Available online at www.sciencedirect.com
ScienceDirect
Materials Research Bulletin 43 (2008) 707–713
Materials Research Bulletin
www.elsevier.com/locate/matresbu

Nonlinear optical properties of *p*-(*N*,*N*-dimethylamino)dibenzylideneacetone doped polymer

A. John Kiran [a], Satheesh Rai Nooji [b], D. Udayakumar [c], K. Chandrasekharan [d,*], B. Kalluraya [b], Reji Philip [e], H.D. Shashikala [a], A.V. Adhikari [c]

[a] *Department of Physics, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India*
[b] *Department of Chemistry, Mangalore University, Konaje, Karnataka 574199, India*
[c] *Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Mangalore 575025, India*
[d] *Lasers and Nonlinear Optics Lab, Department of Science and Humanities, National Institute of Technology Calicut, Calicut, Kerala 673601, India*
[e] *Optics Group, Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore 560080, India*

Received 17 December 2006; received in revised form 22 March 2007; accepted 30 March 2007
Available online 5 April 2007

Abstract

A bis-chalcone derivative, *p*-(*N*,*N*-dimethylamino) dibenzylideneacetone was synthesized. Its third-order nonlinear susceptibility was determined to be as high as 10^{-12} esu by employing single beam *Z*-scan and degenerate four wave mixing techniques using Nd:YAG 7 ns laser pulses at 532 nm. The compound was doped in to poly(methylmethacrylate) matrix and the third-order nonlinearity was investigated by using *Z*-scan technique. The nonlinear refractive index of the doped polymer is found to be negative, and its magnitude is of the order of 10^{-10} esu. The results show that the compound exhibits strong reverse saturable absorption and a good optical limiting property and hence may be used as a promising dopant material. The study on concentration dependence of nonlinear optical parameters has been presented.

Keywords: A. Organic compounds; A. Optical materials; A. Polymers; D. Optical properties

1. Introduction

Organic molecules with large third-order optical nonlinearities are required for photonic applications including all-optical switching, and eye and sensor protection. The nonlinearity in these molecules has been found to originate from a strong delocalization of π-electrons along the length of the molecules [1–4]. Among various organic compounds reported for nonlinear optical (NLO) properties, chalcones have received considerable interest as materials for second-order NLO applications due to their ability to crystallize in noncentrosymmetric structure and their blue light transmittance [5–6]. Some of these chalcone derivatives possess noticeable third-order nonlinearity. However, they cannot be directly used in practical devices since they can get degraded when exposed to intense laser beams. One can overcome this problem and make effective use of these materials in devices by doping them into a polymer matrix, as

* Corresponding author. Tel.: +91 495 2287343; fax: +91 495 2287250.
E-mail address: csk@nitc.ac.in (K. Chandrasekharan).

0025-5408/$ – see front matter
doi:10.1016/j.materresbull.2007.03.030

this can enhance the opto-chemical and opto-physical stability as well as mechanical and thermal properties, while retaining the NLO properties and linear optical transparency [7].

Here we report on the experimental investigation of third-order NLO properties of *p*-(*N*,*N*-dimethylamino) dibenzylideneacetone (DDBA) doped poly(methylmethacrylate) (PMMA). The compound is a derivative of dibenzylideneacetone, which is a very good precursor for the preparation of many types of heterocyclic compounds of medical and biological importance. The $\chi^{(3)}$ of dibenzylideneacetone has been shown to enhance by the $N(CH_3)_2$ substitutions at its *para*-positions [8]. This compound fall in to the group of so-called intramolecular charge transfer compounds which have a large nonlinear electronic polarization that is caused by a large dipole moment change from a ground state to an excited state by optical excitation. Such compounds are expected to possess advantages such as high solubility in organic solvents and matrix polymers and ease of sample preparation, as well as the possibility of giving a high $\chi^{(3)}$ value ($>10^{-12}$ esu) [9]. PMMA has been selected as a matrix because it is a hard, rigid but transparent polymer with glass transition temperature of 125 °C, and an average molecular weight of 60,000. PMMA has physical durability which is far superior to that of other thermoplastics and it is tougher than polystyrene [10]. The third-order NLO property of the compound alone in dimethylformamide (DMF) has been studied using the single beam *Z*-scan and degenerate four wave mixing (DFWM) experimental methods using 7 ns laser pulses at 532 nm, while that of compound doped PMMA has been investigated by *Z*-scan technique. Both *Z*-scan and DFWM experiments were performed on the sample in order to compare the value of third-order nonlinear susceptibility ($\chi^{(3)}$) obtained by two techniques. The concentration dependence of NLO properties of the sample doped PMMA has also been presented.

