Lasing and Stimulated Emission in π-Conjugated Polymers

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Invited Paper

***Abstract*—Recent studies of lasing and stimulated emission in luminescent π-conjugated polymers performed by our group are presented. Optical properties of cylindrical high-Q polymer microcavities are discussed. The emission spectra of plastic microring and microdisk lasers are measured and analyzed. Light-emitting polymer microdiodes are demonstrated as possible candidates for electrically driven plastic lasers. In addition, two unusual regimes of stimulated emission characterized by narrow laser-like spectral lines are demonstrated in thin waveguiding polymer films. These regimes may be associated with random optical feedback introduced by light scattering inside the polymer films and amplified Raman scattering, respectively.**

***Index Terms*—Microcavities, polymer lasers, stimulated emission.**

I. Introduction

THE FIELD OF π-conjugated polymers, or conducting polymers, has soared with diverse applications during the last two decades. When it was realized that these polymers can be efficiently doped with both n- and p-type ions, then applications such as metal shielding were envisioned. Later on, when the doping proved to be reversible, rechargeable batteries were sought. π-conjugated polymers in their neutral or undoped state became interesting when it was realized that they possess large, resonant, third-order optical nonlinear coefficients; this discovery led to potential applications, such as fast optical switches, modulators, and logic computer elements. When intense photoluminescence (PL) was found in poly (p-phenylene vinylene) (PPV), new polymer applications appeared such as light-emitting diodes (LED's) and other large-area display elements. The latest application sought to be realized using π-conjugated polymers is lasers [1], [2].

Photopumped lasers based on polymers in solutions were already demonstrated in 1992 [3]. It was assumed that PL quenching, typically observed in laser dyes, would prevent the realization of population inversion in solid polymer films. However, during the International Conference on Synthetic Metals'96 (ICSM'96) meeting in Utah, researchers in the field of conducting polymers were surprised to hear that laser action could be achieved even in solid polymer films [4]. Since then, the field has exploded with studies focused on laser action in different polymers [5]–[7] using a variety of optical cavities [8]–[11]. The main goal of these studies is to obtain lasing in organic thin films, in general, and conducting polymers, in particular, by charge injection. This will be quite a coup in the optical industry, since the PL wavelength and, thus, the laser color can be easily tuned in polymers to span the entire visible spectral range. In this paper, we describe our studies aimed toward the realization of this goal.

There are two classes of π-conjugated polymers: luminescent and nonluminescent. The optical properties of the luminescent polymers are very similar to those of regular organic laser dyes, such as rhodamine or coumarin. The primary excitations in these polymers are excitons, which may produce PL with a high quantum yield η, defined as the ratio between the number of emitted photons to the number of absorbed photons. Typically, the radiative decay of excitons has to compete with various channels of nonradiative decay. As a result, η is always less than unity. In our studies, we have focused on two varieties of luminescent conducting polymers with particularly high PL yields, namely dioctyloxy-PPV (DOO-PPV) [12] with $\eta \approx 0.2$ and poly (1-phenyl-2-p-n-butylphenylacetylene) (PDPA-nBu) [13] with $\eta \approx 0.4$. Their backbone structure, optical absorption, and PL spectra are shown in Fig. 1. The Stokes-shifted PL bands, which are broadened by both homogeneous (phonons) and inhomogeneous (disorder) contributions, appear in the spectral range where the ground state absorption is weak. Therefore, a simple exciton model has been adopted to describe the optical transitions responsible for absorption and emission in these polymers, as shown in the configuration coordinate diagram of Fig. 2(a). According to this model, the lowest excitations in π-conjugated polymers form a four-level system, where transitions $1 \rightarrow 2$ and $3 \rightarrow 4$ describe the absorption and emission processes, respectively [12]. The phonon-assisted relaxation transitions $2 \rightarrow 3$ and $4 \rightarrow 1$ are very efficient and occur within 100 fs and 1 ps, respectively. On the other hand, the exciton lifetime, i.e., the decay (mostly nonradiative) time of level 3, is in the range of 100 ps to 1 ns in our polymer films, as illustrated in Fig. 2(b). We conclude that it is possible to achieve population inversion

