Laser Properties Of Luminescent Conducting Polymers In Open Resonators

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ABSTRACT

We have investigated the lasing properties of several luminescent conducting polymers, i.e. DOO-PPV and the bi-substituted polyacetylenes PDPA-nBu, and PH$_x$PA, dissolved in various polar and non-polar solvents. PPV polymers emit with high quantum efficiencies in broad emission bands centered in the orange/red region of the spectrum, depending on the solvent, and the PDPA polymers emit in the blue/green region. Our tested laser resonators include polymer solutions excited with 100 ps pulses from a regeneratively amplified mode-locked Nd:YAG laser. We obtain pulsed, low- threshold (μJ-level) laser operation with repetition rate of up to 1 kHz. Resulting mainly from recent refinements in material quality, the DOO-PPV laser characteristics appear to be significantly improved compared to laser results reported originally in the literature. The dependencies of threshold pump energy and output versus input power characteristics on material parameters (type of solvent, polymer concentration) are investigated for a fixed optical gain length. The results are compared with the standard Rhodamine 590 organic dye system used in the same wavelength regions. We have observed that the well known phenomenon of "concentration quenching" in dye molecules does not happen in polymers. Spectral narrowing in PDPA-nBu solution, emitting near 500 nm, is also obtained for the first time.

Keywords: lasing, amplified spontaneous emission, spectral narrowing, conducting polymers

1. INTRODUCTION

Recently luminescent semiconducting polymer materials have gained considerable attention due to their potential as active materials in bright-light solid-state optical display devices. Chemical tuning permits, in principle to generate optical emission throughout the whole visible range of the spectrum, including the red/gree/blue primary colors. The first laser oscillation with a polymer system in the liquid phase near 600 nm was realized about 5 years ago using MEH-PPV[1]. In the following years, novel high-efficiency copolymers and other PPV derivatives extended the laser emission to the blue spectral region[2,3]. The efficiency of these polymer materials appears to be comparable to those of the well known and widely used dye laser materials in the visible wavelength region. A strong advantage of the polymers compared to dyes is their promise of operating not only in liquid but also in the solid phase[4]. In this study we have investigated the emission properties of several new polymers with potential for emission in the blue and green wavelength region. Also, we evaluate their performance in relation to the previously developed PPV systems as well as the widely used Rhodamine 590 "standard".

2. EXPERIMENTAL

As active materials we used poly(1-phenyl-2-p-n-butylphenylacetylene) or PDPA-nBu, poly (1-hexyl-2-phenyl acetylene) or PH$_x$PA, poly(2,5-dioctyloxy p-phenylenevinylene) or DOO-PPV, and for comparison Rhodamine 590. Solutions were prepared by dissolving the respective powder materials in methanol, chloroform, toluene, or xylene solvents, and placing them into an optical-quality quartz cuvette. The cuvette, having 1cm^2 cross section, was placed into an optical resonator formed by a flat high reflector and a flat output coupling mirror (R =95%). The mirror separation was ~ 3 cm. The solutions were transversely excited by 100 ps pulses from a Nd:YAG regenerative amplifier operating at 532 or 355 nm, respectively, with pulse repetition rates variable between 100 Hz and 1 kHz. In order to realize a pencil-shaped excitation volume, the laser beam was expanded and focussed onto the cuvette with a cylindrical lens, thus producing a focal line with ~ 100 μm vertical width (Fig. 1). Using knife edges, the horizontal length of the focal

SPIE Vol. 3148 • 0277-786X/97/$10.00

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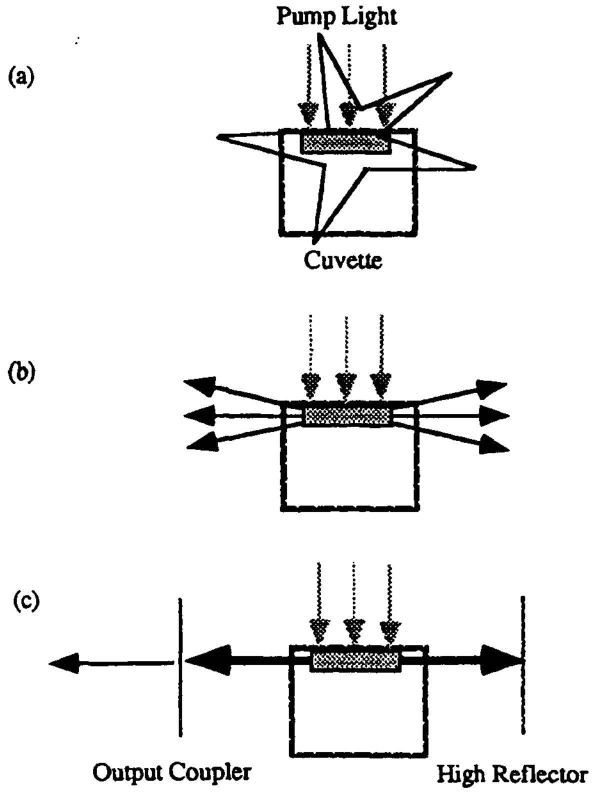

