

Solvent Effect on the Third-Order Nonlinearity and Optical Limiting Ability of a Stilbazolium-like Dye

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ABSTRACT

Stilbazolium-like dyes, which contain different heterocyclic groups as electron donors and an *N*-methylpyridinium iodide group as an electron acceptor, are very interesting optical limiting materials. These materials exhibit low linear absorption, but potentially very strong nonlinear absorption at high intensities. In this paper, the results from investigations of the third-order susceptibilities and nonlinear refractive indices of a stilbazolium-like dye, *trans*-4-[2-(pyrryl)vinyl]-1-methylpyridinium iodide (PVPI), in different solvents using degenerate four wave mixing (DFWM) and Z-scan techniques with 6.8 ns laser pulses at 532 nm are reported. The molecular second-order hyperpolarizability of PVPI increases from 1.6×10^{-31} esu in methanol to 3.4×10^{-29} esu in chloroform, a factor of 212. The third-order nonlinearity of this compound is dominated by nonlinear absorption, which leads to strong optical limiting of nanosecond laser pulses. The strength of the optical limiting is dramatically influenced by the solvent used, with limiting decreasing in the order chloroform>dichloromethane, 1,2-dichloroethane>methanol, acetonitrile. While both nonlinear absorption and nonlinear scattering contribute to the optical limiting, nonlinear absorption is the dominant mechanism.

Keywords: Stilbazolium-like dyes, third-order susceptibility, molecular second-order hyperpolarizability, nonlinear refractive index, optical limiting, solvent effect, degenerate four wave mixing, Z-scan

1. INTRODUCTION

In recent decades, there has been a growing need for optical limiting materials and devices to protect optically sensitive elements from laser damage. In general, an optimal nonlinear optical (NLO) material for optical limiting has a low loss, a high nonlinearity, a fast response time, a large dynamic range and a broadband spectral response. A variety of materials such as semiconductors,¹ carbon black suspensions,² organic polymeric and monomeric materials,³ liquid crystals,⁴ and photorefractive crystals⁵ have been investigated for these applications. Devices based on these materials exploit various linear and nonlinear phenomena, including induced scattering, nonlinear absorption (reverse saturable absorption, two-photon absorption, and free-carrier absorption), nonlinear refraction (self-focusing and self-defocusing), photorefractive, and total internal reflection.⁶ Among these materials, organic materials exhibiting nonlinear absorption are currently of interest because of their large third-order nonlinearities, instantaneous response times, high damage thresholds, ease of processing and structural modification, and their applicability over a wide range of wavelengths. Extensive work has been reported on the optical limiting, based on their reverse saturable absorption, of various organic materials such as indanthrone derivatives and oligomers,^{7,8} porphyrins,^{9,10} phthalocyanines,^{11,12,13} and organometallic compounds.^{14,15} However, the linear transmittance for these reverse saturable absorbers is significantly less than unity.

Most recently, two-photon absorption (TPA) dyes are receiving special attention because of their high transmission at low incident intensity in most of the visible spectral range. Materials possessing large two-photon absorptivities, such as

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dialkylamino stilbazolium iodide and bis-donor stilbenes, have been reported by Prasad^{16,17,18} and Perry¹⁹ recently. TPA based optical limiting of nanosecond and picosecond pulses has also been investigated by these two groups. Studies performed by Reinhardt and co-workers²⁰ revealed that nonlinearities of chromophores could be enhanced by introducing aromatic heterocyclic groups as electron donors and acceptors to inherently polarize a π electron system to which they were attached. This gives us an indication that changing the dialkylamino benzene ring to nitrogen, oxygen or sulfur containing five-membered heterocyclic rings might enhance the third-order nonlinearity of stilbazolium dyes. Following this concept, a series of stilbazolium-like dyes that contain five-membered rings with nitrogen, oxygen, and sulfur as electron donors and methylpyridinium iodide as electron acceptor have been synthesized, and we have begun to study their nonlinear optical properties.