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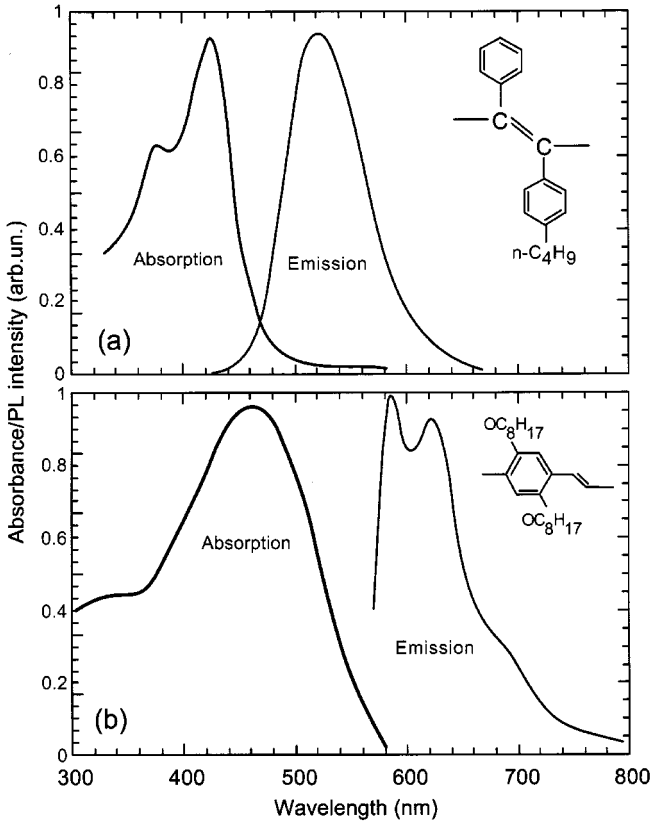

Fig. 1. Absorption and emission spectra of (a) PDPA-nBu and (b) DOO-PPV films. Insets show the corresponding polymer repeat units.

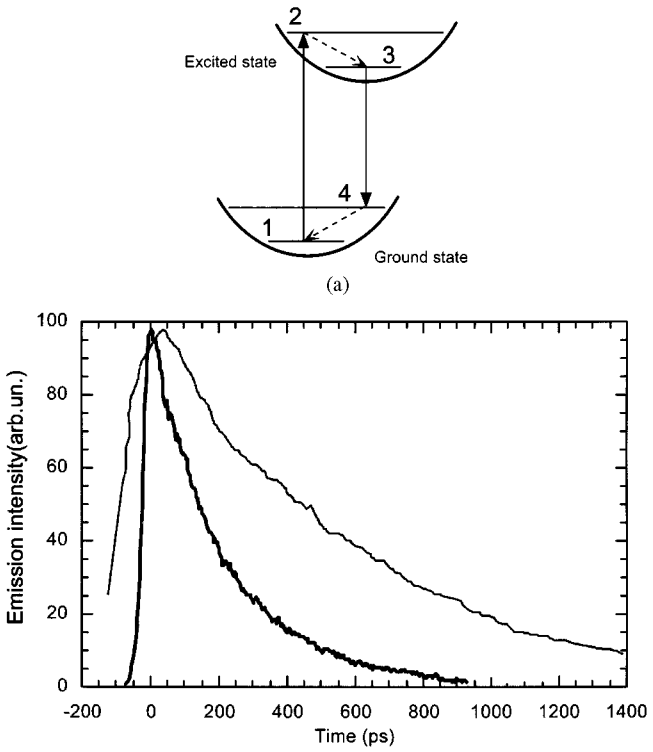

Fig. 2. (a) Configuration coordinate diagram of energy levels (numbered 1 through 4) in luminescent conducting polymers; solid arrows indicate optical transitions corresponding to absorption and emission processes, respectively. (b) Time-resolved PL in DOO-PPV (thick line) and PDPA-nBu (thin line) films.

between levels 3 and 4 and thus satisfy the main requirement for a laser medium.

The polymer residual absorption $\alpha_{\rm res}$ at the optical frequency between levels 3 and 4 determines the threshold excitation density that is necessary for the population inversion and, consequently, lasing [14]. It is preferable, therefore, to have $\alpha_{\rm res}$ as low as possible. However, one of the primary requirements for a polymer laser medium is its high PL yield. It has been noticed that, in general, η is determined not only by the exciton lifetime, but also by the exciton generation yield. The later may also be less than unity due to the formation of interchain excitations [15], [16] and other nonradiative species. It is essential, therefore, for achieving high η to have both long exciton lifetime and low generation yield of nonemissive excitations. The last fundamental condition influencing the performance of a polymer as a laser medium is the spectral extent of the excitonic photoinduced absorption (PA) in photopumped lasers and current induced absorption (IA) of polarons in electrically driven lasers. The PA or IA spectrum may overlap with the spectrum of the stimulated emission and thus cancel the total optical gain. It has been shown that the PA and SE spectra of singlet excitons in DOO-PPV are well separated [12], indicating that this polymer can be a good candidate for photopumped laser media.

II. Lasing

A. Cylindrical Polymer Microlasers

True lasing was first demonstrated in a Fabry–Perot resonator using a dilute solution of MEH-PPV [3], a polymer with optical characteristics similar to those of DOO-PPV. Analogous results were obtained later with solutions of other π-conjugated polymers [17], [18]. Early time-resolved studies have shown that, unlike laser dyes, conducting polymers do not experience concentration quenching and, therefore, may exhibit optical amplification, or gain, even when they are prepared as thin films [19]. However, because the absorption length in neat, undiluted polymer films is much shorter than that in solutions, it is much more difficult to use thin films as gain media in open laser cavities formed with external mirrors [6], [7]. Thus, work in this area has mainly concentrated on microstructures, such as planar [1], [9] and cylindrical microcavities [8], [20], distributed feedback (DFB) lasers [10], [11], and other configurations using thin waveguiding films [21]–[24].

