The role of imine derivatives in enhancing the third-order optical nonlinearity in PMMA films for photonic applications

P. SUDHEESH[a], D. MALLIKHARJUNA RAO[b], K. N. SHARAFUDEEN[c], K. CHANDRASEKHARAN[d]
[a]*Department of Physics, V.T.M.N.S.S College, Dhanuvachapuram, Thiruvananthapuram,Kerala, India-695503*
[b]*Nano and display research laboratory, School of Nanoscience and Technology,National Institute of Technology Calicut, Kerala, India-673601*
[c] *Kuwait College of Science and Technology, Doha District, Kuwait-27235*
[d]*Laser and nonlinear optics laboratory, Department of Physics, National Institute of Technology Calicut, Kerala, India-673601*

We report the third-order nonlinear optical properties of organic thin films of Imine derivatives doped Poly (methyl-methacrylate). Z-scan techniques with 7ns Nd: YAG laser pulses at 532 nm were employed for the measurements. The effect of guest/host concentration on nonlinear absorption has been studied. The compounds exhibited good optical limiting as well. The present works indicate that these materials are promising candidates for photonics applications.

(Received January 6, 2015; accepted April 6, 2017)

Keywords: Imine derivatives, PMMA, Nonlinear optics, Optical Limiting

1. Introduction

The increasing applications of modern communication systems in our day-to-day life have inspired a great interest in the development of photonic devices which are able to carry and process an optical signal. The research has been focused on the third-order nonlinear optical (NLO) properties of materials, on which such devices are based, which proportional to the third-order nonlinear optical susceptibility [1]. Nonlinear optical thin films are currently developed and studied for future photonic applications due to their fast response time and good compatibility with fabrication of waveguide and integrated optical devices [2, 3]. Organic materials having large nonresonant nonlinear polarizability are promising candidates for developing waveguiding devices and are being studied extensively [4-10]. Imine (IM) derivatives have revealed to be an important class of NLO materials in recent past [11-13]. Poly (methyl-methacrylate) (PMMA) is an interesting polymeric media for integrated optics and optical fibre fabrication. The polymeric waveguides have been successfully obtained using PMMA or PMMA based media in the visible spectral range [14-20]. The main challenge to use organic materials for nonlinear optics is to create molecules that have large third-order NLO properties and assemble these molecules in to a solid state material. Since PMMA possess high optical, themal and mechanical damage resistance, we can use it as a host material [21-23].

Despite its advantages, PMMA, by itself cannot be used as a NLO material because it has a low value of nonlinear susceptibility. In this paper, we discuss our attempt to improve the third-order NLO properties of PMMA thin films by doping it with Imine derivatives.

2. Experimental

The Imine (IM) derivatives, also known as Schiff base derivatives, were prepared as per the standard procedure [24, 25]. The molecular structures of the compounds N (4-trifluoromethyl) benzylidine aniline (IM1), N (4-trifluoromethyl) benzylidine (2-chloro) aniline (IM2), N (4-dimethylamine) benzylidine 3-isopropoxyaniline (IM3) are shown in Fig.1. To prepare IM1doped PMMA thin films (IM1/PMMA), IM1 and PMMA were dissolved separately in dimethyl formamide (DMF) and both solutions were mixed together and stirred for 3-4 hrs by using a magnetic stirrer. Then the IM1/PMMA films were made using a spin coating unit (SPIN -150, STS) and the film was annealed at 70^0C for 3 hrs. The same procedure is adopted to prepare IM2/PMMA and IM3/PMMA thin films. The doping concentration of IM in the PMMA by weight was 5%. The thickness of the films were measured with a dial guage (ID-C150MB, MITUTOYO ABSOLUTE) and uniform thickness of $\sim 25\mu m$ was obtained. The linear absorption spectra for all the films were obtained by using UV-VIS spectrophotometer (SCHIMADZU 2400PC Series) are shown in Fig. 2