The interest of our group in these materials arises not only from the potential of these compounds to be two-photon absorption dyes, but also from the high sensitivity of their linear absorption spectra to the nature of the solvent. The latter property provides the possibility of adjusting the optical windows by changing the solvents, which may offer the potential of tuning an optical limiter to a desired spectral range. This would be a very attractive feature for optical limiting applications.

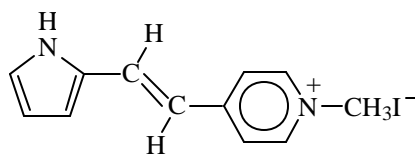


Figure 1 Chemical structure of PVPI

In this paper, we report the results of our investigations of the third-order susceptibility and optical limiting characteristics of a new stilbazolium-like dye, *trans*-4-[2-(pyrrol)vinyl]-1-methylpyridinium iodide (PVPI) (structure shown in Fig. 1) in different solvents using 6.8 ns laser pulses at 532 nm. The molecular second-order hyperpolarizabilities and the nonlinear refractive indices were measured using DFWM and Z-scan techniques. The nonlinear transmissions of PVPI in different solvents have been studied and possible mechanisms contributing to the optical limiting have also been investigated. As will be shown in this paper, changing the solvent not only affects the linear absorption spectra, but also has a dramatic influence on the nonlinearity and optical limiting characteristics of the compound.

2. EXPERIMENTS

The PVPI was synthesized in Professor Wang's lab and was characterized by UV-Vis, IR, ¹H-NMR, MS and elemental analysis.²¹ PVPI was dissolved in five different solvents, methanol, acetonitrile, 1,2-dichloroethane, dichloromethane and chloroform to make to the concentration of 5×10^{-4} mol/L. All of the solvents were purchased from Aldrich Chemical Company. Methanol and 1,2-dichloroethane were spectrophotometric grade and were used without further purification. Acetonitrile, chloroform and dichloromethane were reagent grade and were distilled before use. Each of the solutions used for the linear absorption spectra measurements and nonlinear optical measurements was freshly prepared and was kept in dark before the measurements. The linear absorption spectra of PVPI solutions in a 1-mm quartz cell were acquired using Shimadzu UV-3101 PC UV-VIS-NIR scanning spectrophotometer.

The nonlinear optical experimental setup was described in detail previously.²² An injection-seeded, Q-switched, frequency-doubled Nd:YAG laser with a temporal pulse width (FWHM) of 6.8 ns and a repetition rate of 10 Hz was used as the light source. The energy from the laser was attenuated through a prism wedge and the combination of half-wave plate and polarizing cube. The attenuated beam was then split into three beams by a prism wedge. One of the reflected beams was used to monitor the incident laser energy, and another one was directed to the top-hat beam Z-scan experiment. The transmitted beam went to either the DFWM setup or the nonlinear transmission setup. Carbon disulfide (CS₂) was used as the reference to calibrate both the DFWM and Z-scan experiments.

For DFWM, the laser intensities at the 5-mm cuvette that contains the sample solution were 5.7-8.8 MW/cm² and 6.3-9.8 MW/cm² for the forward and backward pumping beams, and 0.47-0.73 MW/cm² for the probing beam. Each experiment was repeated twice. In the Z-scan experiment, the reflected beam from the prism wedge was expanded to ~12 mm in diameter and subsequently passed through a 2.88-mm diameter aperture. Then, the top-hat beam was focused by a

