464 (1991).
13. F. Kajzar and J. Messier, *Thin Solid Films*, **132**, 11 (1985).
14. J. -C. Baumert, G. C. Bjorklund, D. H. Jundt, M. C. Jurich, H. Looser, R. D. Miller, J. Rabolt, R. Sooriyakumaran, J. D. Swalen, and R. J. Twieg, *Appl. Phys. Lett.*, **53**, 1147 (1988).