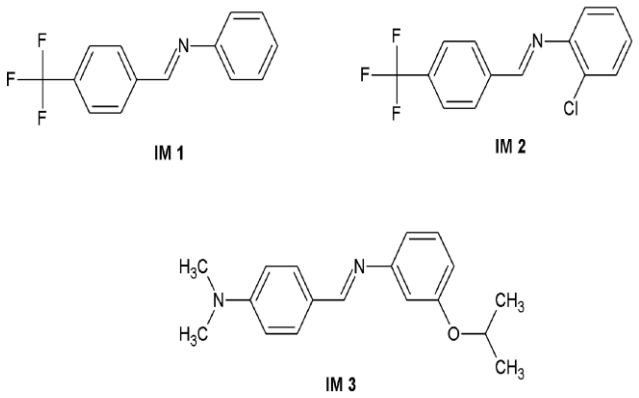

Fig. 1. Structure of Imine derivatives

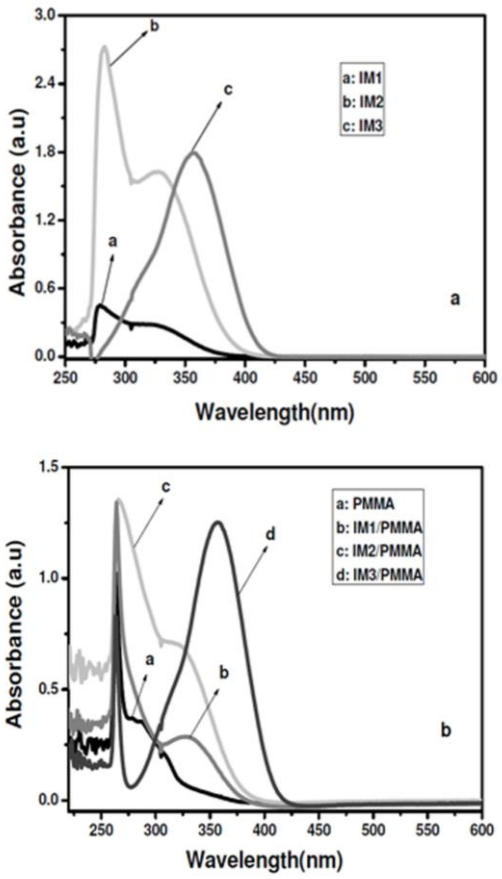

Fig. 2. Linear absorption spectra of a) pure IM and b) IM/ PMMA thin films

Single beam Z-scan technique were used to measure the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) of all the films [26]. A Q- switched Nd: YAG laser with a pulse width of 7ns at 532 nm and at a repetition rate of 10Hz was employed in the experiment. The laser beam was focused on the samples by a lens (f = 0.25m). The input on- axis irradiance for Z- scan study was 0.415GW/cm^2. The effect of guest/host (IM/PMMA) concentration on nonlinear absorption was studied. Optical limiting studies were performed by keeping the sample at the focus by varying the input energy and by monitoring the output energy. The Rj-7620 energy ratio meters were used for simultaneous measurement of incident and transmitted energies.

3. Results and discussion

In the closed aperture Z-scan experiment, the transmittance is affected by both nonlinear refraction and nonlinear absorption, so the determination of n_2 is less straight-forward from the closed aperture measurement. Thus for obtaining pure nonlinear refraction effect, it is then required to split the effect of nonlinear absorption by performing open aperture Z-scan experiment. The method of division of closed aperture experimental data by the open aperture data has been employed to extract pure nonlinear refraction curve [26]. Z-scan traces for the composite films are shown in Fig. 3 and 4. The theoretical fit to the Z-scan curves as per the literature [26] yield the values of β and n_2.

The peak to valley configuration of pure nonlinear refraction Z-scan curves of the films suggests that the sign of nonlinear refractive index is negative, indicating a self-defocusing effect. Now we can extract the value of third-order nonlinear optical susceptibility ($\chi^{(3)}$) from $n_2$and β [26].