$f=20$ cm best form lens to a waist of $45.1 \mu\text{m}$ at the focal point (using equation $w_0=1.22\lambda f/d$, where d is the diameter of the aperture in front of the focal lens), which corresponds to a Rayleigh length of 12 mm. This allowed the samples contained in the 2-mm sample cell to be treated as thin samples. A prism wedge was placed after the sample to allow for simultaneous measurement of the open and closed aperture Z-scan. The limiting aperture was located 65-cm from the focal plane, and less than 3% of the beam was transmitted by this aperture. Z-scan measurements on each of the solutions were repeated at least twice on different days. The lens used in the nonlinear transmission measurement was a 30-cm plano-convex lens ($F/300$), the beam waist at the 2-mm sample cell was $\sim 200 \mu\text{m}$. To measure the scattering lights from the samples, a black-coated metal piece was placed after the sample cell to block the major beam. An $f=12.5$ cm 2" lens was used to collect the scattering light to a J4-09 series Molectron joule meter. Experiments were repeated three times on fresh solution, each time on different days.

3. RESULTS AND DISCUSSIONS

3.1 Linear absorption spectra

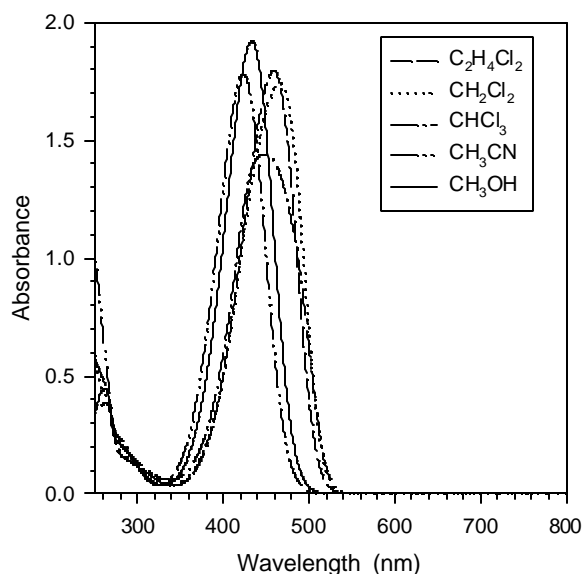


Figure 2 Linear absorption spectra of PVPI in different solvents in 1-mm cell. Concentration of the solutions is 5×10^{-4} mol/L.

One important criteria in evaluating the utility of an optical limiting material is whether it shows broad band spectral response, i.e., if it is transparent at low intensities while exhibiting a large nonlinearity at high intensities over a broad band spectral range. The first step in evaluating the potential of PVPI for optical limiting applications was to measure the linear absorption spectra of PVPI in five different solvents at concentrations of 5×10^{-4} mol/L in a 1-mm cell. The results are shown in Fig. 2.

The lowest energy absorption peak appears at 423.5 nm in acetonitrile (CH_3CN), 433.5 nm in methanol (CH_3OH), 446.5 nm in chloroform (CHCl_3), 457.5 nm in 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$), and 465 nm in dichloromethane (CH_2Cl_2), respectively. Above 550 nm, the solutions are completely transparent. Thus, as the polarity of the solvent is increased, the absorption peak has a hypsochromic shift of over 40 nm, and the optical window over which nonlinear absorption could occur becomes 40 nm broader. Chloroform, dichloromethane and dichloroethane solutions of PVPI exhibit slight linear absorption at the wavelength (532 nm) used in our nonlinear optical studies, thus reverse saturable absorption could possibly occur. This was verified by the Z-scan and nonlinear transmission measurements described subsequently.

The blue-shift of the absorption peak in polar solvents implies that the energy level of the ground state is reduced more by solvent interaction than is that of the excited state, indicating that the ground state is more polar than the excited state. This is probably due to the electron transfer from the five-membered nitrogen atom to the carbon atom in the excited state. The large change in the dipole moment in the excited state can result in very large nonlinear optical effects.