Figure 1. Emission patterns of laser-excited polymer solutions; top view. The excited volume of the active material is of semi-cylinderical shape (hatched box) and emits light in three distinct emission patterns:
(a) Spontaneous emission: light is uniformly emitted in all directions .
(b) Amplified spontaneous emission: large fraction of light is emitted into a filement-like pattern with high divergence.
(c) Laser emission: light is emitted with feedback from external cavity mirrors into a well defined beam emerging from output coupler with reduced divergence.
In all cases the active material is placed in a quartz cuvette^{2}with 1 cm cross section . Reflectivity of output coupler 95% and that of high reflector 99.5% .
Excitation: 532 or 355 nm; 100 ps; 100 Hz repetition rate.

line could be varied up to about 5 mm in length thus allowing us to observe the emission pattern of the active materials as function of gain length. To avoid feed back from the walls of the cuvette, the cuvette was slightly tilted with respect to the excitation line. The emission was observed perpendicular to the excitation direction using suitable imaging optics, a monochromator, and optical detectors. To follow the evolution of the optical emission from low-power excitation to sufficiently high power levels at which spectral narrowing, amplified spontaneous emission (ASE) and laser oscillation set in, a variable filter wheel placed in the excitation beam path was used for the excitation power adjustment. All polymer solutions were compared to the laser behavior of Rhodamine 590 using identical setups.

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3. RESULTS AND DISCUSSION

The main optical parameters of the materials investigated in this work, as well as their gain cross section, σ, and the measured ASE and laser parameters are summarized in Table 1. The absorption and emission characteristics of Rhodamine 590 are illustrated in Figs. 2-5. Excitation of the dye solution with 532 nm leads to efficient excitation close to the absorption maximum (Fig. 2). The low-power emission occurs as ~ 35 nm wide band, centered at 565 nm, with ~100 % quantum efficiency. Under continuing pump power increase, the emission evolves from spontaneous emission to amplified spontaneous emission and laser oscillation, and is shown in terms of its spectral characteristics in Fig. 3 (a), (b) and (c), respectively. Starting from the broad (~35 nm) spectral width of spontaneous emission, curve (a), the width narrows to about 20 nm with the onset of ASE, curve (b), and finally reaches a minimum value of ~ 8 nm after onset of laser oscillation, curve (c). The emission patterns for these three cases vary drastically and can be easily distinguished by visual observation. Up to a certain threshold intensity level, the emission is radiated spontaneously and can be seen to be present in all directions. At the threshold level, ASE sets in, characterized by a small, diverging, filament of light which emerges parallel to the axis of the pencil-shaped excitation volume but exceeds the length of the excitation pencil. Finally, under laser condition, this filament extends throughout the whole cuvette, past the wall/air interfaces to the resonator mirrors, exhibits reduced divergence, and a well collimated laser output beam spot can be seen on a screen behind the output coupling mirror. In the case where laser oscillation is avoided by removal of the resonator mirrors, the quantitative changes of the output intensity and spectral width under continuous power increase evolve from spontaneous emission through strongly amplified spontaneous emission and follow the behavior shown in Fig. 4. For these results an experimentally determined optimum dye concentration of ~0.5 mg/ml was used. While a threshold intensity is observed for ASE, the spectral width decreases gradually to a final value of ~ 7 nm, which is close to the value for laser emission.

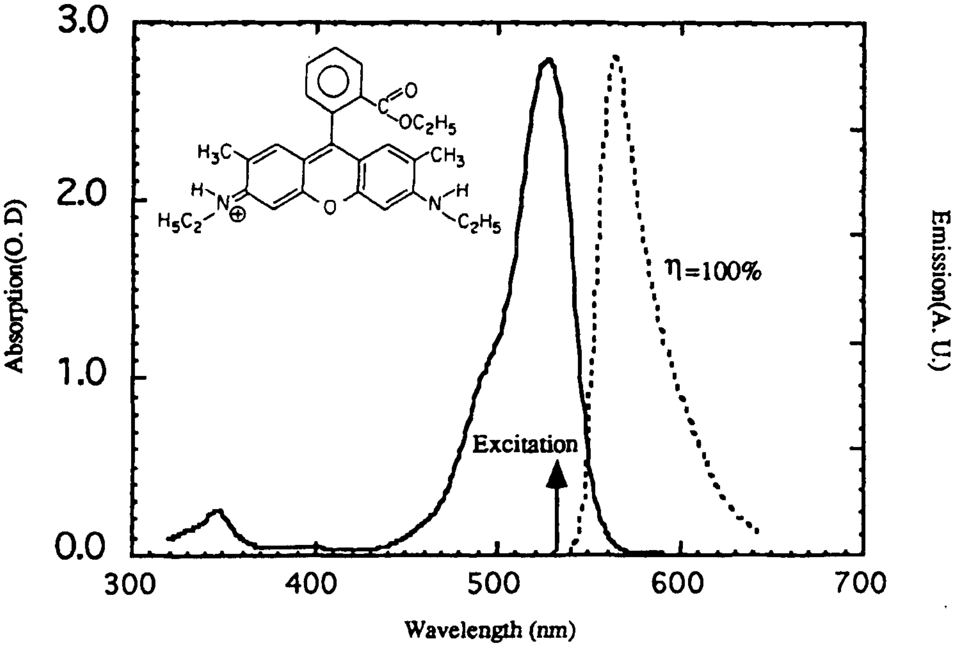

Figure 2. Absorption (solid line) and emission (dashed line) spectra of Rhodamine 590 dye dissolved in methanol. Excitation wavelength is 532 nm. Inset shows the chemical structure of Rhodamine 590.

