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Published in:
Applied Physics Letters

DOI:
10.1063/1.113368

Publication date:
1995

Citation for published version (APA):
Brouwer, H. J., Krasnikov, V. V., Hilberer, A., Wildeman, J., & Hadziioannou, G. (1995). Novel high efficiency copolymer laser dye in the blue wavelength region. Applied Physics Letters, 66(25), 3404-3406. https://doi.org/10.1063/1.113368

Novel high efficiency copolymer laser dye in the blue wavelength region

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(Received 30 November 1994; accepted for publication 21 April 1995)

The lasing performance and wavelength tunability of a novel high efficiency copolymer poly[(2, 5, 2″, 5″-tetraoctyl)-*p*-terphenyl-4,4″-ylene vinylene-*p*-phenylene vinylene], TOP-PPV, pumped with third harmonic radiation of a Nd:YAG laser, was studied in various organic solvents. The results were compared with Coumarin 120 and Coumarin 47 in ethanol under identical experimental conditions. The efficiency of the TOP-PPV copolymer in hexane exceeds that of both coumarin dyes with more than 50%. The laser emission of the polymer dye in hexane is tunable in the wavelength region between 414 and 456 nm ($\Delta\lambda = 38$ nm). © *1995 American Institute of Physics.*

In 1990, research in the field of semiconducting conjugated polymers led to the introduction of the first polymer light emitting diodes based on poly[*p*-phenylene vinylene].[1,2] This observation of electroluminescence triggered intensive research by numerous groups and resulted in the elaboration of various other semiconducting polymer light emitting diode (LED) devices with impressive efficiency[3] and color tunability.[4,5] It was realized that the high photoluminescence quantum yield of conjugated polymers made them promising candidates for active laser media in the liquid or solid state. Furthermore, due to their good processability and mechanical properties, polymeric dyes have a potential advantage as active gain media in dye doped polymeric optical devices. Laser action of a semiconducting polymer (MEH-PPV) in the liquid state[6,7] operating in the yellow/red wavelength region was achieved for the first time in 1992. The reported lasing performance of this polymer was comparable to that of the most efficient laser dye Rhodamine 6G.

In this letter we demonstrate for the first time the lasing performance of a novel highly efficient copolymer poly[(2,5,2″,5″-tetraoctyl)-*p*-terphenyl-4,4″-ylene vinylene-*p*-phenylene vinylene],[8] TOP-PPV, in the blue wavelength region. In Fig. 1 (inset top right) the structure of the repeat unit is given. The TOP-PPV copolymer ($M_n = 2.6 \times 10^3$, $M_w = 4.5 \times 10^3$) has a well-defined conjugated backbone, consisting of regularly alternating terphenylene (TOP) and *p*-phenylene-vinylene (PPV) blocks. The presence of four octyl side chains provides solubility of the conjugated form in common polar solvents such as tetrahydrofuran (THF) and chloroform. The polymer exhibits a high thermal stability, up to 420 °C under nitrogen. Figure 1 shows the absorbance ($\lambda_{\max} = 357$ nm) and emission ($\lambda_{\max} = 440$ nm) spectra of a solution of the TOP-PPV copolymer in hexane (10 mm quartz cell). Photoluminescence quantum yields as high as $M_F \sim 0.8-0.9$ were obtained in solution[8] (THF, hexane) which gave a clear indication of the possibility of lasing action.

The energy conversion efficiency measurements were performed using a linear nondispersive cavity in a quasilongitudinal pumping arrangement. The experimental setup is schematically depicted in Fig. 2. The cavity is defined by a concave metallic rear mirror and a flat dielectric output coupler (transmittance $T = 81\%$, $\lambda = 360-460$ nm) separated by a distance of 95 mm. The pump source was a Nd:YAG laser, Quanta-Ray GCR 130-50, operating at tripled frequency ($\lambda = 355$ nm, *p*-polarized, pulse width $= 8$ ns) with a repetition rate of 1 Hz. In order to prevent laser generation from the cell walls and to minimize Fresnel losses, the dye cell (path length 10 mm) was tilted with respect to the pumping beam. The angle between the pumping and generated beam was approximately 7°. The input and output pulse energy was monitored with two calibrated pyroelectric detectors (Coherent LMP 5, Molectron J3-02, respectively). The spectral characteristics of the laser and luminescence output were measured with an Optical Multichannel Analyzer (Princeton Instruments). In the case of the tuning range measurements a quartz prism was incorporated between the rear mirror and the dye cell as a dispersive element. Wavelength tuning was achieved by rotation of the rear mirror.