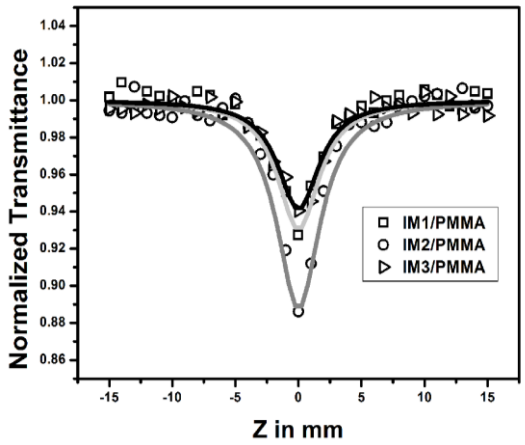

Fig. 3. Open aperture Z-scan curves for IM/ PMMA thin films

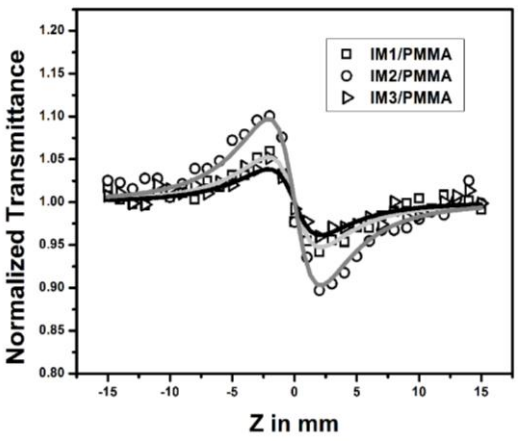

Fig. 4. Pure nonlinear refraction Z-scan curves for IM/PMMA thin films

The nonlinear induced polarization per molecule is described by the microscopic susceptibility that is the hyperpolarizability [9]. For third-order effects, the corresponding hyperpolarizability (γ_h) can be calculated from the literature [27,28]. The NLO parameters of IM/PMMA films estimated in this study are listed in Table 1.

Table 1. Experimentally determined nonlinear optical parameters of IM/ PMMA thin films

Samples	$n_2(10^{-16} m^2W^{-1})$	$\beta(10^{-9} mW^{-1})$	$\chi^{(3)}(10^{-19} m^2V^{-2})$	$\gamma_h(10^{-45} m^5V^{-1})$
IM1/PMMA	5.32	2.12	1.43	3.84
IM2/PMMA	9.83	3.67	2.63	7.04
IM3/PMMA	3.89	1.74	1.06	2.84

The obtained value of $\chi^{(3)}$ of pure PMMA was very low, which has been estimated to be of the order $10^{-22} m^2V^{-2}$ .On the other hand , the value of $\chi^{(3)}$ of PMMA containing Imine derivatives, which are highly soluble in PMMA solution was of the order $10^{-19} m^2V^{-2}$ .This shows the enhancement of NLO coefficient of the film by three order of magnitude. This value of $\chi^{(3)}$ is comparable to or larger than poly diacetylene thin films, cyclic conjugated structures like phthalocyanines, porphyrin derivatives and stilbazolium derivatives which are well-known class of optical materials for photonics and biophotonical applications [9, 29-32]. The γ_h is estimated to be of the order $10^{-45}m^5V^{-1}$ for the samples, which is about two orders magnitude greater than that of other organic molecules [27].

FTIR studies were carried out to analyze the chemical interactions between IM and PMMA. The characteristic vibration bands of PMMA observed at 1736 cm^{-1} due to ─C═O stretch and 1366 cm^{-1} for ─C─O stretch. The bands found at 3013 cm^{-1} and 2971 cm^{-1} correspond to the C─H stretching of the methyl group (CH_3) while the bands at 1215 cm^{-1} and 1356 cm^{-1} are associated with C─H symmetric and asymmetric stretching modes, respectively. We also observed a change in peak at 1736 cm^{-1} towards lower frequency region, which indicates the interaction between ─C═O functional group of PMMA and azomethine group of IM.

In support with the FTIR analysis, slight shift in absorption spectra has been observed from UV-Vis study (π─π^* transitions) is due to interaction azomethine group of IM with carbonyl function of PMMA [33-36]. From the FTIR and UV-visible spectral observations it can be concluded that the significant interactions has been developed between PMMA and IM. Thus a conjugation network could be introduced in PMMA by donor-acceptor-donor IM derivatives and which leads to the enhancement in the nonlinear optical properties of PMMA films. The observed nonlinearities in IM/PMMA films are in accordance with the structural characteristics of IM derivatives [37].

