# Spectral broadening properties of amplified spontaneous emission from a copolymer

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## Abstract

The spectral broadening properties of the amplified spontaneous emission (ASE) generated by a soluble copolymer, Poly[1,8–octane-dioxy–2,6–dimethoxy–1,4–phenylene–1,2–ethenylene–1,4–phenylene–1,2–ethenylene–3,5–dimethoxy–1,4–phenylene](CNMBC-Ph), were investigated. The features of the ASE spectra of the CNMBC-Ph solution demonstrated that the broadening of the ASE spectra is inhomogeneous. The inhomogeneous broadening is supposed to originate mainly from the imperfect configurations of the conjugated polymer with the one-dimensional periodic structure and the spacial inhomogeneous distribution of the chromophores due to disordered distribution of polymers in solution. The influence of inhomogeneous broadening on laser performances was discussed. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Copolymer; Linewidth; Amplified spontaneous emission; spectral broadening; Inhomogeneous broadening

## 1. Introduction

Conjugated polymers are potential materials for applications in optoelectronic devices such as organic light-emitting diodes (OLED), lasers, field-effect transistors, solar cells and displays owing to their high photoluminescence efficiency and gain, large Stokes shift which minimizes self-absorption, wide tunable wavelength range and ease of fabrication and integration into devices [1–10]. Many groups have investigated the photoluminescence of various luminescent polymers [8–12]. Among the investigations, stimulated emission and spectral narrowing of the polymers, such as PPV derivatives, attract intense interest recently, and raise hope for electrically pumped plastic lasers. In addition, the polymers with such high efficiency of fluorescence may become novel promising laser dyes, especially those with blue light emission.

In recent years, the researches on spectral narrowing of various polymers under optically pump conditions and the mechanism of the spectral narrowing have been reported. Diverse configurations for obtaining lasing action in optically pumped polymers have been proposed and developed [13–19]. Obviously, the change of spectral linewidth is an important parameter in all of these researches. In this work,

using 355 nm picosecond pulses of a Nd:YAG laser as the excitation source, we investigated the spectral linewidth changes of amplified spontaneous emission of a soluble polymer, Poly[1,8–octanedioxy–2,6–dimethoxy–1,4–phenylene–1,2–ethenylene–1,4–phenylene–1,2–ethenylene–3,5–dimethoxy–1,4–phenylene](CNMBC-Ph)(the structure of which is shown in Fig. 1) in tetrahydrofuran (THF) solution, as a gain medium under different pump energy. In particular, variations of the spontaneous emission spectra of CNMBC-Ph that corresponding to those of the ASE spectra were monitored. Judging from the changes of the ASE spectral linewidth, we interpret that the spectral broadening of CNMBC-Ph in solution was mainly attributed to inhomogeneous broadening, differing from small molecular laser dyes. The origin of the inhomogeneous broadening and its influence on laser performance were analyzed and discussed.

## 2. Experimental methods

CNMBC-Ph power was dissolved in THF and experiments of this work were all performed in air at room temperature. The absorption and photoluminescence emission spectra of CNMBC-Ph in solution were measured with Shimadzu Dual-Wavelength/Dual-Beam Recording Spec-

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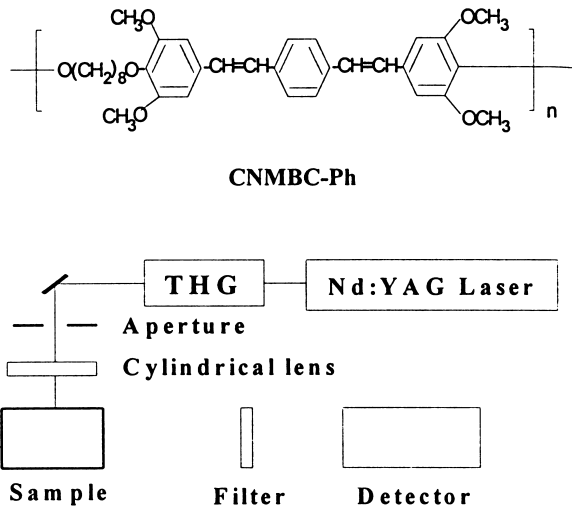
**CNMBC-Ph**



Fig. 1. Chemical structure of CNMBC-Ph and experimental set-up.

trophotometer UV-3000 and Hitachi Spectrophotometer F4500, respectively.

