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Laser emission from a solid conjugated polymer: Gain, tunability, and coherence

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Over the last few years, there has been a considerable effort to achieve lasing from solid-state conjugated polymers. Here, we present measurements on tunable laser emission from an optically pumped solid-state π-conjugated polymer blend system placed into an external cavity. We measured the threshold characteristics, the tunability range, and the coherence properties of the laser. By means of femtosecond pump-probe spectroscopy we recorded the gain spectra of the material and investigated their intensity dependence and temporal evolution. Our measurements allow us to shed light on the fundamental question of the gain mechanism in this class of materials. [S0163-1829(98)50308-6]

Photonics as an analog to electronics describes a technology in which photons instead of electrons are used to store, transmit, and process information. It has been labeled as a key technology of the 21st century.[1] Electro-optics of semiconductors and organic materials is an emerging multidisciplinary field and plays a major role in photonics. Organic materials are currently at the forefront of intense research in nonlinear optics because of their relatively large nonresonant optical nonlinearity. Conjugated polymers comprise an important material system, combining the structural and mechanical properties of polymers with optoelectronic properties commonly associated with inorganic semiconductors.[1–4] The lower fabrication costs and ease of processing polymers compared with conventional semiconductors have led to an inclusion of these materials in hybrid optoelectronic devices. Following the discovery of electroluminescence in conjugated polymers[5] a new field has opened up in which considerable attention has been given to the photophysical and electro-optical properties of these materials due to their potential application in light-emitting devices.[6–9] An important recent development was the observation of laserlike emission from a poly(p-phenylenevinylene) (PPV) layer incorporated in an optical microcavity.[10] Stimulated emission from a variety of PPV derivatives and gain narrowing after photopumping above a certain threshold have also been demonstrated.[11–14] Only very recently, tunable laser emission from an alternating block copolymer blend has been reported.[15] However, it is not yet clear if similar results can be obtained by injecting electrons and holes in a diode structure containing a neat polymer film, because (i) intrachain excitons that act as the emissive species are quenched in the vicinity of metal electrodes, (ii) nonemissive excitations like, e.g., triplet states are mainly excited, (iii) the current densities necessary to obtain a population inversion might be in the order of the damage threshold of these materials, and (iv) the trap density is usually higher in neat films compared to blend systems.

Compared to conventional laser materials, conjugated polymers offer important advantages. Static disorder, which is inherent in these materials, leads to a distribution of conjugation lengths. This again results in an inhomogeneously broadened density of localized states (DOS). After photoexcitation, the primarily generated excitations (intrachain singlet excitons) undergo a random walk within the inhomogeneously broadened DOS and relax towards energetically lower lying sites.[16] This ultrafast energy relaxation together with the strong electron-vibron coupling in these materials leads to a relatively large spectral shift between absorption and emission.[17,18] Hence, there is only a small spectral overlap between absorption and emission and reabsorption of the luminescence, which would pose an obstacle on using this class of materials as active laser media, and can be excluded for the largest part of the emission. Moreover, the inhomogeneous broadening and the strong electron-vibron coupling lead to a spectrally broad net gain that allows wavelength tuning of the laser emission. Additionally, only small concentration quenching, large absorption coefficients, and large cross sections for stimulated emission are observed.[19] Interchain transfer of excitations into nonradiative decay channels can be minimized by blending the optically active phenyl-substituted poly-(p-phenylenevinylene) into an inert matrix polymer.[20] The formation of interchain excitons, which would quench stimulated emission, can also be reduced by excitation into the low-energy tail of the DOS.[21,22]

Here, we report on a polymer gain material that is diluted in an inert matrix in order to study the intrinsic optical properties not masked by, e.g., fast energy transfer into defect states. The π-conjugated polymer we examined is a phenyl-substituted poly-(p-phenylenevinylene) (PPPV), synthesized via Heck reaction. PPPV was blended into a polymethylmetacrylat (PMMA) matrix in a ratio of 0.1% by weight. The refractive index of PMMA is 1.49. For the laser experiments we used a block of the polymer blend system with a thickness of 3 mm and length of 12 mm. The end faces are polished.