The microring and microdisk structures are schematically shown in Fig. 3. In both cases, a thin, uniform polymer film forms the entire cavity of the laser. The main advantage of such microlasers is the ease with which they can be produced, particularly the microring lasers. Typically, an optical fiber was dipped into a saturated chloroform solution of DOO-PPV or PDPA-nBu, which, after quick evaporation, uniformly coated the fiber and produced a complete cylinder of ~1 μm in thickness, 100 μm or more in length, and a diameter D predetermined by the size of the fiber. Alternatively, any other cylindrical substrate could be used with equal success, e.g., lasing was demonstrated using metal wires and also polyaniline fibers [25], [26]. The fabrication of microdisks was slightly more difficult: thin spin coated films were photolithographically etched to produced microdisk arrays of various diameters [27]. The substrate was

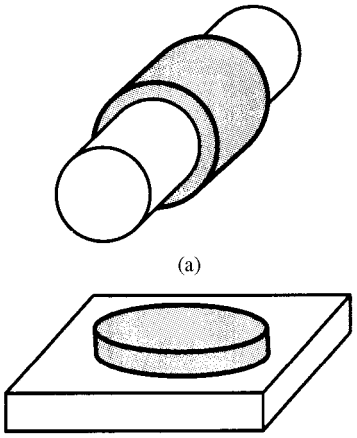

Fig. 3. Plastic cylindrical microcavities. (a) Microring. (b) Microdisk.

usually either quartz or indium tin oxide (ITO) coated glass. The full description of microlaser fabrication and the experimental setup is given elsewhere [26], [27].

An important advantage of a cylindrical microcavity is its relatively high finesse, or quality factor Q. The light in such cavities is confined inside the gain medium by total internal, practically lossless reflections [28]; the radiation leakage is due to the cavity surface curvature and light scattering from imperfections. In comparison, a planar microcavity always experiences losses due to imperfect reflections from the two highly reflective mirrors forming the microcavity [1], [9]. Optical modes inside a cylinder are given by the solution of the two-dimensional (2-D) Helmholtz equation [29]

$$\left(\nabla^2 + n_{\text{eff}}^2 \omega^2 / c^2\right) \psi = 0 \tag{1}$$

where

- n_{eff} effective refractive index describing propagation of a mode in the plane of the cylinder;
- ω optical radial frequency;
- c speed of light in vacuum;
- ψ magnetic (electric) field along the cylinder axis of a transverse electric (magnetic) TE (TM) mode.

The boundary conditions can be approximated by setting $\psi = 0$ at the edge of the cylinder [29]. The solutions of (1) are given by

$$\psi = J_M \left(n_{\text{eff}} \omega_{M,N} \cdot r/c\right) e^{iM\theta} \tag{2}$$

where

- J_M Bessel function of the first kind;
- r, θ radial and angular cylindrical coordinates, respectively;
- M mode order;
- N mode radial number.

In (2), the $\omega_{M,N}$ are given by the solution of the following equation:

$$J_M \left(n_{\text{eff}} \omega_{M,N} \cdot R/c\right) = 0 \tag{3}$$

where R is the radius of the ring or disk.

Equation (3) can be used only as an approximation to describe the modes of the polymer microring and microdisk lasers. First, these microcavities are not perfect cylinders; therefore, it is important to include waveguiding effects, which can be achieved by using n_{eff} as an effective refractive index of the polymer waveguide. Second, a physically meaningful solution of (1) should have a nonzero magnitude at the boundary, i.e., $\psi(R) \neq 0$; it is expected, however, that $\psi(R) \approx 0$ for large M. The solution of (1) with nonzero boundary conditions has been given elsewhere [30], [31].

The cavity Q factor can be generally defined as $Q = \omega t_c$, where t_c is the decay lifetime of a cavity mode [32]; thus, the longer the photon lifetime is inside the cavity, the higher Q is. The value of Q may be influenced by various contributions, and, near the laser threshold, it is given by [29]

$$Q^{-1} = Q_{\text{cav}}^{-1} + Q_{\text{scat}}^{-1} + Q_{\text{abs}}^{-1}. \tag{4}$$