On the basis of the absorption spectrum of CNMBC-Ph, excitation wavelength of 355 nm was employed in the experiments. The pump source was an active mode-locked Nd:YAG laser, operating at tripled frequency ($\lambda = 355$ nm, pulse width = 300 ps) with a repetition rate of 3 Hz. A cylindrical lens was used to shape the excitation beam into a stripe with a width of approximately 200 μm and a length of about 5 mm. An aperture before the cylindrical lens was used to fix the size of the optical beam and make sure the stripe was not changed in the experiments. The ASE spectra of CNMBC-Ph in the solution of 3 mg/ml were collected from one end of the stripe at various pump intensities. In the meantime, the fluorescence emission spectra were monitored in the direction of about 45° with respect to the stripe. The spectra were detected with a home-made system with a spectral resolution of 2 nm. The set-up is schematically depicted in Fig. 1.

## 3. Results and discussions

Fig. 2 shows the ASE and spontaneous emission spectra of CNMBC-Ph (in the solution of 3 mg/ml) under different pump energies. It was supposed that the ASE originated from the main vibration band. The linewidth (FWHM) of the ASE in this paper was taken for the main vibration. When the excitation energy was below 22 μJ, ASE did not occur, as shown in Fig. 2a. When the excitation energy was 25 μJ, which was slightly higher than the threshold of 22 μJ, as shown in Fig. 2b, the ASE spectrum could be deleted from one end of the stripe. The center wavelength of the ASE spectrum is at 456 nm. In the meantime, in the emission spectrum recorded in the direction at an angle of 45° with respect to the stripe (Fig. 2b) a small dip at the band of the ASE was observed. In Fig. 2c, an obvious collapse

appeared in the fluorescence spectrum when the pump energy was 40 μJ.

The spontaneous emission profile of the Fig. 2c was obviously modified owing to the occurrence of ASE. After subtracting $I_c(\lambda)$ from $I_a(\lambda)$, where $I_a(\lambda)$ and $I_c(\lambda)$ denote the spontaneous emission profiles of Fig. 2a,c, respectively, we obtained a new profile shown in Fig. 3. The linewidth of this profile is 34 nm, which is broader than that of the ASE spectrum obtained from the stripe end. It appears that ASE occurring from other directions besides the two stripe ends and the ASE spectrum distributions of the other directions are different from that of the two stripe ends. Therefore, the profile of Fig. 3 gives a superposition of the ASE spectra from every direction. Fig. 4 which gives the ASE output
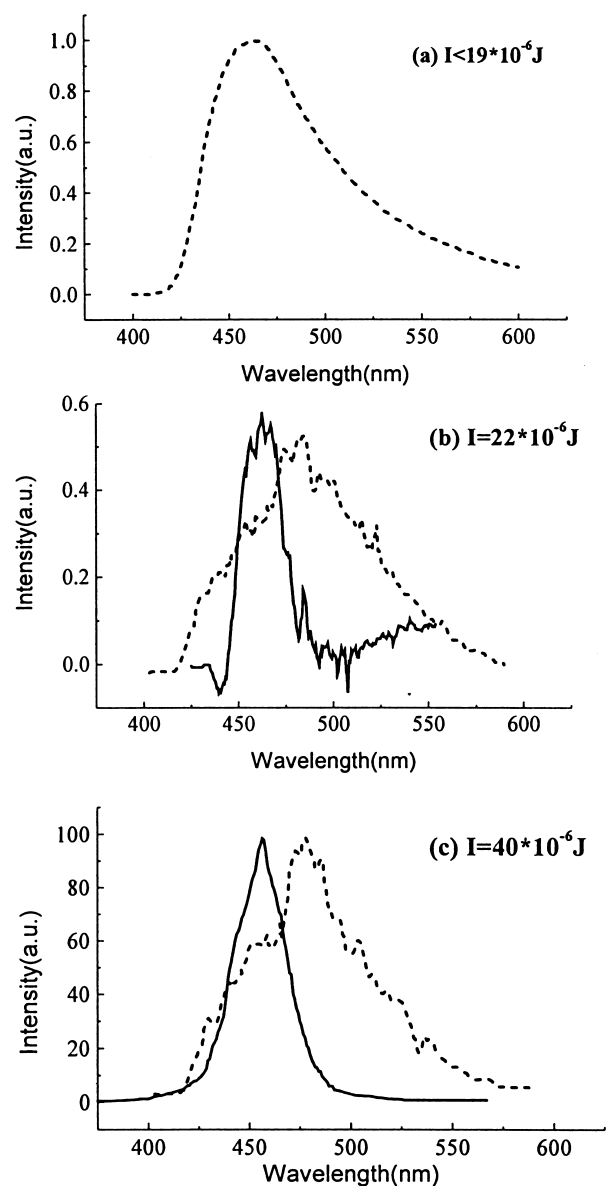