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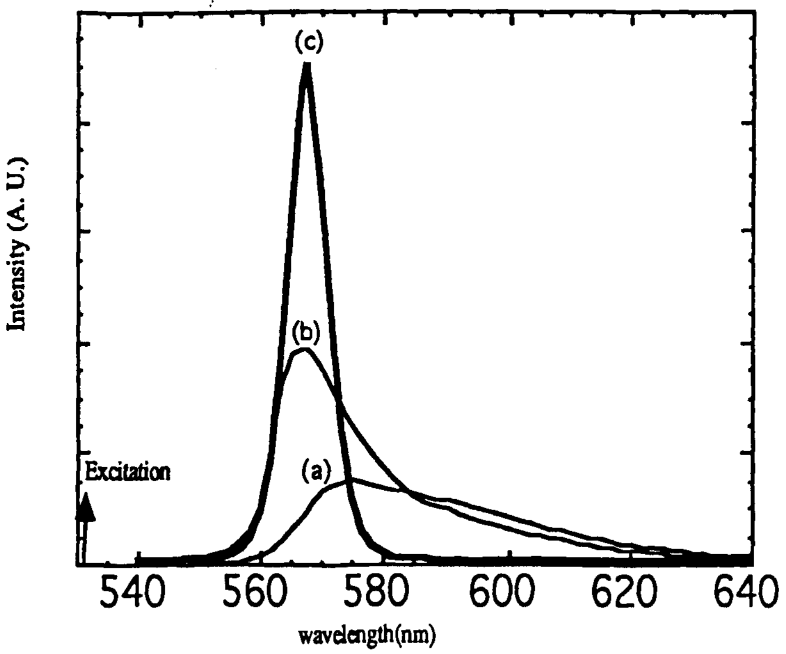

Figure 3. Spectral narrowing of Rhodamine 590 dye in methanol observed under excitation with 100 ps pulses at 532 nm; repetition rate is 100 Hz.
(a) Spontaneous emission at low excitation. $E_{pump} < 5$ µJ.
(b) Amplified spontaneous emission at $E_{pump} > 5$ µJ.
(c) Laser emission at $E_{pump} = 100$ µJ.

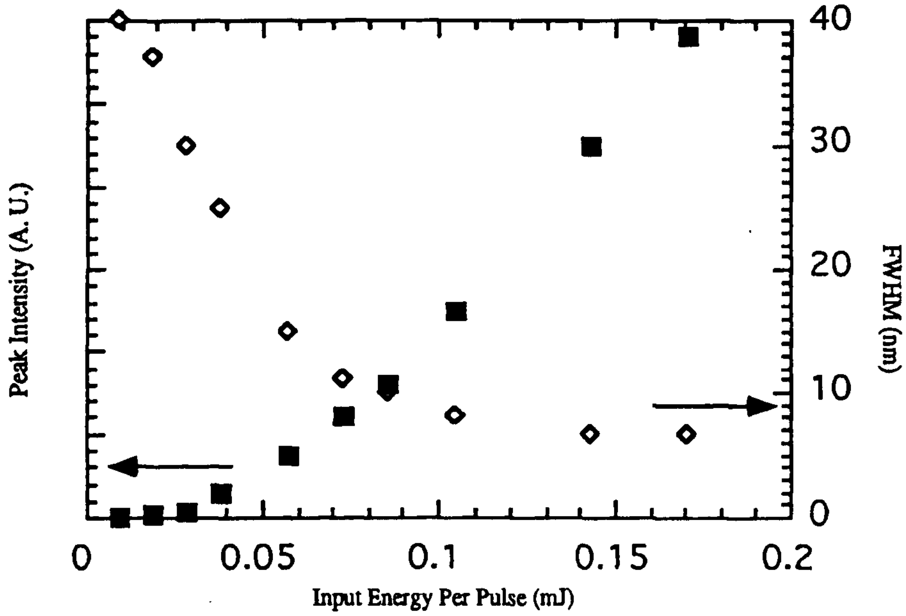

Figure 4. Output peak intensity (filled squares) and spectral width of emission (open squares) measured as function of pump pulse energy for Rhodamine 590 in methanol.
Excitation: 100 ps; 532 nm; repetition rate 100 Hz.