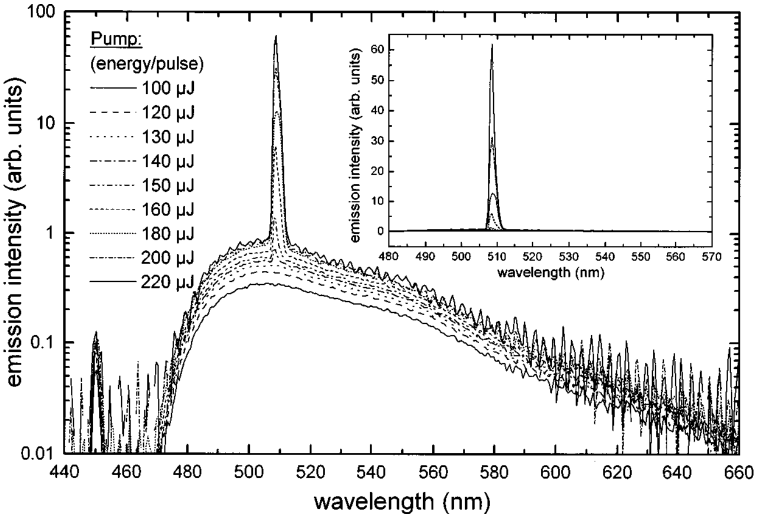

FIG. 1. Emission spectrum of the PPPV/PMMA laser depending on the pump-pulse energy (the peak at 450 nm is due to scattered pump light); the inset shows the same spectra on a linear scale.

The sample was placed into a conventional pulsed dye-laser resonator in Hänsch configuration suitable for transverse pumping. The sample was fixed under an angle of 87° with respect to the resonator axis in order to avoid backreflection. The resonator consists of a holographic grating (2400 lines/mm and $\simeq 60\%$ efficiency) in Littrow configuration acting as a high reflector and a dielectric mirror with a reflectivity of 20% as output coupler. The cavity length is about 4.5 cm, which results in approximately 30 round-trips during a pump pulse.

As a pump source we used an excimer pumped dye laser. The pump pulses had a temporal width of about 10 ns at a rate of 10 Hz and pulse energies in the range from 100 to 250 μJ at a wavelength of 450 nm. The absorption depth of the sample at 450 nm is about 0.2 mm. The pump beam was focused onto the sample with a cylindrical lens ($f = 25$ mm) resulting in a total energy density of 32 to 81 mJ/cm^2 per 10-ns pump pulse. Taking into account that the lifetime of the excited states in our material is about 770 ps, the effective energy density is lower by a factor of at least 13. Furthermore, lifetime shortening due to the stimulated emission process will reduce the effective energy density even further.

Emission from the polymer laser was spectrally resolved with a 0.27 m monochromator and detected with a liquid nitrogen cooled optical multichannel analyzer system. All laser measurements were performed at room temperature under standard atmosphere. Under these conditions and at pump-pulse energies of 230 μJ, the operating lifetime of the laser, measured as the time at which the output power dropped to 50% of its initial value, was about 6 min corresponding to 4000 pulses.

The evolution of the emission spectra as a function of pump energy per pulse is shown in Fig. 1. At low pump energies the emission intensity depends linearly on the pump energy and no spectral changes are observed. The shape of the spectra resemble the photoluminescence (PL) spectrum, except for the high-energy part, which is suppressed by reabsorption effects due to the transverse pumping configuration. However, upon increasing the pump energy above a certain threshold of 150 μJ per pulse a narrow peak emerges out of the inhomogeneously broadened emission spectrum. The peak intensity rises nonlinearly with the pump energy (Fig. 2), reaching a maximum two orders of magnitude above the maximum intensity of the PL-like broad emission spectrum. Simultaneously, a dramatic drop of the spectral linewidth occurs: The linewidth drops from $\Delta\lambda \approx 70$ nm (for the PL-like emission) down to $\Delta\lambda = 0.55$ nm (Fig. 2), which is close to the minimum linewidth $\Delta\lambda = 0.3$ nm determined by the cavity properties. The threshold behavior of the output intensity accompanied with the emission narrowing is one characteristic indication for lasing. A photograph of the PPPV/PMMA laser in operation is shown in Fig. 3(a).