The nonlinear absorption process in organic materials is mainly due to free carrier absorption, direct Multiphoton absorption or excited state absorption (ESA) and reverse saturable absorption (RSA). In the case of nanosecond regime, this can be explained using the five level model described in the literature [38-40]. If the mechanism belongs to simple two-photon absorption (TPA), β should be a constant that independent of the on axis irradiance I_0. If the mechanism is direct three photon absorption, β should be a linear increasing function of I_0 and the intercepts on the vertical axis is zero [41]. In the present study it is seen that for all the films β is decreasing with increasing intensity as shown in Fig. 5. The fall in β with increasing $I_0$is a consequence of RSA [42].

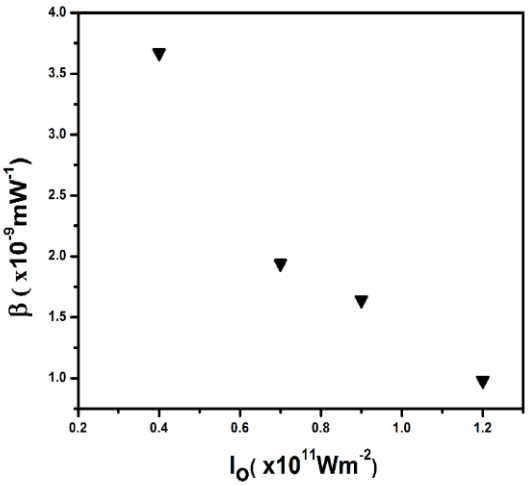

Fig. 5. The fall in β with increasing I_0 within the IM2/PMMA thin film

The ground state cross-section (σ_g) and excited state cross section (σ_{ex}) for all the samples determined from the method described in reference [43]. The values obtained for σ_{ex} and σ_g for all the compounds are in the order of 10^{-24} cm^2 and 10^{-25} cm^2 respectively. The value of σ_{ex} is found to be larger than the value of σ_g $\left(\sigma_{ex} > \sigma_g\right)$ which is in agreement with the condition for observing

RSA [42]. Therefore we attribute the observed nonlinear absorption to the RSA for all the films.

The concentration dependence of theβ was also studied. For the concentration dependence studies, the PMMA films were prepared with different weight percentages (1, 2, 5 and 10%) of the IM. The values of β increases with concentration of IM in PMMA, because the film with higher concentration possess more molecules per unit volume and correspondingly they exhibit higher NLO parameters. Fig. 6 shows the variation of β with IM2 concentration in PMMA.

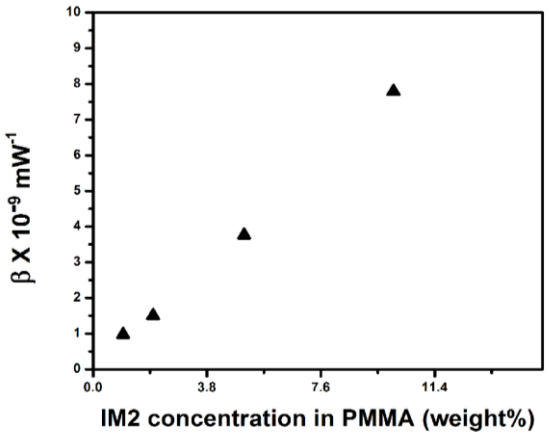

Fig. 6. Concentration dependence of β with IM2 wt% in PMMA thin film

The optical limiting behavior of the films is shown Fig. 7. The experiment shows that the best limiting behavior is observed for the IM2/PMMA film, which exhibits strongest nonlinear absorption among the films. RSA is the main mechanism for the fims to produce an optical limiting effect .