Q_{cav}^{-1} describes radiation losses determined by the cavity geometry for a given mode, Q_{scat}^{-1} is due to scattering from imperfections inside and on the surface of the cavity, and Q_{abs}^{-1} is determined by the self-absorption of a cold gain medium and is defined as $Q_{\text{abs}} = 2\pi n/\alpha_{\text{res}}\lambda$, where n is the refractive index and α_{res} is the absorption coefficient at the emission wavelength λ. Q_{cav} is known to strongly depend on M and N [33]. It is maximized for $N = 1$ and the corresponding modes are called whispering gallery modes, for which, at $M > 20$, we find that $Q_{\text{cav}} > 10^4$ [29]. In our measurements of both microring and microdisk lasers made from pristine polymer films, we have found that typical Q values are of the order of $3 \cdot 10^3$ [20], [25]. We have concluded that, despite rather high Q_{cav} values, the Q of a polymer microcavity is usually limited by scattering losses and material absorption, Q_{scat}^{-1} and Q_{abs}^{-1}, respectively. Q_{scat}^{-1} can be somewhat minimized by making smoother microcavity surfaces and purifying the polymer solution. Q_{abs}, on the other hand, is determined by α_{res} and thus is difficult to change. However, it is possible to dilute the polymer by mixing it with other less lossy and optically neutral media, which may lower α_{res} and, therefore, increase Q_{abs}. This has been successfully demonstrated with various blends of organic dyes, oligomers [34]–[37], and polymers [5], [6].

B. Experimental Results

The microring polymer lasers on optical fibers were photoexcited from one side by 100-ps-long pulses at 532 nm (for DOO-PPV) or 355 nm (for PDPA) produced by a Nd : YAG laser amplifier at repetition rates of 0.1–1 kHz [20], [26]. The microring emission was collected by a lens from the other side of the ring and analyzed using a triple spectrometer with a spectral resolution of ~0.1 nm. The spectra were recorded using a cooled charge coupled device (CCD) array detector. The excitation area (~50 μm) was smaller than the lateral size of the cylinder microring; therefore, the ring cavity did not provide any lateral confinement (along the cylinder axis) for the laser modes. However, due to high intrinsic losses in the polymer film, the modes were gain-guided and thus well confined to the portion of the microring containing the photoexcited area. We further ignore any complications (e.g., mode distortions) that could arise from one-sided asymmetrical excitation of these microcavities.

Fig. 4(a) shows the emission spectra obtained from a PDPA-nBu microring deposited on a fiber with $D = 125$ μm. The broad, featureless PL band at low excitation intensities I is

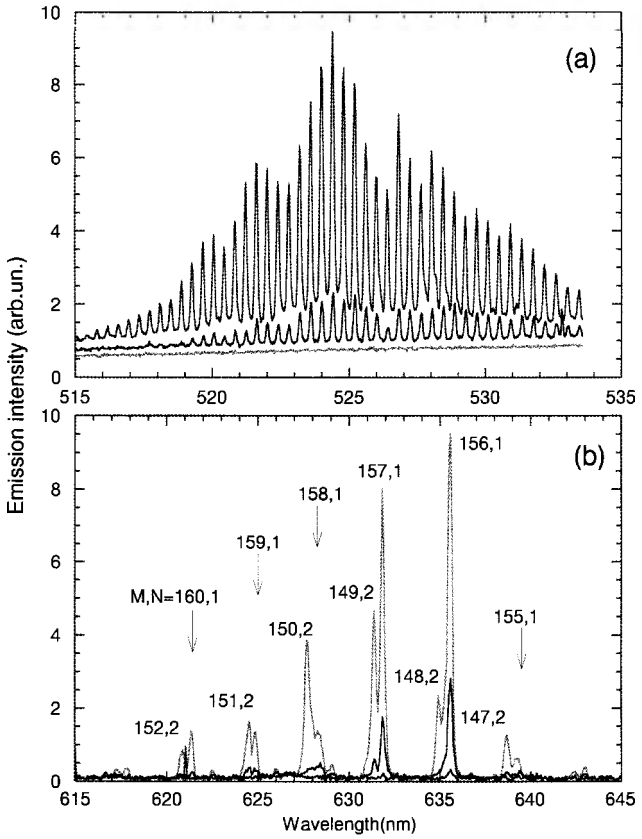

Fig. 4. (a) Emission spectra from a PDPA-nBu microring on a $\varnothing 125$-μm optical fiber at different excitation intensities; excitation energies from top to bottom are 1, 0.7, and 0.6 μJ, respectively. (b) Emission spectra from a DOO-PPV microring on a $\varnothing 20$-μm fiber; excitation energies are 165, 90, and 65 nJ, respectively. M and N indices are assigned to each laser line (see text).

transformed into a multimode ring laser spectrum at higher I. This transition into the lasing regime is accompanied by a kink in the emission intensity versus I dependence at the threshold excitation intensity I_o [20], [25]. The wavelength of each laser mode $\lambda_{M,N}$ is given by the solution of (3), which can be equivalently rewritten as $n_{\text{eff}}\omega_{M,N}R/c = X_{M,N}$, where $X_{M,N}$ are the zeros of the Bessel function. The latter may be further simplified for $N = 1$ by substituting $X_{M,1} \approx M$ (for large M) as follows:

$$M\lambda_M = 2\pi R n_{\text{eff}}. \tag{5}$$

Equation (5), in fact, describes the longitudinal modes of a ring resonator formed by the thin polymer waveguide with the total length of $2\pi R$. TE modes (polarization is in the plane of the waveguide and parallel to the fiber axis) with $N = 1$ have the highest Q and thus the lowest I_o. These modes may dominate the spectrum of the microring laser for very thin polymer films, which can be seen in Fig. 4(a) (see also [20]). From (5), we obtain an expression for the intermodal separation $\Delta\lambda = \lambda_{M-1} - \lambda_M$ as

$$\Delta\lambda = \frac{\lambda^2}{2\pi R n_{\text{eff}}}\left(1 - \lambda\frac{\partial n_{\text{eff}}}{\partial\lambda}\right)^{-1}. \tag{6}$$