3.2 DFWM Study

The third-order susceptibility of PVPI was measured in three different solvents: chloroform, dichloroethane and methanol. The intensity dependence of the conjugate signal of each solution was measured, and a nearly cubic correlation was found for each of the solution (shown in Fig. 3), indicating a third-order nonlinear process. All of the measurements were conducted within the cubic power range. For each solvent, the conjugate signal of a series of solutions with the concentration of $10^{-5} - 10^{-4}$ mol/L was measured, and was compared with that of the reference materials, CS_2 , under identical conditions. The $c^{(3)}$ value of the solution was then calculated using the following equation²³

$$c_{\text{sample}}^{(3)} = c_{\text{ref}}^{(3)} \left(\frac{I_{\text{sample}}}{I_{\text{ref}}} \right)^{1/2} \left(\frac{n_{\text{sample}}}{n_{\text{ref}}} \right)^2 \left(\frac{l_{\text{ref}}}{l_{\text{sample}}} \right) \left(\frac{a l}{e^{-a l/2} (1 - e^{-a l})} \right) \quad (1)$$

where I is the intensity of the conjugate signal, n is the refractive index of solution, l is the sample path length, and a is the linear absorption coefficient for the solution at 532 nm. The subscript *ref* refers to CS₂, for which $c_{\text{xxxx}}^{(3)} = 6.8 \times 10^{-13} \text{ esu}^{24}$ at 532 nm was used.

The $c^{(3)}$ value of the solution is normally assumed to be the sum of those of the solvent and the solute. The molecular second-order hyperpolarizability of the solute, g_{solute} , is related to the macroscopic nonlinear optical parameter $c^{(3)}$ by equation (2)²⁵

$$c_{\text{solution}}^{(3)} = L^4 (N_{\text{solvent}} g_{\text{solvent}} + N_{\text{solute}} g_{\text{solute}}) \quad (2)$$

where N_{solute} and N_{solvent} are the number densities of molecules of the solute and solvent per mL, which is proportional to the concentration of the solution, and L is the local field correction factor given by $(n^2+2)/3$.

It is obvious that there is a linear correlation between the $c^{(3)}$ value and the concentration of solutions. This is shown in Fig. 4. From the slope of each plot, the g_{solute} can be extrapolated. Table 1 shows the g value and the linear absorption cross-section of PVPI at 532 nm in different solvents.

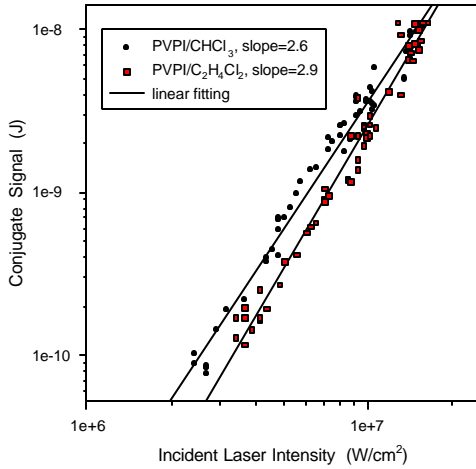


Figure 3 Conjugate signal versus incident laser intensity for chloroform and dichloroethane solutions of PVPI in 5-mm cell. The linear coefficient of confidence $r=0.98$ for both plots.

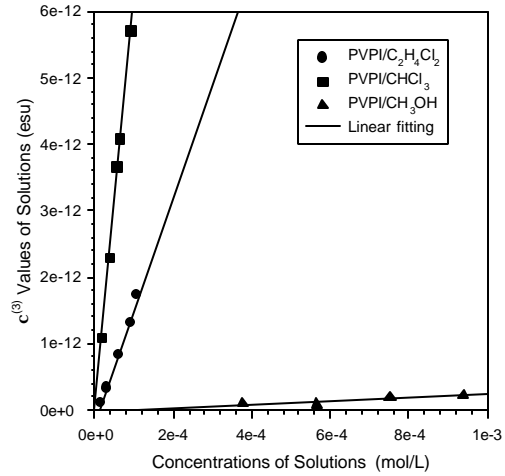


Figure 4 $c^{(3)}$ value versus concentration curve for PVPI in different solvents. The linear coefficient of confidence $r=0.995$.