2. Experimental

p-(*N*,*N*-dimethylamino) dibenzylideneacetone was synthesized according to the procedure given in the literature [11]. It was then purified by recrystallization from ethanol. DDBA and PMMA were taken in the powder form and dissolved in DMF. The concentration of the dopant in PMMA matrix was varied from 2.5% to 15% (sample I: 2.5%; sample II: 5%; sample III: 10%; sample IV: 15%). The structure of DDBA is as shown in Fig. 1. The linear absorption spectrum of DDBA in DMF (10^{-2} mol/L) recorded with the fiber optic spectrometer model SD2000 (Ocean Optics Inc., USA) is shown in Fig. 2. The linear refractive index of the sample was obtained by using an Abbe refractometer.

2.1. Z-scan measurements

Z-scan [12] is a technique that is particularly useful when the nonlinear refraction is accompanied by nonlinear absorption. This method allows the simultaneous measurement of both nonlinear refractive index and nonlinear absorption coefficient. Basically, the method consists of translating a sample through the focus of a Gaussian beam and monitoring the changes in the far field intensity pattern. Because of the light-induced lens-like effect, the sample has the tendency to recollimating or defocusing the incident beam, depending on its z position with respect to the focal plane. By properly monitoring the transmittance change through a small aperture placed at the far-field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector (open aperture), one can measure the intensity dependent absorption as a change of transmittance through the sample.

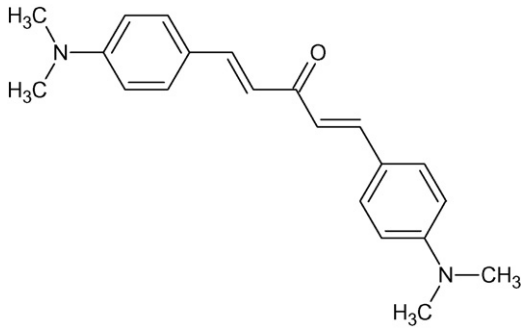

Fig. 1. Structure of DDBA.

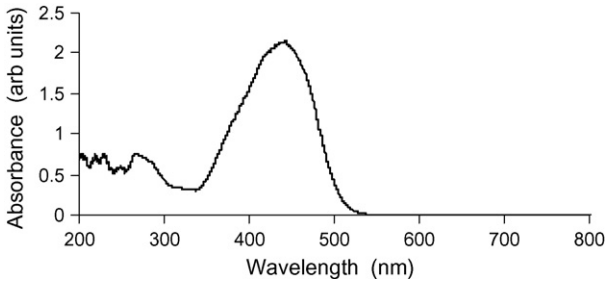

Fig. 2. Linear absorption spectrum of DDBA in DMF solution (1×10^{-2} mol/L).