Assuming negligible dispersion, from Fig. 4(a) we find that, for PDPA-nBu films, $n_{\text{eff}} \approx 1.75$. We note that the spectrum in Fig. 4(a) may be used to determine $\partial n_{\text{eff}}/\partial\lambda$, if n_{eff} can be measured independently.

Fig. 4(b) shows the emission spectra of a DOO-PPV microring laser with $D = 20$ μm. These spectra cannot be adequately described by (5), since more than one set of longitudinal modes is observed. However, it is possible to model them using (3) for the two lowest order TE modes with $N = 1$ and $N = 2$ (TM modes were not observed in thin microrings). As a result of such modeling, M and N indexing numbers can be assigned to each laser line, as shown in Fig. 4(b). The only fitting parameter is n_{eff}, which we find (assuming near zero dispersion) to be 1.68 and 1.677 for $N = 1$ and $N = 2$, respectively. Higher order waveguided modes (with $N = 2$) are expected to have lower n_{eff} values due to their deeper penetration inside the glass fiber.

In order to avoid light propagation inside the optical fiber, we used thin metal wires as a cylindrical core for the microring [25]. Although an absorptive metal surface may quench stimulated emission and prevent lasing, a thicker (>5 μm) polymer film helps to isolate the modes from the metal core and thus minimize optical losses [25], [26]. Fig. 5(a) shows the emission spectra obtained from a DOO-PPV microring ($D = 35$ μm) deposited on a $\varnothing 25$-μm aluminum wire. At low excitation intensities, the spectrum is dominated by a single set of equidistant longitudinal modes; however, it can be seen from Fig. 5(a) that, at higher intensities, additional modes with a higher threshold appear in the emission spectrum. Assuming negligible dispersion, from $\Delta\lambda$ of Fig. 5(a) we calculate that $n_{\text{eff}} = 2.23$, which is significantly higher than the value estimated from Fig. 4(b), where $n_{\text{eff}} \approx 1.7$. Lower n_{eff} for the thinner microrings on glass fibers indicates that the lasing modes in the these cavities are not confined to the polymer film, but also partly propagate inside the glass core, where the refractive index is low (~1.4). The modes in thick microrings, however, are fully contained inside the polymer and therefore have higher n_{eff}.

We found that polymer microdisk lasers behave similarly to thick microring lasers. Typically, a single microdisk with a diameter ranging from 8 to 128 μm was photoexcited by a focused laser beam from the Nd : YAG laser amplifier, producing 100-ps or 10-ns pulses at 532 nm. The polymer emission was collected in the plane of the microdisk using the same experimental setup used for the microring laser measurements. Unlike microrings, however, microdisks provide good lateral confinement for the lasing modes. In addition, it is easy to achieve a complete and uniform excitation of the whole microdisk area. The mode structure of the disk microcavity is also described by (3). In fact, the spectra of the microdisk lasers are virtually indistinguishable from those of microrings, as shown in Fig. 5(b). Using (6) and again assuming zero dispersion for the DOO-PPV microdisk laser shown in Fig. 5(b) with $D = 16$ μm, we calculate $n_{\text{eff}} = 2.22$, which is close to the value of n_{eff} obtained for thick DOO-PPV microrings deposited on metal wires.

The emission spectra of polymer microlasers shown in Figs. 4 and 5 were obtained using 100-ps pulse excitation. Although the duration of such excitation is much longer than the photon lifetime in the microcavity ($t_c = Q/\omega \sim 1$ ps), it is of the order of the exciton lifetime in the polymer film and therefore may not be considered quasi-continuous [37]. We studied the effects of longer pulse excitation and found that the 10-ns exci-