In comparison with the effect of the solvent on the linear absorption cross-section (ranging from $1 \times 10^{-19} \text{ cm}^2$ in methanol to $2 \times 10^{-18} \text{ cm}^2$ in chloroform), the solvent exhibits a much more pronounced effect on the third-order nonlinearity. The g value of PVPI in chloroform is 212 times larger than that of PVPI in methanol. This dramatic change in g value could be either due to different excited state population gratings in the solvents, or to a ground-state absorption induced thermal effect, or to a combination of the two effects.

To gain additional information about the nonlinear optical response mechanisms, DFWM studies were carried out with the probe beam polarized orthogonally to the pump beams. Although a phase conjugate signal was observed with this arrangement for the reference material CS₂, no conjugate signal was observed within experimental error for any of these three solutions. This indicates that the main contribution to the NLO response of PVPI solutions may originate from the static

grating²⁶ (excited state population grating²⁷ or thermal grating) that should vanish when the probe beam polarization is orthogonal to that of the pumps.

Table 1 Linear absorption cross-sections (S_0), g values and nonlinear refractive indices of PVPI in different solvents

Solvents	S_0 (10^{-18} cm ²)	g (10^{-31} esu)	gS_0 (10^{-13} esu/cm ²)	n_2^* (10^{-18} m ² /W)	Re $c^{(3)*}$ (10^{-13} esu)
CHCl ₃	2.0	340	170	-9.8	-8.7
CH ₂ Cl ₂	1.5	–	–	-8.4	-7.2
C ₂ H ₄ Cl ₂	0.6	79	132	-5.3	-4.7
CH ₃ OH	0.1	1.6	16	ND	ND

* n_2 and Re $c^{(3)}$ are measured in 5×10^{-4} mol/L solutions.

3.3 Z-scan measurement

In order to determine the sign of $c^{(3)}$ and to investigate the relative contributions from its real and imaginary parts, Z-scan²⁸ studies were conducted in 5×10^{-4} mol/L solutions of PVPI in chloroform, dichloromethane and dichloroethane in a 2-mm cell.

The real part $c^{(3)}$ is related to the nonlinear refraction coefficients by²²

$$\text{Re } c^{(3)} \text{ (esu)} = \frac{cn_0^2}{720p^2} n_2 \text{ (m}^2/\text{W)} \quad (3)$$

where

$$n_2 \text{ (m}^2/\text{W)} = \frac{\Delta\Phi_0 I}{2p L_{\text{eff}} I_0} \quad (4)$$

In this equation, $L_{\text{eff}} = \frac{(1 - e^{-aL})}{a}$, where a is the linear absorption coefficient, c is the velocity of light in vacuum, and n_0 is the linear refractive index of the solution. $\Delta\Phi_0$ and I_0 are the on-axis ($r = 0$), peak ($t = 0$) nonlinear phase shift and the intensity with the sample at focus ($Z=0$), respectively. For a Gaussian spatial and temporal distribution,

$I_0 = \frac{4\sqrt{\ln 2} E_{\text{total}}}{\sqrt{p^3} w_0^2 t}$, where E_{total} is the incident energy on the sample after the reflection from the front surface of

the cell is taken into account, w_0 is the beam waist of radius at the focal point, t is the pulsewidth (full width at half maximum). The sign of $\Delta\Phi_0$ and hence n_2 is determined from the relative position of the peak and valley with Z .

For a top-hat beam Z-scan, ΔF_0 can be obtained from the measured peak-valley transmittance difference ΔT_{p-v} by a simple empirical equation²⁹

$$\Delta\Phi_0 = 2.7 \tanh^{-1} \left(\frac{T_{pv}}{2.8(1-S)^{1.14}} \right) \quad (5)$$

where S is the transmittance of the aperture in front of the detector for a closed aperture measurement.