The lasing performance of TOP-PPV was studied in three solvents; tetrahydofuran, hexane, and *p*-xylene (Merck, spectroscopic grade). In the case of hexane (a poor solvent for TOP-PPV) the solution was filtered over an 0.2 μm filter to remove undissolved compound. The reference laser dyes

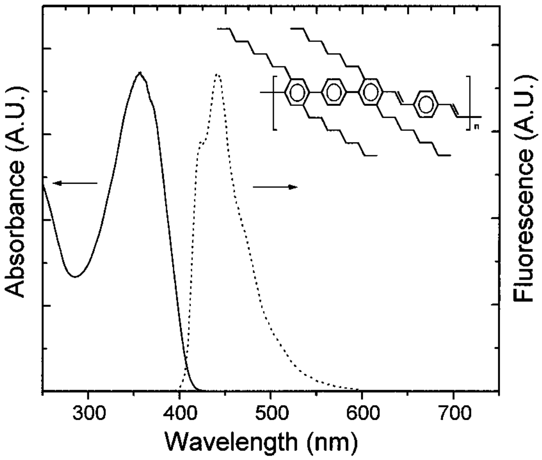

FIG. 1. Absorbance and emission spectra of the TOP-PPV copolymer in hexane. Inset (top right-hand side): the chemical structure of the TOP-PPV repeat unit.

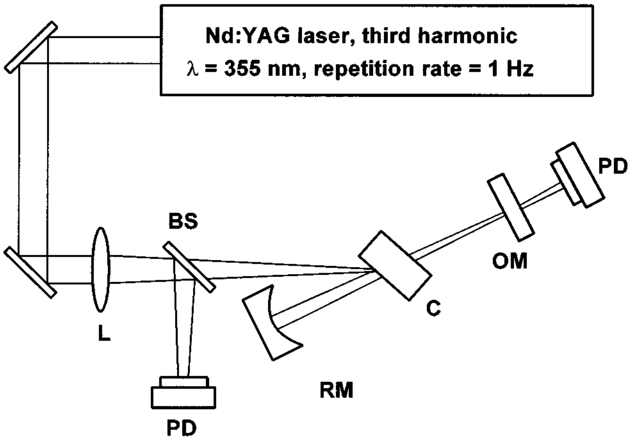

FIG. 2. Experimental setup: L, lens; BS, beam splitter; PD, pyroelectric detector; RM, concave rear mirror; C, flow cell; and OM, dielectric output mirror.

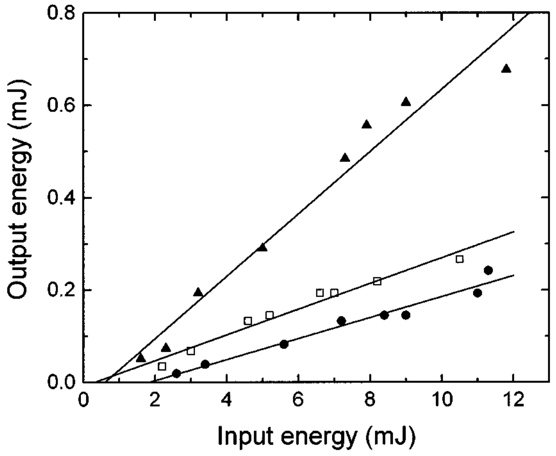

FIG. 4. Plot of the output pulse energy of the dye laser as funciton of the input pulse energy of the Nd:YAG pump beam in case of ▲, TOP-PPV copolymer in hexane; □, TOP-PPV copolymer in *p*-xylene; and ●, Coumarin 120 in ethanol. The slope of the lines represents the energy conversion efficiency.

Coumarin 120 and 47 (Lambdachrome LC 4400 and LC 4700) were used in ethanol solution (Merck, spectroscopic grade). All prepared solutions had a transmittance of 1% at $\lambda = 355$ nm, measured in a standard 10 mm quartz cuvette on a SLM aminco 3000 diode array spectrometer. Concentration dependent measurements at fixed pump energy indicated that the transmittance ($T = 1\%$) of the dye solutions were in the region of optimum efficiency.

Clear evidence of laser action of the TOP-PPV copolymer is shown in Fig. 3. When the pump energy exceeds the threshold energy of lasing, intense blue light with a narrow spectral bandwidth [7 nm, full width at half-maximum (FWHM)] was emerging from the output coupler. The spectrum of the spontaneous emission was obtained after blocking the rear mirror of the cavity to interrupt the feedback system. The wavelength of laser generation coincides with the maximum of the fluorescence emission spectrum.