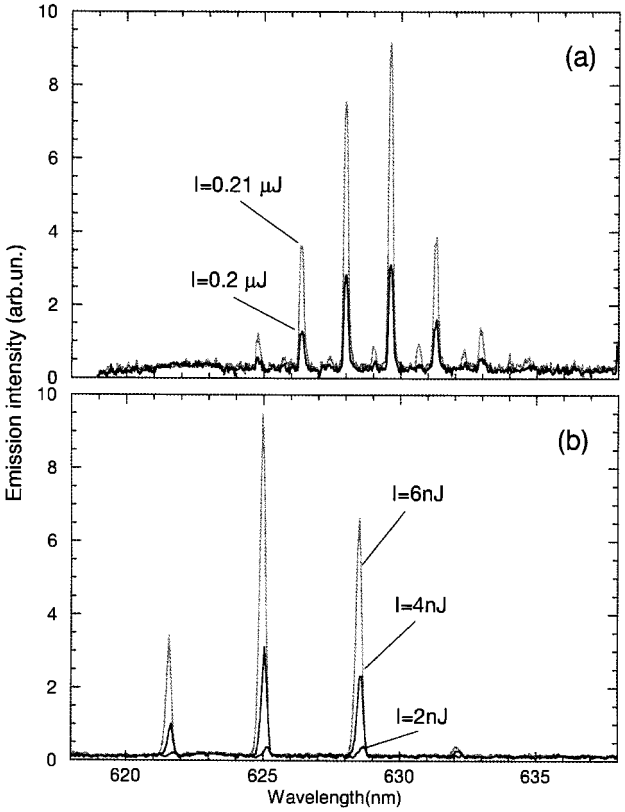

Fig. 5. (a) Emission spectra from a DOO-PPV microdisk with $D = 35$ μm on a ∅25-μm Al wire at two different excitation intensities. (b) Emission spectra from a thin DOO-PPV microdisk with $D = 16$ μm at three different excitation intensities as indicated.

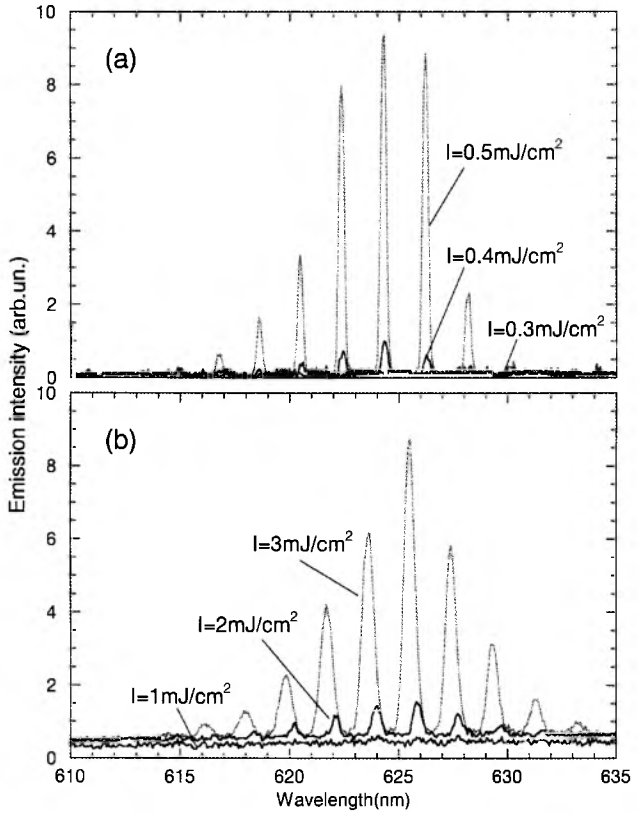

Fig. 6. Emission spectra of a DOO-PPV microdisk with $D = 32$ μm at different excitation intensities using (a) 100-ps pulse excitation and (b) 10-ns pulse excitation.

tation also resulted in efficient lasing. In Fig. 6, we compare the emission spectra obtained from a single DOO-PPV microdisk ($D = 32$ μm) using (a) 100-ps pulses and (b) 10-ns pulses. The mode structures in both cases are essentially identical. The main difference is the pronounced broadening and blue-shift of the laser lines in the case of 10-ns excitation. The blue-shift may still be observed with 100-ps pulses. Both of these effects are highly detrimental to the performance of any laser. The apparent explanation might be excessive heating of the polymer film, since most of the excitation energy is, after all, spent on heating of the polymer film and the longer pulse excitation does provide more energy. The spectral blue-shift (decrease of λ_M), however, indicates that either D or n_{eff} decrease as I increases, and this cannot be explained by an increase in temperature. We thus speculate that the blue-shift is caused by lowering of the polymer refractive index at high excitation densities. Also, the substantial line broadening in the case of long pulse excitation can be attributed to the reduction of the Q factor, which may be due to either microcavity deformations caused by overheating or additional absorption losses from triplet exciton population build-up.

C. Micro-LED's with Cylindrical Geometry

Our group has been engaged in studying micro-LED's with cylindrical geometry [27], [38]. As pointed out above, microlasers with cylindrical geometry may have a high Q value that is limited only by α_{res} of the gain medium. We have therefore fabricated a variety of cylindrical micro-LED's and studied their properties at low current densities with the aim of achieving laser action when using current injection at a much higher density in a pulsed current regime.