The Q-switched Nd:YAG laser with a pulse width of 7 ns at 532 nm was used as a source of light in the *Z*-scan experiment. The experiment was performed using a Gaussian beam. A lens of focal length 26 cm was used to focus the laser pulses into a 1 mm quartz cuvette containing the sample solution. The resulting beam waist radius at the focused spot was 19.6 μm. This corresponds to the Rayleigh length of 2.274 mm. Thus the sample thickness of 1 mm was less than the Rayleigh length and hence it could be treated as a thin medium. The scan was obtained with a 50% ($S = 0.5$) aperture and at a pulse energy of 16 μJ, which corresponds to a peak irradiance of 0.355 GW/cm^2. In order to avoid cumulative thermal effects, data were collected in single shot mode [13]. The experiments were performed at room temperature. The optical limiting measurements were carried out when the sample was at focal point by varying the input energy and recording the output energy. The incident and the transmitted energies were measured simultaneously by two pyroelectric detectors with Laser Probe Rj-7620 Energy Ratiometer.

2.2. DFWM experiment

Four-wave mixing refers to the interaction of four waves in a nonlinear medium via the third-order polarization. When all the waves have same frequency, it is called as degenerate four wave mixing. There are several geometries used in studying this phenomenon. One of such geometries used in our experiment is the backward geometry or the phase conjugate geometry. Here, two counter-propagating strong beams are called as forward pump beam and the backward pump beam. A third wave called the probe beam is incident at small angle θ to the direction of the forward pump. A fourth beam, called the conjugate beam, is generated in the process and propagates counter to the probe beam [14].

In our DFWM experiment we used 7 ns pulses at 532 nm from the second harmonic output of a Q-switched Nd:YAG laser. The laser energy at the sample was varied by the combinations of neutral density filters. Sample was taken in a 1-mm thick glass cuvette, with concentration of 10^{-2} mol/L. We used the standard backward geometry for $\chi^{(3)}$ measurement, consisting of two strong, equal energy counter-propagating pump beams and a weak probe beam incident at a small angle ($\sim 4^\circ$) to one of the pumps. A small portion of the pump beams was picked off and measured by a photodiode to monitor the input energy. The DFWM signal generated in the sample solution was separated by a second photodiode. The photodiode signals were averaged over a number of laser shots and displayed by a Tektronix TDS2002 digital storage oscilloscope.

3. Results and discussion

3.1. Z-scan studies

The linear absorption spectrum of the sample dissolved in DMF shows that 532 nm is away from the resonance wavelength. Open aperture curve, as shown in Fig. 3, yields the details of nonlinear absorption for sample III (concentration of 10% in matrix). The solid line is a theoretical fit of experimental data to equation as described in reference 15. The excited state cross-section σ_{ex} can be measured from the normalized open aperture *Z*-scan data [15]. We assume that the molecular energy levels can be reduced to a three level system in order to calculate σ_{ex}. Molecules are optically excited from the ground state to the singlet-excited state. The molecules from this state relax either to the ground state or the triplet state, when excited state absorption can occur from the triplet to the higher triplet-excited state.

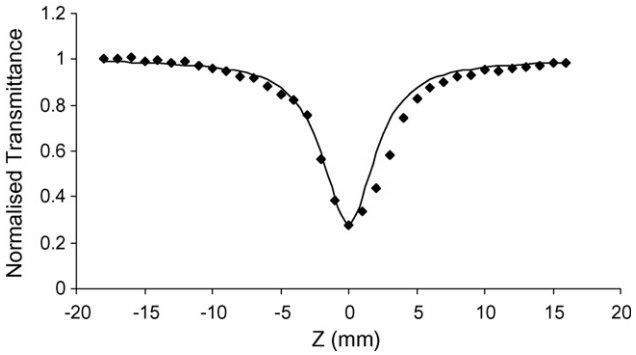

Fig. 3. Open aperture curve for sample III. Solid line is a theoretical of experimental data with $\beta = 57.5$ cm/GW.