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To investigate the influence of the dye concentration on the ASE behavior, we measured the emission spectra of a variety of solvents ranging in concentration from ~0-8 mg/ml. The results are shown in Fig. 5 in terms of the effect of the dye concentration on the ASE threshold intensity and spectral width. Drastic changes are observed for the ASE spectral width, which reaches a minimum value of ~ 5 nm over a relatively narrow concentration range from about 0.3 - 1 mg/ml. As is apparent in Fig. 5, the threshold intensity increases above this optimum concentration and reaches again the same level as at very low concentration. This phenomenon is well known in dye photophysics and has been dubbed "concentration quenching" in the literature[5]. We speculate that the dye molecules strongly interact at high concentration to form aggregates, which consequently reduce the oscillator strength of the transition between the lowest-lying excited state level and the ground state. This happens also for small oligomers, such as 6T (6 thiophene repeat units), and it has been thoroughly studied in J- and H- aggregates in the literature. We will see below that the same phenomenon does not occur in π-conjugated polymers.

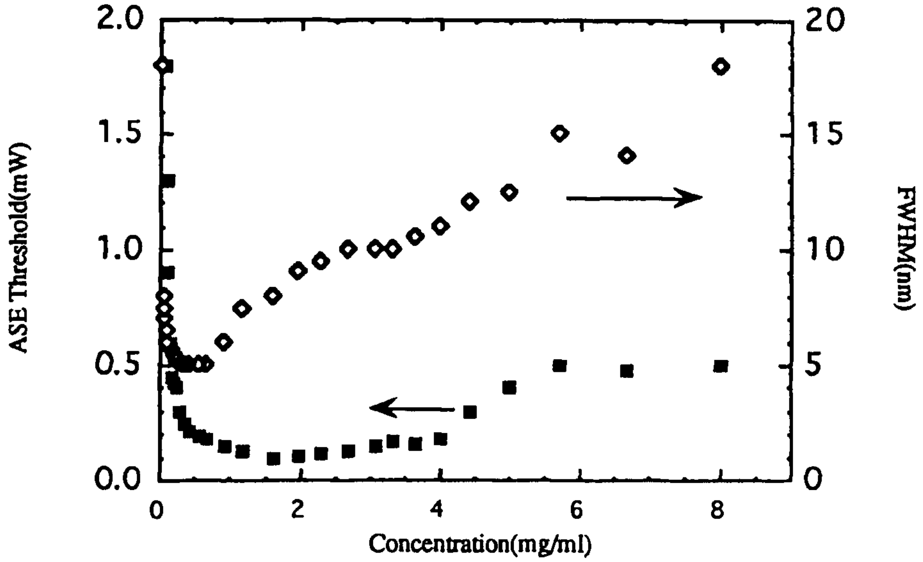

Figure 5. Change of amplified spontaneous emission threshold intensity (filled squares) and band width (open squares) with concentration for Rhodamine 590 dye in methanol.
Increase of ASE threshold intensity and band width after increase of concentration beyond optimum value of ~ 0.5 mg/ml is the consequence of the "concentration quenching" effect.

The first polymer system we investigated is PDPA-nBu dissolved in xylene. The low-intensity absorption and emission spectra are shown in Fig. 6. This system absorbs in the near UV and exhibits emission in the blue/green spectral region. Using 355 nm excitation and the same setup as described earlier, we observed under power increase the emission behavior illustrated in Fig. 7. Starting from a low-intensity spectral width of ~ 90 nm (curve a), we obtain ASE at a pump threshold energy of 8 μJ (curve b). With increasing pump power the spectral width decreases to ~20 nm (curve c). The ASE threshold energy is about the same as for Rhodamine 590; however, the threshold concentration required for laser operation is significantly higher (~factor of 100) and therefore the PDPA-nBu/xylene system forms a highly viscous liquid. The inhomogeneities of the liquid caused strong beam distortions and no attempts were made to obtain laser oscillation.

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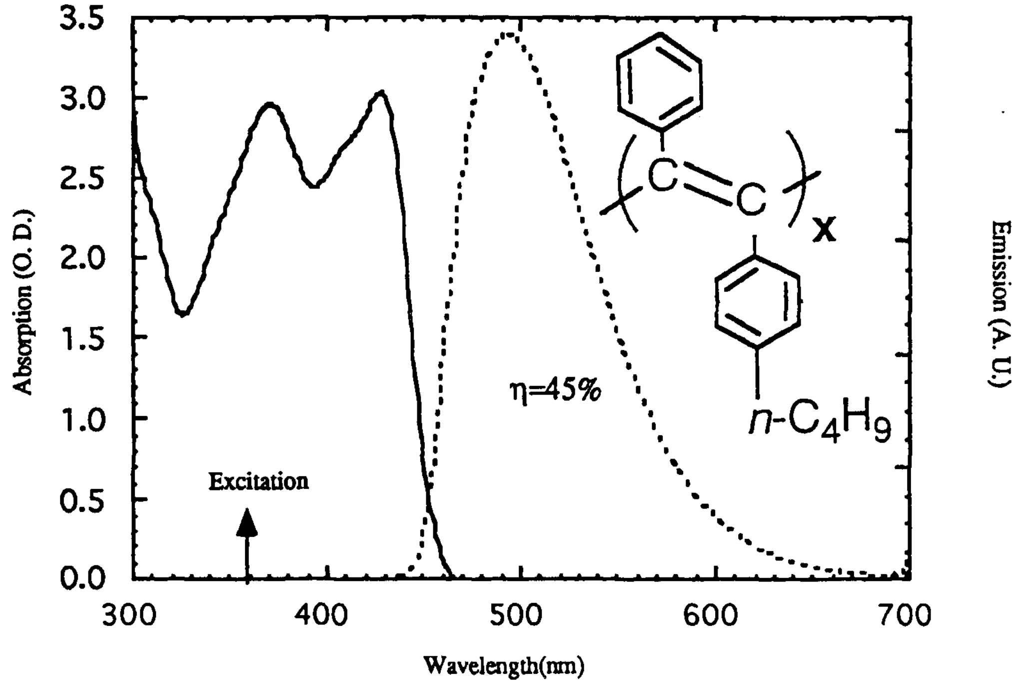