While the emission of our device is isotropic below the

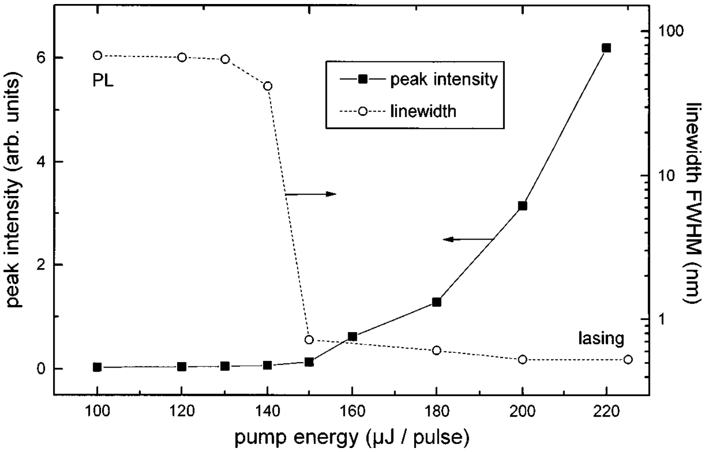

FIG. 2. Peak intensity of the emission spectra (at 508.5 nm) and spectral linewidth of the emission (full width at half maximum, FWHM) depending on the pump-pulse energy.

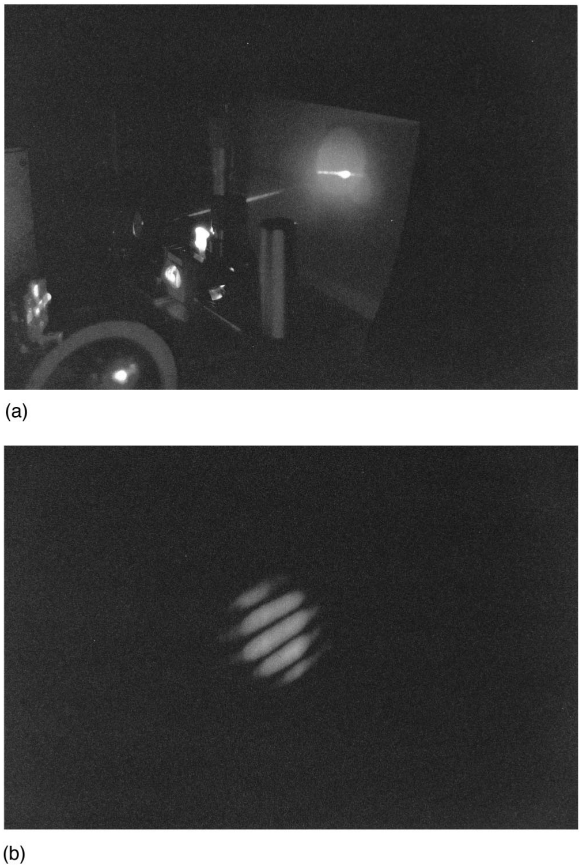

FIG. 3. (a) Photograph of the PPPV/PMMA laser in operation; (b) photograph of the interference fringes observed after guiding the emission beam through a Michelson interferometer.

threshold, a highly collimated beam is emitted above the threshold. The beam divergence angle is $\theta \approx 5$ mrad (0.3°). Light scattered from a surface shows speckles, pointing to a high degree of coherence. The bright and dark areas observed at the surface are associated with constructive and destructive interference of the light scattered at the irregularities of the surface, respectively. This speckle pattern is a consequence of the coherence of the laser emission. The temporal coherence is measured with a Michelson-interferometer setup. The incident beam is split by a 50:50 beam splitter and then directed into the two arms of the interferometer. Coherent superposition of the two light fields on an observation screen leads to constructive and destructive interference, resulting in a fringe pattern as shown in the photograph [Fig. 3(b)]. The visibility of these fringes can be taken as a criterion for the coherence of the two beams. Hence, varying the length of one arm of the interferometer leads to a direct measurement of the coherence length l_{coh}. We measured a coherence length of $l_{\mathrm{coh}} = 500$ μm corresponding to a coherence time of about $\tau_{\mathrm{coh}} = l_{\mathrm{coh}}/c = 1.7$ ps. This rather short duration is probably limited by scattering at sample inhomogeneities. Lifetime shortening due to the stimulated emission and/or dephasing effects might contribute as well.