For calibration of the Z-scan measurements, CS₂ was run as a reference material at the input energy of 62.7 – 79.0 μ J. The measured peak-valley transmittance difference, ΔT_{p-v} , was 0.25 – 0.522, which gives a calculated ΔF_0 of 0.250 – 0.527. From this, an averaged n_2 value of 5.40×10^{-18} m²/W, namely 1.05×10^{-11} esu was obtained by using the conversion

formula,³⁰ $n_2 \text{ (esu)} = \left(\frac{cn_0}{80p} \right) n_2 \text{ (MKS)}$, which is in excellent agreement with the reported values of $1.3 \pm 0.3 \times 10^{-11}$

esu.³¹ The Re $c^{(3)}$ was then calculated to be 6.0×10^{-13} esu.

A typical open aperture and closed aperture Z-scan experimental data taken in dichloromethane solution is shown in Fig. 5. The open aperture curve clearly demonstrates a strong nonlinear absorption. The pronounced asymmetry in the closed aperture curve indicates that nonlinear absorption plays a dominant role in the third-order nonlinear process of the

PVPI/CH₂Cl₂ solution. The peak-valley shape of the pure refraction curve suggests that the refractive index change is negative. For an absorptive media measured in nanosecond regime, the negative sign usually implies that thermally induced changes in refractive index dominates the refractive index change in solution.

As shown in Fig. 4(b), the peak-valley transmittances difference $\Delta T_{p-v}=0.66$ corresponds to an on-axis phase change of 0.67. Thus, the nonlinear refractive index n_2 is obtained to be $-8.4 \times 10^{-18} \text{ m}^2/\text{W}$ using equation (4), yielding a $\text{Re } c^{(3)}$ value of $-7.2 \times 10^{-13} \text{ esu}$. The Z-scan experimental results in PVPI/CHCl₃ and PVPI/C₂H₄Cl₂ solutions are quite similar to that in dichloromethane solution. The nonlinear refractive indices for the two solutions are calculated to be $-5.3 \times 10^{-18} \text{ m}^2/\text{W}$ for the PVPI/C₂H₄Cl₂ solution at an input energy of 81.2 μJ , and $-9.8 \times 10^{-18} \text{ m}^2/\text{W}$ for the PVPI/CHCl₃ solution at an input energy of 77.4 μJ , yielding $\text{Re } c^{(3)}$ values of $-4.7 \times 10^{-13} \text{ esu}$ and $-8.7 \times 10^{-13} \text{ esu}$, respectively. These values are summarized in Table 1. Experiments performed on pure solvents show neither nonlinear absorption nor nonlinear refraction.