Figure 4 shows the ordinary linear dependence of the output pulse energy of the dyes as function of the input pulse energy of the Nd:YAG laser. This plot clearly demonstrates that the conversion efficiency (7%) of TOP-PPV in hexane is significantly higher than in all other cases. The conversion efficiencies and lasing wavelengths for all dyes are given in Table I. The efficiencies of TOP-PPV in THF and *p*-xylene (1.8% and 2.8%, respectively) are comparable to that of the coumarin dyes. As expected, the lasing wavelength for TOP-PPV in THF and *p*-xylene are red shifted (bathochromic shift) with respect to hexane due to increasing solvent polarity. The lasing bandwidth of the TOP-PPV polymer was approximately 7 nm in all solvents. The bandwidth of both coumarin dyes was almost twice larger, 12 nm. During all measurements no visible signs of photodegradation were observed.

The results of the wavelength tunability measurements are shown in Table I. For the TOP-PPV copolymer in hexane the tuning curve and the fluorescence spectrum are plotted in Fig. 5. From this plot it can be seen that the tuning curve follows the shape of the emission spectrum in the wavelength region with the highest emission cross section (414–452 nm), due to the small overlap between absorbance and emission band. The wavelength tuning range of TOP-PPV in hexane $\Delta\lambda = 38$ nm) was the highest among all dye/solvent systems measured, which demonstrated the superior efficiency of this polymer solution. It should be mentioned that the bandwidth of laser generation was 3 nm (FWHM) in all

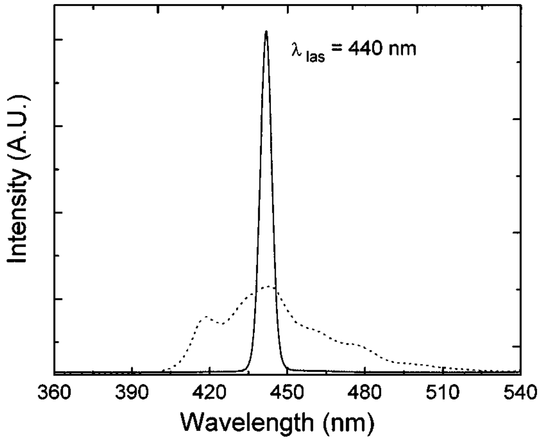

FIG. 3. Spontaneous (dotted) and stimulated (solid) emission spectra of TOP-PPV in hexane as measured with the linear nondispersive cavity.

TABLE I. Comparison of the laser characteristics of Coumarin 47, 120, and TOP-PPV.

Dye	Solvent	λ_{las}[a] (nm)	Efficiency[a] (%)	Tuning range[b] (nm)
TOP-PPV	THF	449	1.8	438–456
	p-xylene	449	2.8	436–456
	hexane	440	6.8	414–452
Coumarin 47	ethanol	451	2.8	444–470
Coumarin 120	ethanol	439	2.3	424–450

[a] Linear nondispersive cavity.
[b] Dispersive cavity.

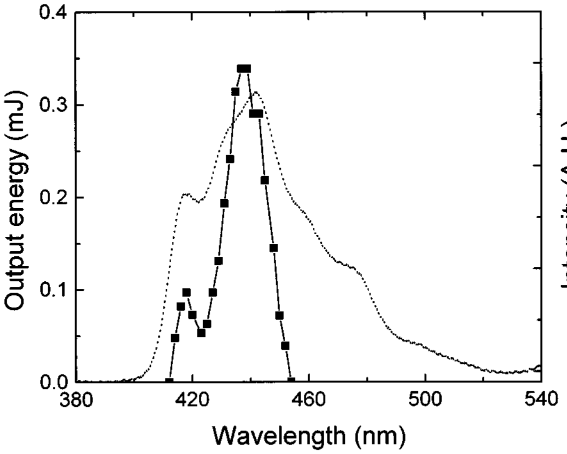

FIG. 5. Tuning curve (-■-) and luminescence spectrum (dashed) of the TOP-PPV copolymer in hexane (pump energy 10 mJ).

cases and was mainly determined by the dispersion of the cavity.

The reason for the higher conversion efficiency of TOP-PPV in hexane is unclear at this moment. Gel permeation chromatography (GPC) of the solution revealed that the molecular weight distribution changed with respect to THF and *p*-xylene. Due to the poor solubility in hexane, only the lower molecular weight species dissolved and as a result the polydispersity (M_w/M_n) decreased from 1.7 (in THF) to 1.17 ($M_n=3.1\times10^3$, $M_w=3.6\times10^3$).

In conclusion, we have demonstrated the performance of a novel high efficiency copolymer laser dye in the blue wavelength region. The conversion efficiency when pumped by third harmonic radiation of a Nd:YAG laser exceeds that of the well-known coumarin dyes in this wavelength region. In the case of the TOP-PPV copolymer in hexane a wavelength tuning range of almost 40 nm was obtained. The lasing performance of this polymer shows considerable promise for the development of stable solid-state dye doped laser materials based on TOP-PPV. This research was financially supported by SON/STW and by the EEC (Human Captial and Mobility program).

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