The change in the intensity of the beam as it passes through the material is given by $dI/dz = -\alpha I - \sigma_{ex}N(t)I$, where I is the intensity, and N is the molecules in the excited state. The excited state density of molecules appears as a result of a nonlinear absorption process whose intensity dependence can be obtained from $dn/dz = \sigma_{ex}I/h\nu$, where ν is the frequency of the laser. Combining the above two equations and solving for the fluence of the laser and over the spatial extent of the beam gives the normalized transmission for open aperture as

$$T = \ln\left(\frac{1 + (q_0/1 + x^2)}{q_0/1 + x^2}\right) \tag{1}$$

where $q_0 = (\sigma_{ex}F_0L_{eff})/(2h\nu)$, F_0 the fluence of the laser at the focus and $L_{eff} = (1 - \exp^{-\alpha L})/\alpha$.

A fit of Eq. (1) to the open aperture data at 532 nm with q_0, yields a value of $\sigma_{ex} = 6.24 \times 10^{-17}$ cm^2 for the sample I. The ground state absorption cross-section of sample I calculated from $\alpha = \sigma_g N_a C$, where N_a is the Avogadro's number and C is the concentration in mol/cm^3, is found to be $\sigma_g = 3.818 \times 10^{-18}$ cm^2. The value of σ_{ex} is larger than the value of σ_g, which is in agreement with the condition for observing reverse saturation absorption [15,16]. The value of σ_{ex} was found to be larger than that of σ_g in all investigated samples. Reverse saturation absorption generally arises in a molecular system when the excited state absorption cross-section is larger than the ground state cross-section. Generally, NLA can be caused by free carrier absorption, saturated absorption, direct multiphoton absorption, or excited state absorption. If the mechanism belongs to the simple two-photon absorption, β should be a constant that is independent of the on-axis irradiance I_0. As if the mechanism is the direct three-photon absorption, β should be a linear increasing function of I_0 and the intercepts on the vertical axis should be nonzero [17]. But Fig. 4 shows that β is decreasing with increasing I_0. The fall-off of β with increasing I_0 is a consequence of the reverse saturation absorption [18]. The two-photon absorption coefficient, β, of sample III calculated from open aperture curve is found to be 57.5 cm/GW.

Fig. 5 shows the closed aperture curve for sample III. The absence of prominent peak in the closed aperture signature indicates a strong absorptive nonlinearity of the sample [12]. Practically, in the case of a closed aperture scan, nonlinear refraction is accompanied by nonlinear absorption. However, in order to differentiate nonlinear

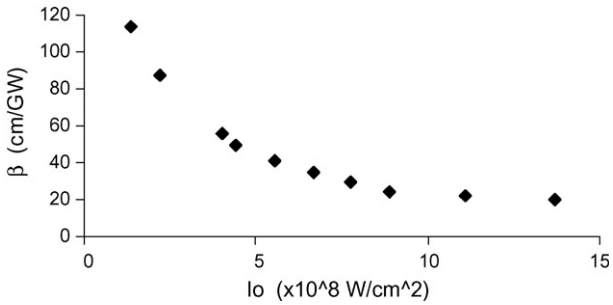

Fig. 4. A fall-off of β with increase in on axis intensity (I_0) within the sample.

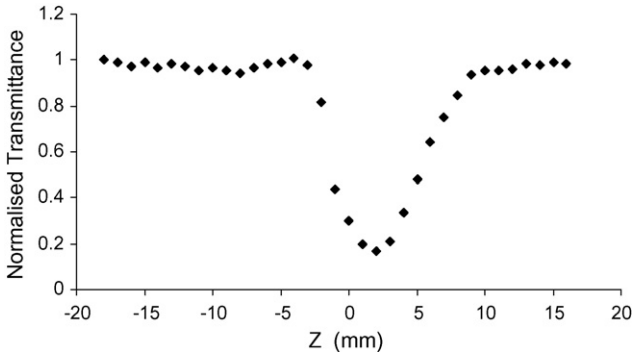

Fig. 5. Closed aperture curve for sample III.