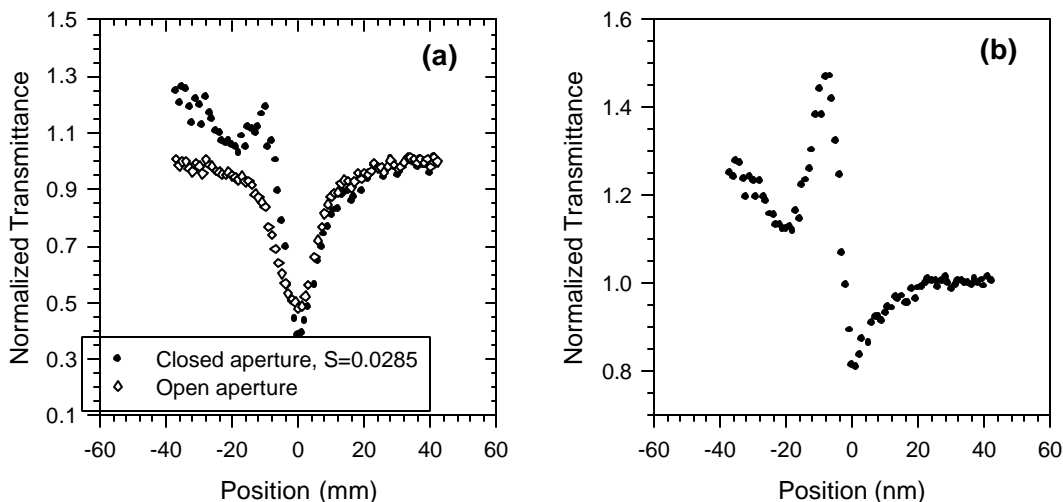


Figure 5 Top-hat beam Z-scan experimental curve for $5 \times 10^{-4} \text{ mol/L}$ PVPI/CH₂Cl₂ solution in a 2-mm cell at an input energy of 81.6 mJ.

- (a) Normalized open aperture and closed aperture experimental data;
 (b) Normalized pure nonlinear refraction curve by the division of the closed aperture data by open aperture data.

3.4 Optical limiting

As shown in the Z-scan open aperture results, PVPI in chloroform, dichloromethane and dichloroethane exhibited significant transmittance drop when the sample was moved to the vicinity of the focal plane. This transmittance drop is generally considered to be due to either nonlinear absorption, nonlinear scattering, or combined effects. Both of these effects are important in improving the optical limiting performance.

To characterize the optical limiting performance of PVPI, we have directly measured the energy transmission as a function of fluence at 532 nm using 6.8 ns laser pulses. The results of PVPI in five different solvents are shown in Fig. 6. The chloroform, dichloromethane and dichloroethane solutions exhibit significant transmittance changes as the input fluence is varied from 0.01 to 6 J/cm², with the chloroform solution showing the best result. The optical limiting threshold³² appears to be 0.006 J/cm², and the transmittance drops to ~8% when the fluence is increased to ~6 J/cm².

As mentioned above, both nonlinear absorption and nonlinear scattering can contribute to the optical limiting. Comparing the optical limiting performance with their corresponding linear absorption at 532 nm, it is observed that the higher the linear absorption, the better the limiting performance. A few percentage changes in linear transmission caused a dramatic difference in nonlinear transmission, strongly suggesting a nonlinear absorption mechanism. However, this still could not rule out the possibility of another mechanism, such as nonlinear scattering, that can also contribute to the limiting performance. To verify this assumption, scattering measurements were performed on each of the solutions using a metal

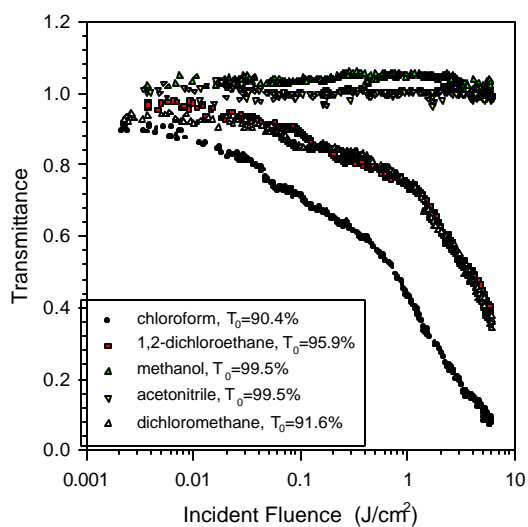


Figure 6 Transmission versus input fluence for 6.8 ns laser pulses for five 5×10^{-4} mol/L PVPI solutions in 2-mm cell.

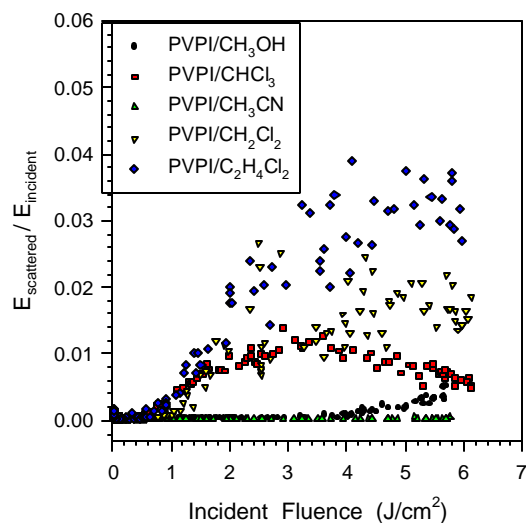


Figure 7 Percentage of scattered energy versus incident fluence of five 5×10^{-4} mol/L PVPI solutions in 2-mm cell for 6.8 ns laser pulses.