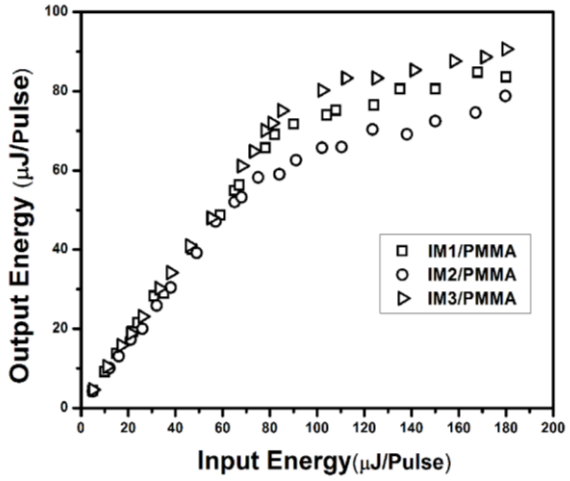

Fig. 7. Optical limiting behavior in IM/PMMA thin films

4. Conclusions

The Z-scan signatures revealed that all the thin films exhibit a self-defocusing effect at 532nm. We have explained an option for increasing the third-order NLO properties of PMMA thin films by three order magnitude with the incorporation of Imine derivatives. The mechanism behind the nonlinear absorption was ascribed to RSA. The materials exhibit good optical limiting properties at the wavelength used. The results conclude that the materials show remarkable optical response in nanosecond regime, which help us in designing suitable materials for optical and photonic device applications.

Acknowledgements

Authors wish thanks to Dr. Soney Varghese, Nano and display research laboratory, School of Nanoscience and Technology and Mr. Siji Narendran N. K, Laser and nonlinear optics laboratory, Department of Physics for providing chemicals and useful discussions to finalize this article.

References

[1] R. W. Boyd, Nonlinear Optics, Academic Press: San Diego (1992).
[2] U. Gurudas, D. M. Bubb, Applied Physics A: Materials and Processing **88**, 255 (2007).
[3] U. Gubler, C. Bosshard, Polymer for Photonics Applications I, Springer, Verlag, Berlin (2002).
[4] S. Kasap, P. Capper, Springer Handbook of Electronic and Photonic Materials Springer, New York (2006).
[5] C. Li, L. Zhang, M. Yang, H. Wang, Y. Wang, Phys. Rev. A **49**, 1149 (1994)
[6] J. W. Perry, K. Mansour, I.Y.S Lee, X. L. Wu, P. V. Bedworth, C. T. Chen, D. Ng, S. R. Marder, P. Miles, T. Wada, M. Tian, H. Sasabe, Science **273**, 1533 (1996).
[7] S. R. Marder, W. E. Torruellas, M. B. Desce, V. Ricci, G. I. Stegeman, S. Gilmour, J. L. Bredas, J. Li, G. U. Bublitz, S. G. Boxer, Science **276**, 1233(1997).
[8] R. W. Munn, C. N. Ironside, Principles and Applications of Nonlinear Optical Materials, CRC Press, London (1993).
[9] H. N. Nalwa, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, USA (1997).
[10] H. Ma, A. K. Y. Jen, L. R. Dalton, Adv. Mater. **14**, 1339 (2002).
[11] P. G. Lacroix, Eur. J. Inorg. Chem. **2001**, 339 (2001).
[12] P. G. Lacroix, S. D. Bella, I. Ledoux, Chem. Mater. **8**, 541 (1996).
[13] J. P. Costes, J. F. Lamere, C. Lepetit, P. G. Lacroix, F. Dahan, Inorg. Chem. **44**, 1973 (2005).