Figure 6. Absorption (solid line) and emission (dashed line) spectra of PDPA-nBu dissolved in xylene. Excitation wavelength is 355 nm. Inset shows the chemical structure of the PDPA-nBu repeat unit.

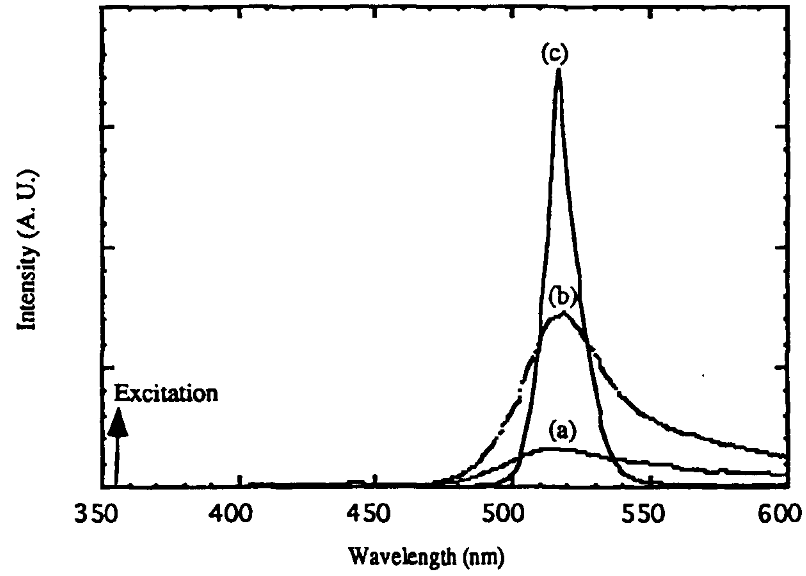

Figure 7. Spectral narrowing of PDPA-nBu in xylene observed under excitation with 100 ps pulses at 355 nm; repetition rate is 100 Hz.

(a) Spontaneous emission at low excitation. $E_{pump} < 5$ μJ.

(b) Amplified spontaneous emission at $E_{pump} \sim 8$ μJ.

(c) Amplified spontaneous emission at $E_{pump} \sim 300$ μJ.

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The second investigated polymer system was PH_xPA. The low-intensity absorption and emission spectra for PH_xPA dissolved in xylene are shown in Fig. 8. This system absorbs in the deep UV and emits in the blue spectral region. In spite of a known high quantum efficiency of the emission we did not observe any spectral narrowing in this material, even at pulse repetition rates as low as 50 Hz. The same negative result was obtained using chloroform as solvent.

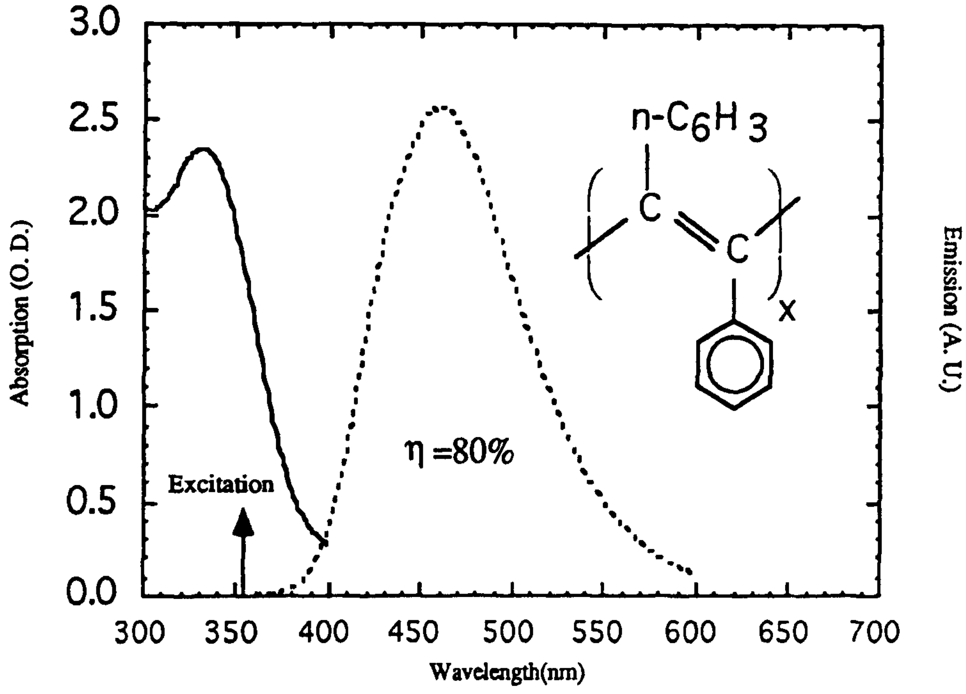

Figure 8. Absorption (solid line) and emission (dashed lin) spectra of PHxPA polymer dissolved in xylene. Excitation wavelength is 355 nm. Inset shows the chemical structure of PHxPA.