piece to block the major beam and a 2" diameter lens behind the sample cell to collect the forward scattering light under the identical conditions as the nonlinear transmission measurements. The results are shown in Fig. 7. Not surprisingly, we observed a nonlinear scattering in most of the solutions. Scattering from chloroform, dichloromethane, and dichloroethane solutions became apparent when the incident fluence was increased above 1 J/cm^2 . Saturation occurred in chloroform solution as the fluence was increased to 3.4 J/cm^2 . This probably arises from reabsorption of the scattering light due to the high nonlinear absorption occurring in the solution. Although the nonlinear scattering is obvious, it does not appear to be the dominant mechanism for optical limiting. We have made this conclusion based on the following two facts. First, even in the dichloroethane solution that exhibited the strongest nonlinear scattering, the measured scattering energy at the higher fluence is only $\sim 4\%$ of the incident energy. In contrast, the transmittance drops to 38% at the highest fluence. The small percentage drop ($<4\%$) induced by the scattering should not be the dominant contributor to the optical limiting. Second, further experiments using a small aperture ($d = 2.4 \text{ mm}$) placed in front of the detector demonstrated that the aperture had no effect on the nonlinear transmission measurements. This strongly suggests that even if nonlinear scattering occurred in the solution, nonlinear absorption is still the dominant effect that contributes to the efficient optical limiting performance. In addition, the nonlinear absorption is more likely to be a reverse saturable absorption rather than two-photon absorption as evident by the fact of that the conjugate signal vanished when the probe polarization was changed orthogonally to that of the pump beams in DFWM studies.

One issue needs to be mentioned is that although the chloroform solution shows the best optical limiting performance, it is also the most unstable solution. The transmission curve representing the second time run on the same chloroform solution appeared to be much lower than the initial measurement on fresh solution. Precipitates were observed several hours after chloroform solutions of PVPI were exposed to the laser beam or to ambient light. The dichloromethane solution behaved in a similar manner with precipitates occurring 1-2 days after exposure to light. The nonlinear scattering may, in part, be explained by the existence of strongly absorbing scattering centers that are present in the solution. A possible origin of these centers is from by-products of the photochemical reactions in solutions. Further studies will be carried out to find out a suitable solvent that can stabilize the compound while maintaining its excellent optical limiting performance.

4. CONCLUSIONS

DFWM, Zscan and nonlinear transmission measurements have been carried out on *trans*-4-[2-(pyrryl)vinyl]-1-methylpyridinium iodide (PVPI) solutions using 6.8 ns laser pulses at 532 nm. The solvents show a dramatic effect on both of the linear absorption spectra and the nonlinear optical properties. The g value of the chloroform solution is 212 times as

larger as that of the methanol solution. Z-scan results demonstrate that thermally induced refractive index changes dominate the changes of the refractive index in the solutions. However, nonlinear absorption is still the predominant effect contributing to the third-order nonlinear process.

Nonlinear transmission studies on different solutions demonstrate that both nonlinear absorption and nonlinear scattering contribute to the optical limiting behavior, with nonlinear absorption being the dominant limiting mechanism. Such cooperative nonlinear effects enhance the nonlinear transmission and are important in improving the optical limiting performance. The fact that reverse saturable absorption exists in the vicinity of the linear absorption band combined with the possible two-photon absorption over the broad transparent band makes PVPI a very promising candidate for broadband optical limiting applications.

5. ACKNOWLEDGEMENT

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