Two kinds of cylindrical micro-LED devices were studied: microdisks and microrings, as shown in Fig. 7(a). For microdisks, we deposited DOO-PPV or PDPA-nBu thin films on good quality ITO substrates for hole injection. The film was then capped with an Al metal layer for electron injection, followed by etching of both polymer and Al layers to produce patterned microdisks of various diameters. For microrings, we coated ITO on optical fibers of various diameters, which were drawn out from commercial multimode silica fibers. ITO layers with a typical thickness of 200 nm and sheet resistance of 10 Ω/□ were prepared by an electron beam evaporation process. Thin polymer films with an estimated thickness of 1 μm were then deposited onto the ITO coated fibers by dipping the fibers into saturated toluene solutions of DOO-PPV. Afterwards, a semitransparent Al layer was deposited in high vacuum of 10^{-4} Pa. The length of the Al electrode was about 2 mm.

The electrical properties of the polymer LED's, such as current–voltage (I–V) characteristics, were measured using Keithley 236 source measuring unit connected to a PC. The emission intensity in the forward biasing mode was detected using a photomultiplier. The emission spectrum was measured

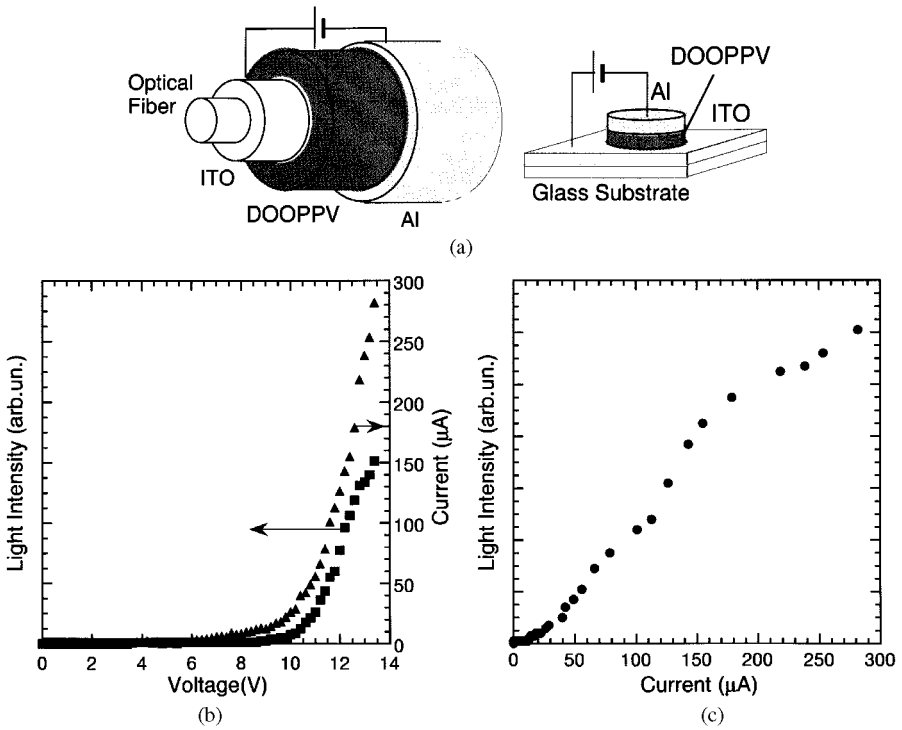

Fig. 7. (a) Microring and microdisk LED devices. (b) Emission–voltage and current–voltage characteristics of a ∅125-μm microring LED with DOO-PPV polymer. (c) Emission–current characteristic of the microring LED.

using a triple spectrometer and an optical multichannel detection system with a liquid nitrogen cooled charge coupled device with ~0.3-m resolution.

Typical I–V and voltage-emission intensity (V–L) characteristics at forward biasing of a ∅125–μm microring LED with DOO-PPV polymer are shown in Fig. 7(b). The LED's exhibited typical rectifying characteristics, in which the ITO and Al layers act as hole and electron injecting electrodes, respectively. The emission onset is seen to occur at about 9 V, but we found that the driving voltages increase with the polymer thickness. As evident in the I–L plot shown in Fig. 7(c), L increases monotonously with I, similarly to DOO-PPV flat-type LED's.

The electroluminescence (EL) spectrum of the microring LED is shown in Fig. 8. As evident from this figure, the EL spectrum is similar to the PL spectrum. It has a broad double hump feature; lasing modes could not be obtained since the injected current density was only about 100 mA/cm^2 dc. We also achieved bright EL from a microdisk LED using up to 2 A/cm^2 dc current density [26]. In order to produce a current-driven organic laser, it will be necessary to use pulsed current sources. We have determined [25] that laser action is possible with submicrosecond light pulses (<200 ns). We may then assume that submicrosecond electrical pulses will be sufficiently short for electrically driven polymer laser diodes. From the laser threshold intensity for our photopumped microlasers, neglecting the polaron absorption and assuming a 5% internal quantum efficiency, we estimate the threshold current density necessary for lasing to be of the order of 10^4 A/cm^2. Such current densities are within the present limits of polymer LED's, where current densities as high as 10^6 A/cm^2 have been recently demonstrated [39].