Finally, we have investigated the emission properties of the polymer DOO-PPV, dissolved in xylene and toluene. The low-intensity absorption and emission spectra are shown in Fig. 9. The absorption peaks at 480 nm and excitation with 532 nm YAG laser radiation is still possible but occurs with significantly reduced efficiency in the long-wavelength shoulder of the absorption. The spectral narrowing results for the DOO-PPV are shown in Fig. 10. All phases of emission behavior from spontaneous emission through laser oscillation are easily obtainable at low pump power levels, in spite of the less efficient excitation compared with Rhodamine 590. The concentration level used in this case was ~5mg/ml and the material oscillates in a single narrow emission at ~590 nm with an output/input characteristics shown in Fig. 11.

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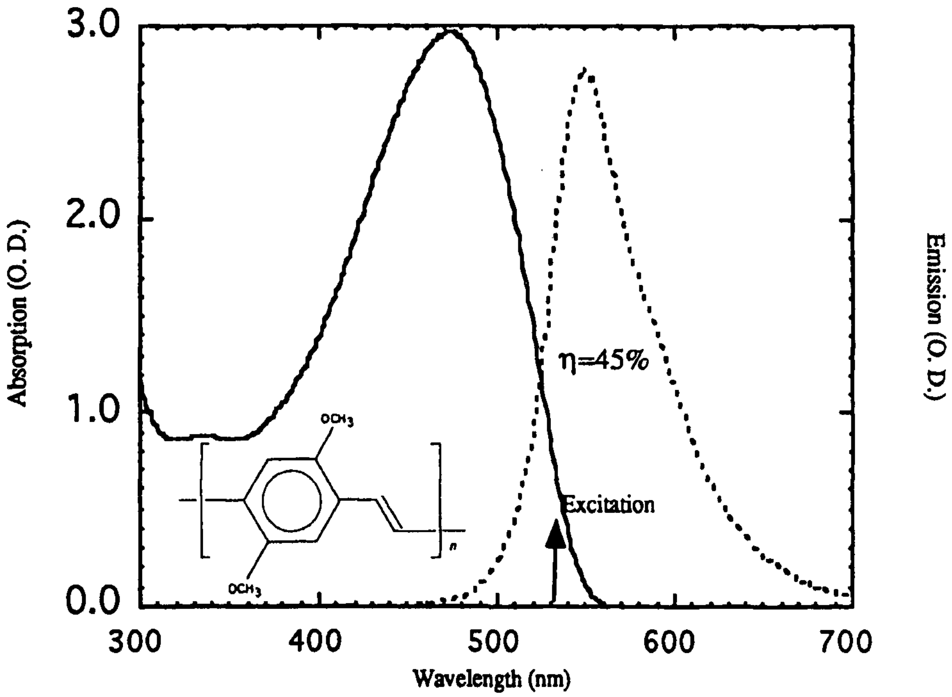

Figure 9. Absorption (solid line) and emission (dashed line) spectra of DOOPPV polymer dissolved in xylene. Excitation wavelength is 532 nm. Inset shows the chemical structure of DOOPPV.

The concentration dependence of the emission reveals a more complicated behavior compared to Rhodamine 590, and is illustrated in Fig. 12 for the onset of ASE. At low DOO-PPV concentration and low laser excitation level (not shown) one observes again the behavior shown in Fig. 9. However, at increasing concentration (curve a) the emission subdivides into two peaks, one at ~560 nm and the other at ~590 nm, and at further increased concentration levels (curves b and c) the 590 peak grows at the expense of the 560 nm peak. At the highest used pump power levels only the long-wavelength peak at ~590 nm is left. The influence of the polymer concentration on the ASE threshold intensity and bandwidth is shown in Fig. 13. While the threshold deceases monotonously with increasing concentration, the bandwidth is seen to reach an optimum low value at ~ 3 mg/ml, increases slightly and finally decreases again towards higher concentration levels. This behavior is in marked contrast to the corresponding behavior of Rhodamine 590 (compare Fig. 5) and indicates the absence of "concentration quenching" effects in this polymer. This observation is consistent with the fact that laser emission can be obtained in fully concentrated solid state thin films of the material[2,3,4].