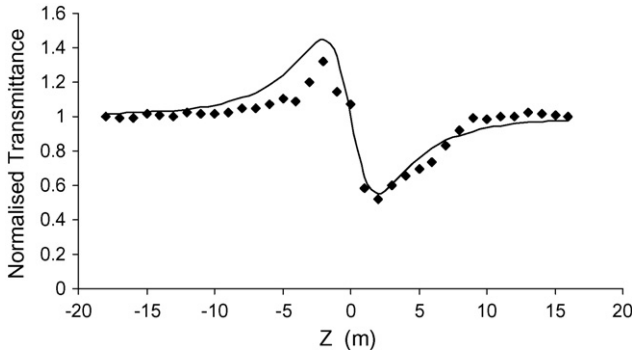

Fig. 6. Pure nonlinear refraction curve for sample III obtained by dividing closed aperture data by open aperture data. Solid line is fitted with $\Delta\Phi_0 = 2.1$.

refraction from nonlinear absorption, one can follow division method described in Ref [12]. Fig. 6 shows the pure nonlinear refraction curve obtained by dividing the closed aperture data by the corresponding open aperture data. The solid line is a fit of experimental data to equation described in Ref [12]. The nonlinear refractive index, n_2, calculated from Fig. 6 is found to be 1.7×10^{-10} esu, and the $Re\chi^{(3)}$ value is found to be 1.83×10^{-12} esu. Further, to determine the contributions of the solvent and PMMA to the observed NLO properties, we conducted *Z*-scan experiment on the pure DMF and PMMA dissolved in DMF. Neither nonlinear refraction nor nonlinear absorption was observed at the input energy used. Hence, any contribution from the solvent and PMMA to the nonlinearity of the samples is negligible. Fig. 7 shows the dependence of β on the concentration of sample in the polymer matrix. The values of n_2, β, real and imaginary $\chi^{(3)}$ for all sample concentrations are shown in Table 1.

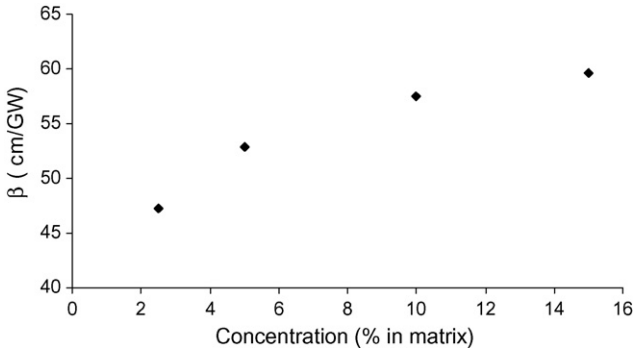

Fig. 7. β vs. concentration of DDBA in polymer matrix.

Table 1
Calculated values of β, n_2, $Re\chi^{(3)}$, and Im $\chi^{(3)}$

Sample	β (cm/GW)	n_2 ($\times 10^{-10}$ esu)	$Re\chi^{(3)}$ ($\times 10^{-12}$ esu)	Im $\chi^{(3)}$($\times 10^{-12}$ esu)
Sample I	48.62	1.375	1.479	0.752
Sample II	52.90	1.552	1.602	0.801
Sample III	57.50	1.700	1.829	0.890
Sample IV	59.60	1.770	1.886	0.886

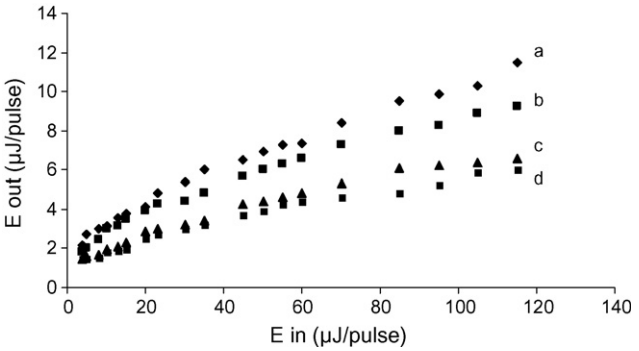

Fig. 8. Optical limiting of nanosecond pulses in DDBA doped PMMA at different concentrations: (a) sample I; (b) sample II; (c) sample III; (d) sample IV.