[14] P. Pantelis, J. Hill, R. Kashyap, Proc. of SPIE Conf. Photopolymer Device Physics, Chemistry and Applications II, San Diego, California, July 24-26 **1559**, 2 (1991).
[15] K. C. Lin, W. Y. Lee, G. Y. Tien, Proc. of SPIE Conf. Solid State Lasers and Nonlinear Crystals, San Jose, CA, USA **2379**, 251 (1995).
[16] D. M. Ruck, S. Brunner, K. Tinschert, W. F. X. Frank, Nucl. Instr. Meth. Phys. Res. B. **106**, 447 (1995).
[17] N. Okamoto, S. Tashiro, Opt. Commun. **66**, 93 (1988).
[18] S. N. Oliver, C. S. Winter, R. J. Manning, J. D. Rush, C. Hill, A. E. Underhill, Proc. of SPIE Conf. Nonlinear Optical Properties of Organic Materials V, San Jose, CA, USA **1775**, 110 (1992).
[19] M. K. Kagami, H. Ito, T. Ichikawa, S. Kato, M. Matsuda, N. Takashashi, Appl. Opt. **34**, 1041 (1995).
[20] K. H. Park, K. M. Yeon, M. Y. Lee, S. D. Lee, D. H. Shin, C. J. Lee, N. Kim, Polymer **39**, 7061(1988).
[21] F. W. Billmeyer, Text Book of Polymer Science; John Wiley and Sons, Singapore (1994).
[22] X. T. Tao, T. Watanabe, K. Kono, T. Deguchi, M. Nakayama, S. Miyata, Chem. Mater. **8**, 1326 (1996).
[23] H. M. J. Zidan, J. Appl. Polym. Sci. **88**, 104 (2003).
[24] I. A. Mohammed, G. Sankar, M. Khairuddean, M. Abu Bakar, Molecules **15**, 3260 (2010)
[25] L. Marin, S. Destri, W. Porzio, F. Bertini, Liq. Cryst. **36**, 21 (2009).
[26] M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan, E. W. Van Stryland, IEEE J. Quantum Electron **26**, 760 (1990).
[27] J. Hein, H. Bergner, M. Lenzner, S. Rentsch, J.Chem. Phys. **179**, 543 (1994).
[28] M. T. Zhao, B. P. Singh, P.N. Prasad, J.Chem.Phys. **89**, 5535 (1988).
[29] S. Tomaru, K. Kubodera, T. Kurihara, S. Zembutsu, Jpn. J. Appl. Phys. **26**, L1657 (1987).
[30] W. Sun, C. M. Lawson, G. M. Gray, C. Zhan, D. Wang, Appl. Phys. Lett. **78**, 1817 (2001).
[31] C. Meloney, H. Byrne, W. M. Dennis, W. Blau, J. M. Kelley, Chem. Phys. **121**, 21 (1988).
[32] S. Guha, K. Kang, P. Porter, J. E. Roach, D. E. Remy, F. J. Aranda, D. V. G. N. L. Rao, Opt. Lett. **17**, 264 (1992).
[33] K. L. Deng, J. Liu, G. Z. Wang, H. Tian, X. B. Ren, H. B. Zhong, P. F. Zhang, Express Polym Lett. **2**, 677 (2008).
[34] A. Balamurugan, S. Kannan, V. Selvaraj, S. Rajeswari, Trends Biomater. Artif. Organs **18**, 41 (2004).
[35] M. Saleem Khan, R. Aman Qazi, M. Said Wahid, African Journal of Pure and Applied Chemistry **2**, 41(2008).
[36] S. Prashant, B. Vasuda, G. Vikesh, Vinod Kumar, J. Polymer-Plastics Technology and Engineering **50**, 1179 (2011).
[37] P. Sudheesh, K. Chandrasekharan, Solid state commun. **152**, 268 (2012).
[38] R. L. Sutherland, Handbook of Nonlinear Optics; Dekker, New York (1996).
[39] C. V. Bindu, S. S. Harilal, V. P. N. Nampoori, C. P. Girija Vallabhan, Appl. Phys. B. **70**, 429 (2000).
[40] W. Feng, W. Yi, H. Wu, M. Ozaki, K. Yoshimo, J. Appl. Phys. **98**, 034301(2005).
[41] S. L. Guo, L. Xu, H. T. Wang, X. Z. You, N. B. Ming, Optik **114**, 58 (2003).
[42] S. Couris, E. Koudoumas, A. A. Ruth, S. Leach, J. Phys. B: Atom Mol. Opt.Phys. **28**, 4537 (1995).
[43] J. M. Hales, J. W. Perry, Organic and Polymeric third-order NLO materials and Device applications , CRC Press, Boca Raton USA (2008).

*Corresponding author: csk@nitc.ac.in