Upon pumping the polymer laser with pump-pulse energies of 270 μJ we obtained output pulse energies of 4.8 μJ at an emission wavelength of 508 nm. This corresponds to a quantum efficiency for the lasing process of $Q_{\mathrm{Las}} \approx 2\%$. Pumping even higher above the threshold, we obtained output energies up to 6 μJ per pulse.

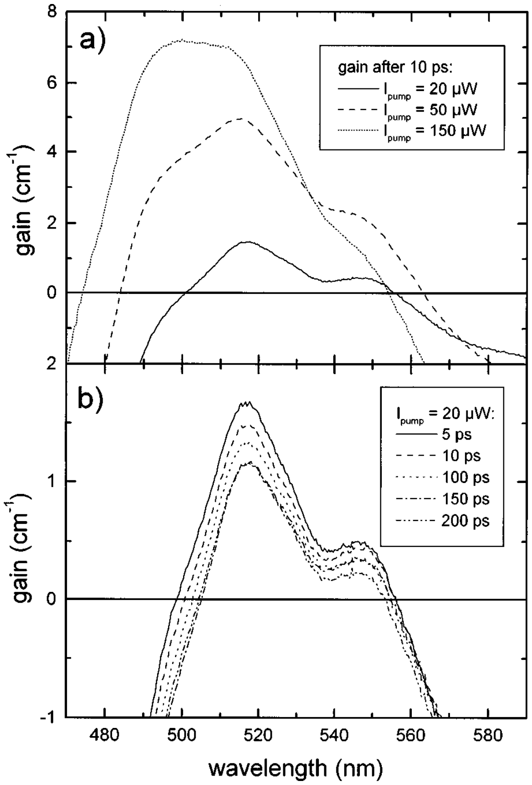

FIG. 4. (a) Gain spectra 10 ps after excitation for three different pump intensities; (b) gain spectra at different time delays after excitation with a pump intensity of 20 μW.

In addition to measuring the emission from the polymer laser, we performed pump-probe measurements in order to record time-resolved gain spectra of the polymer blend system. In these experiments the sample was a freestanding film with a thickness of about $L = 180$ μm. The sample was kept under vacuum to minimize photo-oxidation. It was excited with frequency-doubled pulses from a Ti:Sapphire regenerative amplifier system. The pump pulses had a temporal width of 200 fs at a 1 kHz repetition rate and pulse energies between 20 and 150 nJ at a wavelength of 400 nm. A white-light continuum, generated by focusing a small fraction of the amplifier output onto a sapphire crystal, was used to detect the photoinduced absorption change $-\Delta \alpha L$ in the sample. Gain spectra were obtained as the difference between the absorption change $-\Delta \alpha L$ and the linear absorption αL, normalized to the sample thickness L.

Figure 4(a) shows the net gain 10 ps after the pump pulse for three different pump intensities. Raising the pump energy per pulse from slightly above the threshold to pulse energies far above the threshold results in both a strong increase and a spectral broadening of the gain. However, for higher pump energies a photoinduced absorption band competes with the low-energy part of the optical gain, leading to the observed change in the intensity distribution of the gain spectrum. The spectral region of the net gain determines the tunability region of the laser. In our setup, tunability is accomplished by a grating in Littrow configuration acting as a high reflector. As shown in Fig. 5(a), the laser emission can be tuned over the gain region. The observed emission intensities for a constant pump-pulse energy follow the gain spectrum. The largest tunability range we observe for the PPPV/PMMA poly-