Samples show strong reverse saturable absorption at 532 nm. Hence, optical limiting based on the reverse saturable absorption can be expected for the nanosecond laser pulses. In Fig. 8 optical limiting behaviors is shown for samples I, II, III, and IV. The nonlinear absorption was observed to increase on going from sample I to IV. Consequently the optical limiting was observed to be the best in sample IV among the four investigated samples. In all these samples, for input energies less than 15 μJ/pulse, the output energy increased linearly with the incident energy. But for energies more than 15 μJ/pulse, the measured output energy deviates from linearity, indicating the occurrence optical limiting. The linear transmittance of these samples at 532 nm was 65–70%.

3.2. DFWM study

Variation of the DFWM signal as a function of the pump intensity the compound dissolved in DMF at a concentration of 1×10^{-2} mol/L is shown in Fig. 9. The signal is proportional to the cubic power of the input intensity as given by

$$I(\omega)\alpha\left(\frac{\omega}{2\varepsilon_0 cn^2}\right)^2\left|\chi^{(3)}\right|^2 I^2 I_0^3(\omega) \tag{2}$$

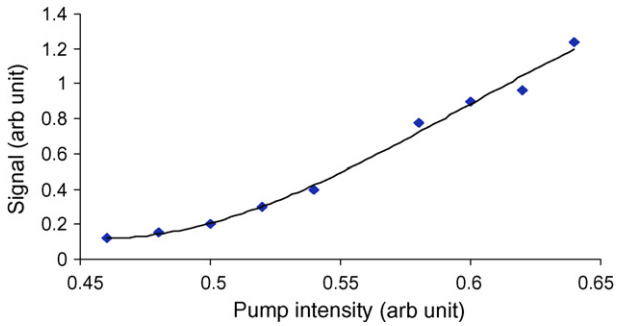

Fig. 9. DFWM signal vs. pump intensity for DDBA in DMF (1×10^{-2} mol/L).

where $I(\omega)$ is the DFWM signal intensity, $I_0(\omega)$ the pump intensity, l the optical pathlength, and n is the refractive index of the medium. The solid curve in the figure is cubic fit to the experimental data. $\chi^{(3)}$ can be calculated from

$$\chi^{(3)} = \chi^{(3)}_{\text{ref}} \left[\frac{I/I_0^3}{(I/I_0^3)_{\text{ref}}} \right]^{1/2} \left[\frac{n}{n_{\text{ref}}} \right]^2 \frac{l_{\text{ref}}}{l} \left(\frac{\alpha l}{(1 - e^{-\alpha l}) e^{-(\alpha l/2)}} \right) \tag{3}$$

where the subscript 'ref' refers to the standard reference CS_2 under identical conditions, α the linear absorption coefficient of the sample and $\chi^{(3)}_{\text{ref}}$ is taken to be 4.0×10^{-13} esu [19,20]. The value of $\chi^{(3)}$ is found to be 1.66×10^{-12} esu and it matches well with the value 1.9×10^{-12} esu obtained for the pure compound in DMF solution by *Z*-scan technique.

The $\chi^{(3)}$ value of the compound is very high and is comparable with the values 1.3×10^{-12} esu, obtained for tricyanovinyl azo dye and 6×10^{-12} esu, obtained for 4-(*N*,*N*-diethylamino)-4′-nitrostilbene (DEANS) [9]. These studies reveal that this compound can be a promising dopant material for doping polymers for photonic device applications.

