

# Stimulated emission in the blue wavelength region from a copolymer containing PPV segment

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## Abstract

The lasing properties of a soluble conjugated polymer, Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethynylene-1,4-phenylene-1,2-ethynylene-3,5-dimethoxy-1,4-phenylene] (CNMBC-Ph) in chloroform solution were investigated. The third harmonic radiation of a Nd:YAG laser was used as the pump light. The stimulated emission with a linewidth of 15 nm was observed in the blue wavelength region with the peak at 450 nm. The threshold pulse peak power was about 2.8 MW/cm<sup>2</sup>. The energy conversion yield of the laser was estimated to be about 3.4%. The maximum peak power of the laser output pulse reached 40 kW. © 2000 Published by Elsevier Science S.A. All rights reserved.

**Keywords:** Stimulated emission; Polymer lasing; Conjugated polymer; Dye laser

## 1. Introduction

Semiconducting conjugated polymers, such as poly(*p*-phenylenevinylene) (PPV) and its derivatives, have become potential materials for applications in optoelectronic devices, such as light-emitting diodes [1–3], field-effect transistors [4] and solar cells [5]. Due to the relatively high photoluminescence (PL) quantum yield, conjugated polymers had stimulated the intensive research on achieving polymer lasers. Moses [6] reported for the first time a dye laser made from conjugated polymer (MEH–PPV) in 1992. Brouwer et al. [7] studied the laser performance and wavelength tunability of TOP–PPV in solution. The efficiency of this copolymer in hexane exceeds that of both coumarin dyes with more than 50%. More recently, polymer lasers in various forms have been investigated under optical excitation [8–10].

Being a new potential kind of active material, conjugated polymers show some advantages compared with other materials. The absorption coefficient of the polymer

is large; the absorption and emission are spectrally separated due to Stokes shift, so the intrinsic loss due to reabsorption is minimal. Conjugated polymers have semiconducting properties and  $\pi$ – $\pi^*$  energy gap can be altered through the modification in the molecular structure. Therefore, conjugated polymers can exhibit emission throughout the whole visible spectrum. In this paper, we present a laser emission in the blue wavelength region from solution of a soluble PPV derivative — Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethynylene-1,4-phenylene-1,2-ethynylene-3,5-dimethoxy-1,4-phenylene] (CNMBC-Ph), which is a kind of copolymer that contains alternating conjugated and non-conjugated blocks. It was shown that blue light can be obtained from this kind of structure due to the fixed conjugation length [11,12]. The chemical structure of CNMBC-Ph and a schematic diagram of the polymer dye laser are shown in Fig. 1.

## 2. Experimental

The active material used here is the chloroform solution of CNMBC-Ph with optimized concentration of  $1.3 \times 10^{-3}$

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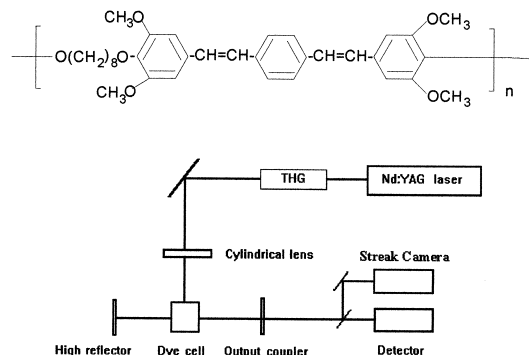


Fig. 1. Chemical structure of CNMBC-Ph and a schematic diagram of the polymer dye laser.

mol/l. After filtering through a 0.2- $\mu\text{m}$  filter to remove impurity, the solution was put into a square spectrophotometric cuvette of  $1 \times 1$  cm dimension, polished on all sides. The cuvette was placed in a resonator composed of two flat mirrors. A flat Al mirror was used as the high reflector, and a polished quartz glass flat with a reflectivity of about 8% is used as the output coupling mirror. To avoid feedback from the walls of the dye cell, the cell was slightly tilted with respect to the cavity axis. The third harmonic radiation of an active mode-locked Nd:YAG laser [wavelength = 355 nm, pulse width (full width at half-maximum, FWHM) = 300 ps, pulse energy = 5–700  $\mu\text{J}$ , pulse repetition rates = 2 Hz] was used as the exciting light. The solution was transversely pumped. The emission of the pump laser is focused on the solution by a cylindrical lens into a  $10 \times 0.2$  mm line area. The cavity length is approximately 1.47 cm, which results in approximately three round trips during a pump pulse. The absorption spectrum was measured with a Shimadzu Dual-Wavelength/Double-Beam Recording Spectrophotometer UV-3000. The PL emission spectrum was recorded with a Hitachi Spectrophotometer F4500. The temporal behavior of the fluorescence emission and the output laser pulses was measured using a M1764 high speed Streak Camera

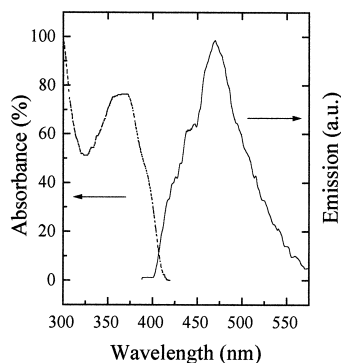


Fig. 2. UV absorption spectrum (dotted line) and PL emission spectrum (solid line) of CNMBC-Ph in chloroform.