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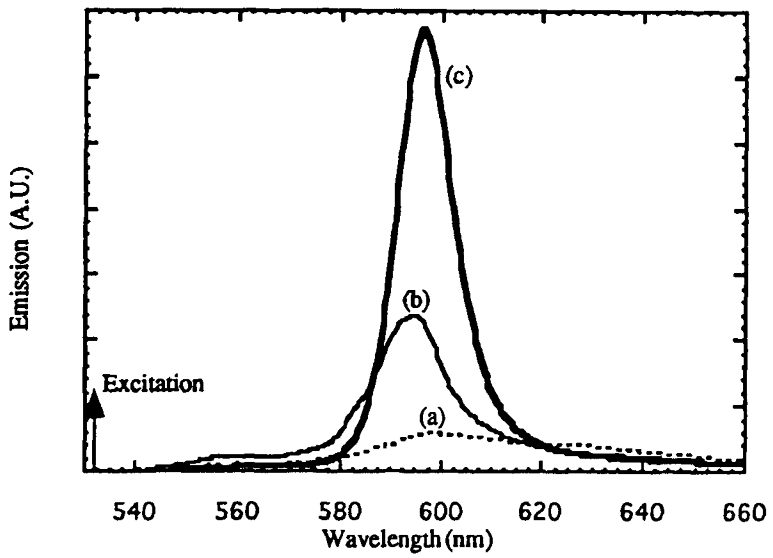

Figure 10. Spectral narrowing of DOOPPV in xylene observed under excitation with 100 ps pulses at 355 nm; repetition rate is 100 Hz.
(a) Spontaneous emission at low excitation. $E_{pump} < 1$ µJ.
(b) Amplified spontaneous emission at $E_{pump} \sim 10$ µJ.
(c) Laser emission at $E_{pump} = 50$ µJ.

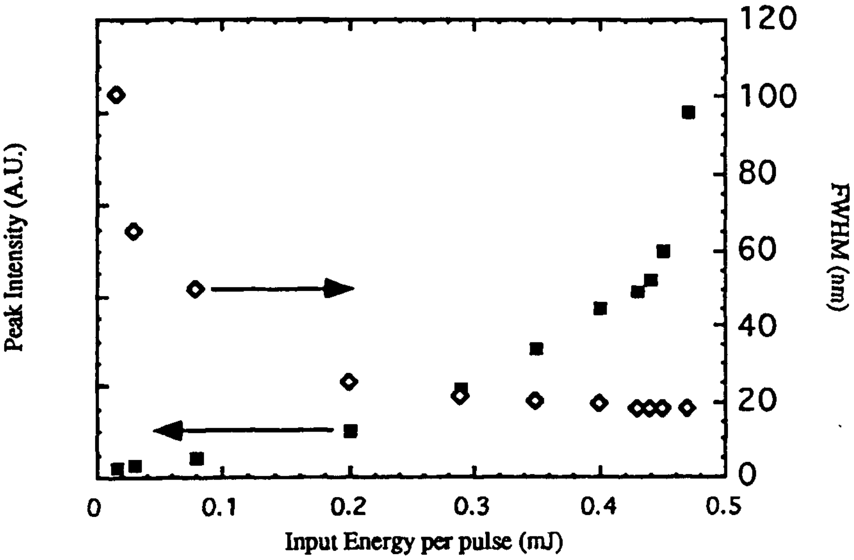

Figure 11. Output peak intensity (filled squares) and spectral width of emission (open squares) measured as a function of pump pulse energy for DOOPPV polymer in toluene
Excitation: 100 ps; 532 nm; repetition rate 100 Hz.

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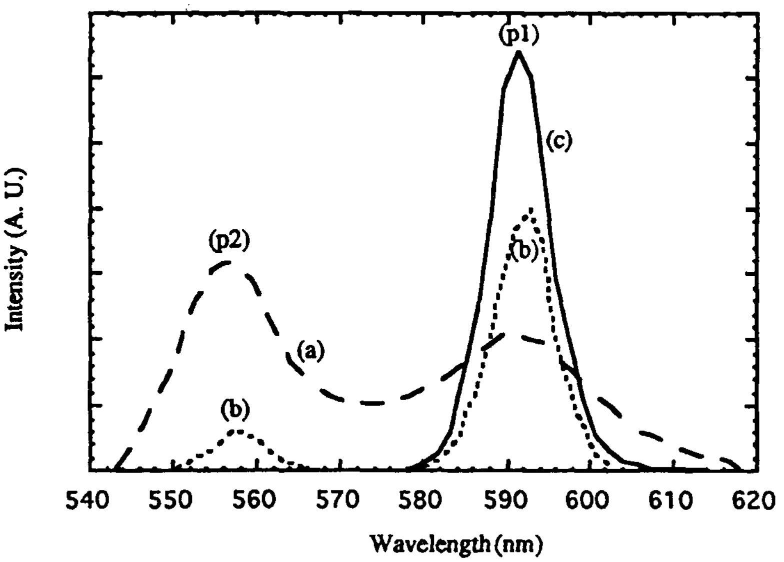

Figure 12. Emission spectra of DOOPPV n toluene at three different concentration levels, C: (a) C =.6 mg/ml ; (b) C = 2.5 mg/ml ; (c) C = 16.5 mg/ml.
Excitation: 532 nm; 370 μJ ; 100 Hz repetition rate.