4. Conclusions

The third-order nonlinear optical properties of *p*-(*N*,*N*-dimethylamino) dibenzylideneacetone were studied by using *Z*-scan and degenerate four wave mixing techniques with 7 ns laser pulses at 532 nm. The compound was doped in to poly(methylmethacrylate) at different concentrations and the third-order nonlinearity was investigated. The $\chi^{(3)}$ value of the compound is high and is comparable with the values obtained for tricyanovinyl azo dye and 4-(*N*,*N*-diethylamino)-4′-nitrostilbene. The *p*-(*N*,*N*-dimethylamino) dibenzylideneacetone doped poly(methylmethacrylate) exhibits strong reverse saturable absorption and good optical limiting properties. This study shows that *p*-(*N*,*N*-dimethylamino) dibenzylideneacetone can be an interesting dopant material and hence can be used in optical limiting applications.

Acknowledgements

Authors wish to thank Dr. G. Umesh, Department of Physics, NITK, for providing laboratory facility for the *Z*-scan experiment. They also thank Mr. Suchand Sandeep, Research Scholar, RRI for his kind help in DFWM studies.

References

[1] S.R. Marder, W.E. Torruellas, M. Blanchard-Desce, V. Ricci, G.I. Stegeman, S. Gilmour, J.-L. Bredas, J. Li, G.U. Bublitz, S.G. Boxer, Science 276 (1997) 1233.
[2] 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 (1996) 1533.
[3] R.W. Munn, C.N. Ironside (Eds.), Principles and Applications of Nonlinear Optical Materials, Chapman and Hall; CRC Press, 1993.
[4] C. Li, L. Zhang, M. Yang, H. Wang, Y. Wang, Phys. Rev. A 49 (1994) 1149.
[5] G.J. Zhang, T. Kinoshita, K. Sasaki, Y. Goto, Y. Nakayama, Appl. Phys. Lett. 57 (1990) 221.
[6] J. Indira, P.P. Karath, B.K. Sarojini, J. Cryst. Growth 209 (2002) 242.
[7] M. Samoc, A. Samoc, B.J. Luther-Davis, Opt. Soc. Am. B 15 (1998) 817.
[8] A. Johnkiran, K. Chandrasekharan, S.R. Nooji, H.D. Shashikala, G. Umesh, B. Kalluraya, Chem. Phys. 324 (2006) 699.
[9] L.H. Hornak, Polymers for Light Wave and Integrated Optics, Marcel Dekker, New York, 1992, pp. 657.
[10] F.W. Billmeyer Jr., Text Book of Polymer Science, 3rd ed., John Willey & Sons, Singapore, 1994.
[11] V.K. Ahluwalia, R. Agarwal, Comprehensive Practical Organic Chemistry Preparation and Quantitative Analysis, Universities Press (India) Ltd., Hyderabad, 2000.
[12] M. Sheik-Bahae, A.A. Said, T.-H. Wei, D.J. Hagan, E.W. Vanstryland, IEEE J. Quant. Electr. 26 (1990) 760.
[13] P. Yang, J. Xu, J. Ballato, R.W. Schwartz, D.L. Carroll, Appl. Phy. Lett. 80 (2002) 3394.
[14] R.A. Fisher (Ed.), Optical Phase Conjugation, Academic Press, New York, 1983.
[15] F.Z. Henari, W.J. Blau, L.R. Milgrom, G. Yahioglu, D. Philips, J.A. Lacey, Chem. Phys. Lett. 267 (1997) 229.
[16] L.W. Tutt, T.F. Boggess, Prog. Quant. Electr. 17 (1993) 299.
[17] S.-L. Guo, L. Xu, H.T. Wang, X.Z. You, N.B. Ming, Optik 114 (2003) 58.
[18] S. Couris, E. Koudoumas, A.A. Ruth, S. Leach, J. Phys. B: At. Mol. Opt. Phys. 28 (1995) 4537.
[19] R. Philip, M. Ravikanth, G. Ravindrakumar, Opt. Commun. 165 (1999) 91.
[20] J.S. Shrik, J.R. Lindle, F.J. Bartoli, M.E. Boyle, J. Phys. Chem. 96 (1992) 5847.