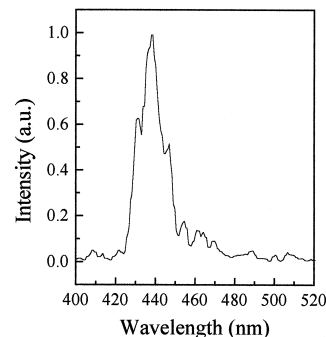


Fig. 3. The lasing spectrum of CNMBC-Ph in chloroform.

with 2-ps response time. All measurements were performed in air at room temperature.

### 3. Results and discussion

The absorption and PL emission spectra of CNMBC-Ph in chloroform are illustrated in Fig. 2. The absorption peak is located at 360 nm, so the excitation of the sample solution with 355 nm is efficient. The PL emission spectrum of CNMBC-Ph in chloroform is a broad emission band in the blue region with a maximum peak at 464 nm. FWHM is about 80 nm.

Fig. 3 shows the lasing spectrum of CNMBC-Ph in chloroform at a pump energy of 25  $\mu\text{J}$ . The measurement of the lasing spectrum was limited by the low resolution (2 nm) of the spectrometer used in this study. When the pump

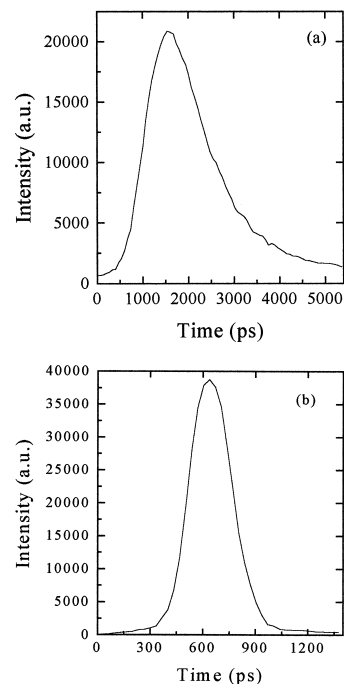


Fig. 4. (a) Temporal behavior of the fluorescence emission. (b) Temporal behavior of the lasing emission from CNMBC-ph in chloroform solution.

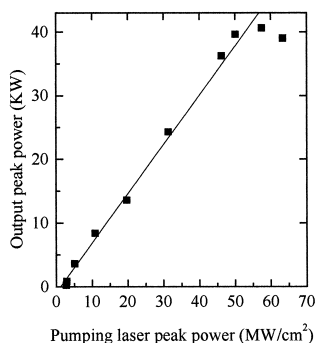


Fig. 5. The laser output pulse peak power vs. pumping-laser pulse peak power.

energy exceeds the lasing threshold, the laser beam spot can be seen on a screen behind the output coupler. When a block is placed between the cuvette and the high reflector of the cavity to interrupt the feedback system, the spot disappeared on the screen. The laser beam observed is a highly directional blue light. The divergence of the laser beam is about 6 mrad. As shown in Fig. 3, the lasing peak is located at 450 nm. FWHM of the lasing spectrum is approximately 15 nm, which shows a wide gain spectrum.

The temporal behavior of the fluorescence emission and the output laser pulses were received using the Streak Camera, which are shown in Fig. 4. The observed spontaneous decay time of the sample solution is 1.1 ns. The pulse width of the lasing output at the pump energy of 25  $\mu\text{J}$  is about 300 ps. The pulse wave form has been treated by utilization of the deconvolution method.

Fig. 5 illustrates the laser output pulse power as a function of the pump pulse power. Below the pump pulse peak intensity of 57  $\text{MW}/\text{cm}^2$ , the output pulse power increases almost linearly to the pump pulse power. For a higher pump pulse power, the laser output power is saturated. The threshold pump intensity is 2.8  $\text{MW}/\text{cm}^2$ . The maximum peak power of the output pulse arrives at about 40 kW. The energy conversion efficiency was estimated to be 3.4%.

## 4. Conclusion

The lasing property of a copolymer containing PPV segment–CNMBC-Ph in chloroform solution was investigated. The stimulated emission with a linewidth of 15 nm was observed in the blue spectral range under excitation at 355 nm. The energy conversion efficiency of the laser was estimated to be about 3.4%. The maximum peak power of the output pulse reached 40 kW.

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