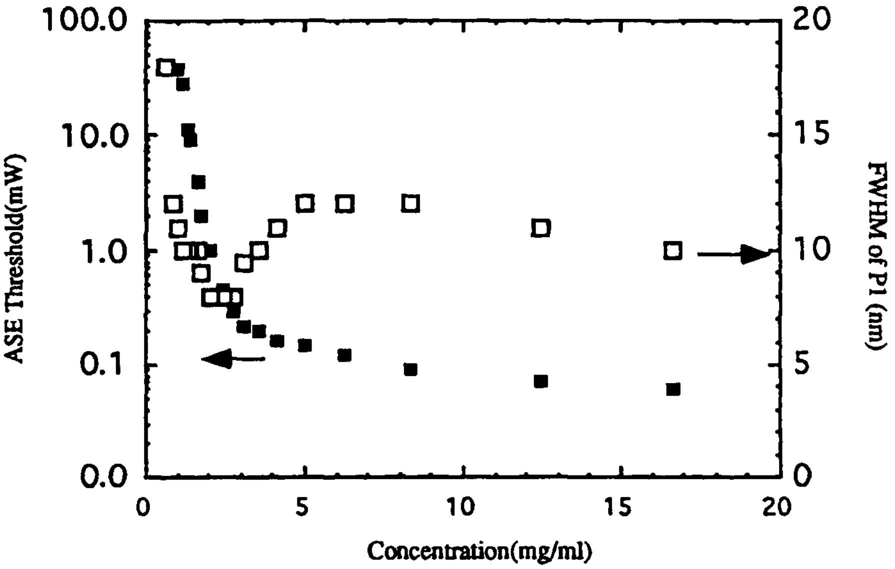

Figure 13. Change of amplified spontaneous emission threshold intensity (filled squares) and spectral width (open squares) with concentration of DOOPPV polymer in toluene.

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Gain medium	Rhodamine 590[1]	PPV-DOO[2]	PDPA-nBu[3]	PH_xPA[3]
$\lambda_{max,abs}$ (nm)	525	470	365 & 427	330
$\lambda_{o\ emiss}$ (nm)	565	550	490	460
η (%)	100	45	45[4]	80[4]
τ_f (ps)	3700	400	600	"800"(predicted)
n	1.33	1.5	1.7	1.7
$\Delta\lambda_{emiss}$ (nm)	35	65	90	95
$\Delta\nu_{emiss}$ (THz)	33	64	112.4	134.7
σ ($10^{-16}cm^2$)	5.8	4.2	2.2	2.2
λ_{pump} (nm)	532	532	355	355
$I_{ASE\ thresh}$ (mJ)	.02	.01	.2	No narrowing
$I_{laser\ thresh}$ (mJ)	.05	.04	.3	
C (mg/mlit)	.5	6	15	
$\Delta\lambda_{ASE}$	20	20	20	
$\Delta\lambda_{laser}$	6	10	Not measured	

1. in methanol , 2. in toluene , 3. in xylene , 4. in film , 5. $\sigma = (\lambda_0^2 \eta) / (8\pi n^2 \tau \Delta\nu)$

Table 1. Summary of results.

4. CONCLUSIONS

In conclusion, we verified the excellent laser potential of the previously known PPV polymer solutions and realized, for the first time spectrally narrowed emission in the green region at 520 nm with a PDPA-nBu polymer in solution. A comparison of the polymer emission properties with those of Rhodamine 590 indicates the insensitivity of polymer amplified spontaneous emission and laser output intensities regarding high concentration levels. In contrast to dye systems this makes them interesting candidates for solid state laser materials.

5. ACKNOWLEDGMENTS

The work at the University of Utah was done at the Utah Laser Institute and supported by DOE grant F6-03-96-FR45490.

6. REFERENCES

1. D. Moses, "High quantum efficiency luminescence form a conducting polymer in solution: novel polymer laser dye", *Appl. Phys. Lett.* **60**, p. 3215, 1992.
2. H.-J. Brouwer, V.V. Krasnikov, A. Hilberer, J. Wildeman, and G. Hadziioannou, "Novel high efficiency copolymer laser dye in the blue wavelength region", *Appl. Phys. Lett.* **66**, 3405 (1995).
3. W. Holzer, A. Penzkofer, S.-H. Hong, A. Bleyer, and D.D.C. Bradley, "Laser action in Poly(m- phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene)", *Advanced Materials* **8**, 974(1996).
4. F. Hide, M. A. Diaz-Garcia, B. J. Schwartz, M. R. Anderson, Q. Pei, and A. Heeger, "Semiconducting Polymers: a new class of solid-state laser materials", *Science* **273**, 1833 (1996); N. Tessler, G. J. Denton, and R. H. Friend, "Lasing from conjugated polymer microcavities", *Nature* **382**, 695 (1996); S. V. Frolov, W. Gellermann, M. Ozaki, K. Yoshino, and Z. V. Vardeny, "Cooperative emission in π-conjugated polymer thin films", *Phys. Rev. Lett.* **78**, 729 (1997).
5. F. P. Schäfer, "Dye Lasers", Topics in Applied Physics, Vol.1, *Springer Verlag*, 1990.

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