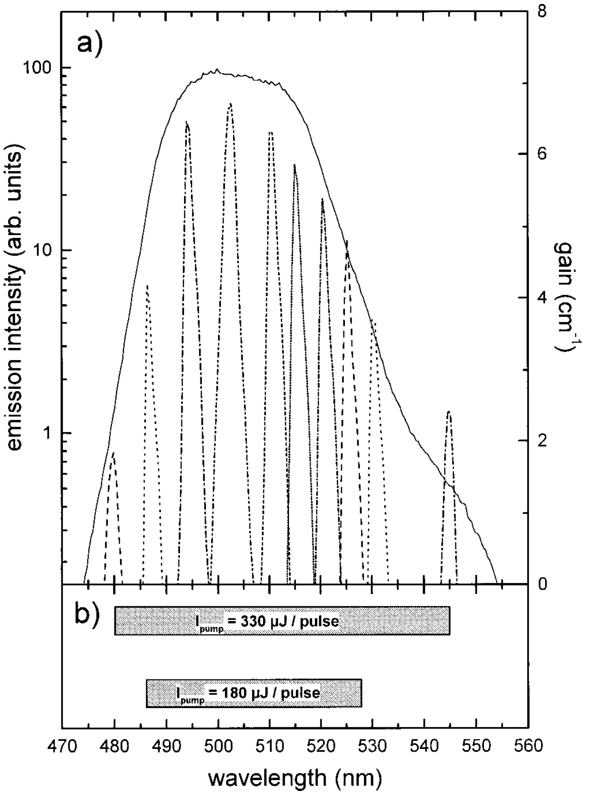

FIG. 5. (a) Laser emission spectra (dotted lines) tuned over the whole tunability range; a gain spectrum (10 ps after excitation with a pump intensity of 150 μW, solid line) is shown for comparison; (b) tunability range of the laser for two different pump-pulse energies.

mer blend is about 65 nm as shown in Fig. 5(b). This is about a factor of 2 larger than the value reported in Ref. 15.

The temporal evolution of the optical gain can be seen in Fig. 4(b). For up to 200 ps, which is the limit of our experimental setup, significant gain is observed: about 70% of its initial value is retained. This corresponds to a decay time of about 750 ps, which agrees reasonably well with the PL lifetime of about 770 ps measured with a streak-camera setup. This indicates that trapping of the primarily generated excitons, which are the emitting species, into nonradiative decay channels is suppressed and results in a high PL quantum efficiency Q_{PL}. Taking into account the intrinsic lifetime $\tau_0 \simeq 1$ ns and using the quantum efficiency relation for radiative transition we end up with $Q_{\mathrm{PL}} = 80\%$, which is one of the highest values reported for conjugated polymers so far.

The gain spectra that are due to stimulated emission are very similar to the steady-state photoluminescence spectrum supporting the assignment of the gain to excitonic optical transitions. The gain spectra show vibronic replicas identical to those observed in the photoluminescence. Typical vibronic energies are around 190 meV. Following the molecular approach[17] in which a conjugated polymer is treated as an array of localized subunits separated by topological faults arising from the inherently present disorder in noncrystalline polymers, the gain mechanism can be explained in the following way: After optical pumping from the ground state ($S_{0,0}$) to an excited Franck-Condon state ($S_{1,\mathrm{vib}}$) an ultrafast vibrational cooling to the pure electronic excited state ($S_{1,0}$) takes place. Due to this ultrafast cooling process, the vibrational sublevels of both the excited state and the ground state are populated according to the Boltzmann distribution. Hence, there is a population inversion between the pure electronic excited state ($S_{1,0}$) and the vibronic sublevels of the ground state ($S_{0,\mathrm{vib}}$). Emission (stimulated or spontaneous) is from $S_{1,0}$ into the nonpopulated $S_{0,\mathrm{vib}}$ states, followed by a second thermalization process into the $S_{0,0}$ state. Despite the perturbing optical transitions, these ultrafast thermalization processes allow the pumped conjugated polymer to exhibit gain and operate as a laser medium.

In conclusion, we have demonstrated tunable laser emission from a solid conjugated polymer blend based on PPPV in an external resonator. The output energy of our laser is up to 6 μJ per pulse. The laser is tunable over a spectral range of about 65 nm. Blending the optically active material in an inert matrix results in a negligible transfer of excitons into nonradiative decay channels. From our measurements we conclude that the PPPV/PMMA blend system is an excellent material for solid-state polymer lasers.

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