Fig. 2. The ASE (solid line) and spontaneous emission (dash line) spectra of CNMBC-Ph in THF solution under different pump intensities (I): (a) $I < 19$ μJ. (b) $I = 22$ μJ. (c) $I = 40$ μJ.
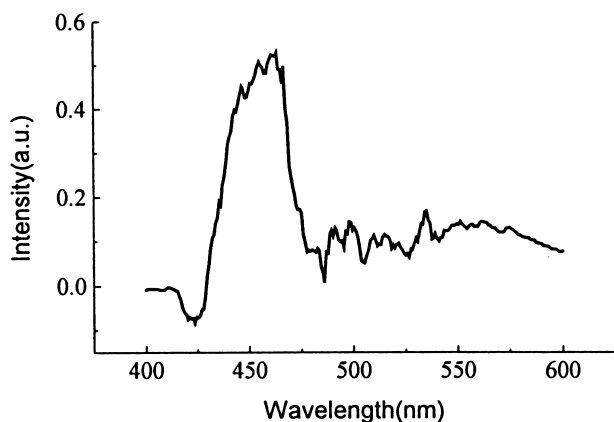
Fig. 3. Difference Spectrum obtained from spontaneous emission spectrum under 19 μJ minus that under 40 μJ.

pulse energy measured from the stripe ends as a function of the pump pulse energy exhibits that the output energy of the ASE is saturated when the pump energy is over 340 μJ. Therefore, the pump energy used to get spectra in Fig. 2c is in the range of small-signal gain; and hence the power broadening linewidth can be neglected. Because the stripe size is constant in the experiment, the spatial broadening also can be neglected. Therefore, the above results demonstrate that the spectral broadening may mainly originate from inhomogeneous one, and that CNMBC-Ph solution is a kind of inhomogeneous broadened laser medium [19–27].

In the case of conventional small molecules laser dyes, each molecule often has only one chromophore. In general, they do not aggregate into oligomer in usually used concentrations of $10^{-3}$–$10^{-5}$ M. In that case, every molecule has a uniform environment, therefore, their spectral broadening mainly originate from homogeneous broadening. As for CNMBC-Ph, its molecular chain is not an absolutely rigid structure; hence, the CNMBC-Ph molecule may not maintain its perfect configuration of an one-dimensional periodic structure whet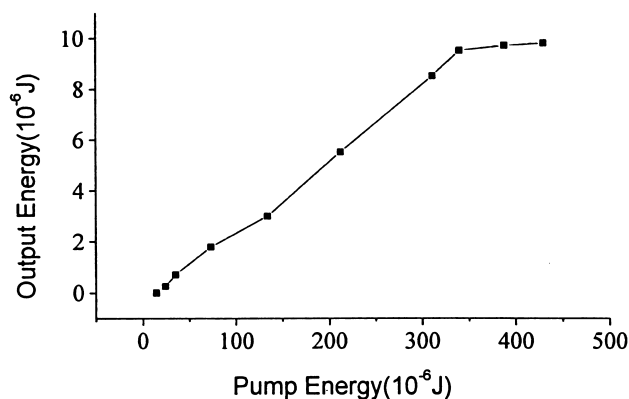her in solution or in film. The imperfect configuration may lead to intrachain chromophores with different environments. Furthermore, disordered distribution of CNMBC-Ph molecules in solution may also bring about the defect concentration of the chromophores in the sample that stems from the interaction among the polymer molecules. The imperfect distribution of the chromophores in the sample which is analogous to the lattice defects would give rise to the inhomogeneous broadening of the ASE spectrum of CNMBC-Ph solution.

In general, single-longitudinal-mode operation is seldom achieved with inhomogeneous broadened gain media. However, because conjugated polymers are high gain active media, it is easy to realize both multi-mode oscillation and single-mode oscillation when suitable polymer laser cavity configurations are employed. In addition, the conjugated polymers have small spontaneous emission lifetimes, typically in a range from sub-nanosecond to a few nanosecond, therefore, their upper laser levels decay quickly, and pump source must have fast-rising and high-intensity output in order to produce a substantial population inversion. This feature of conjugated polymers may be a crucial obstacle to using when conjugated polymers in fabricating electrically pumped laser.



Fig. 4. The ASE output energy vs. pump energy.

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