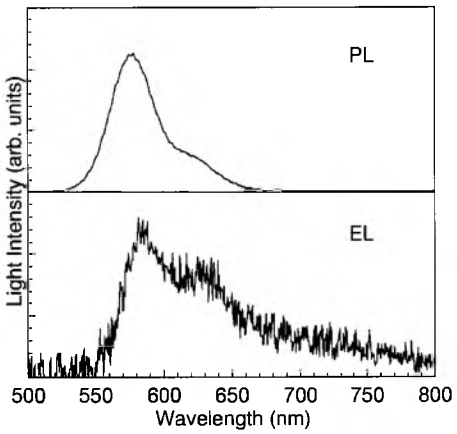

Fig. 8. EL spectrum of the DOO-PPV microring LED.

III. Irregular Regimes of Stimulated Emission

A. Mirrorless Laser-Like Emission

In the absence of an optical cavity, a gain medium is expected to exhibit amplified spontaneous emission (ASE), [14], [40], a stimulated emission process without a feedback mechanism that would otherwise lead to lasing. ASE typically results in emission spectral narrowing and exciton lifetime shortening, both of which have indeed been observed in thin polymer films [12]. Our recent close examination of stimulated emission in polymer waveguides [41], however, has shown that the ASE model might not be adequate to fully describe the observed phenomena. In our measurements, we used the experimental apparatus already described in Section II. Thin DOO-PPV films, spin-coated on

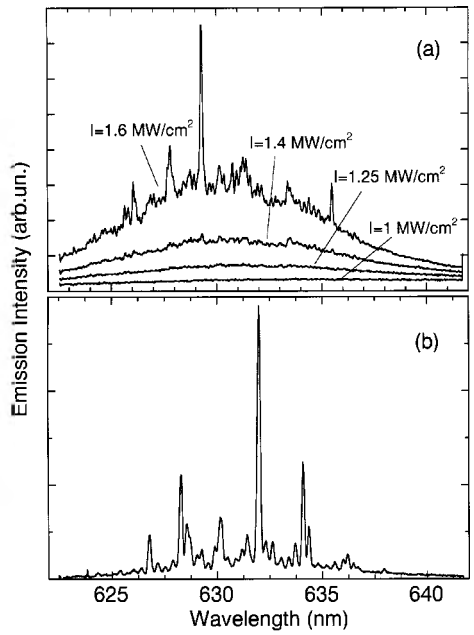

Fig. 9. Stimulated emission spectra of a DOO-PPV film obtained using a stripe-like excitation area with the length L of 1 mm and width of 30 μm. Spontaneous emission (a) at different excitation intensities and (b) at $I = 2$ MW/cm2 from a different excited area of the same DOO-PPV film.

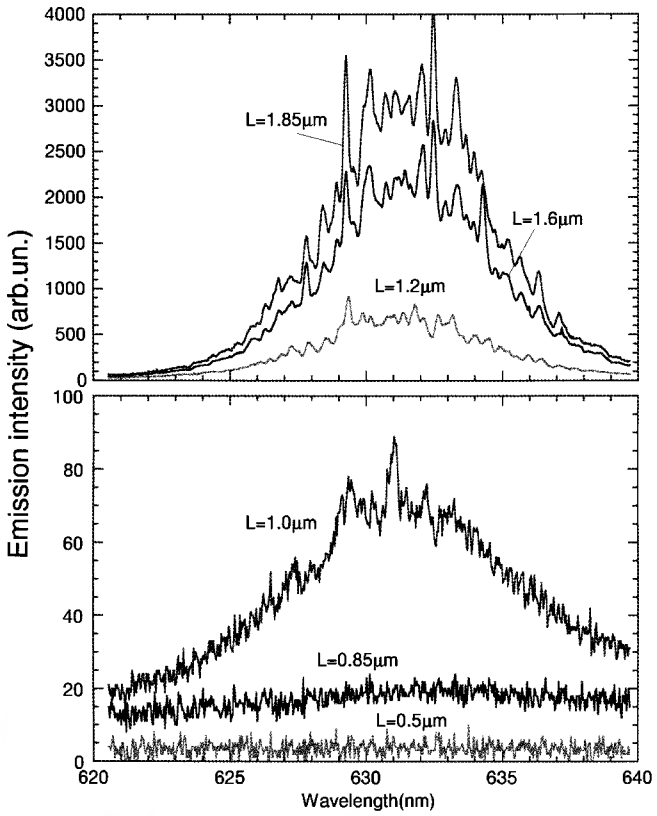

Fig. 10. Emission spectra from a DOO-PPV film in the stripe excitation geometry at $I \sim 1$ MW/cm2 for various L as shown in the insets.

flat quartz substrates, were photoexcited using an excitation area in the shape of a thin stripe with length L and width a [41]. The polymer emission was collected in the direction along the stripe axis; as reported previously [14], stimulated emission predominantly occurred in this direction.

Fig. 9(a) illustrates typical emission spectral narrowing observed in one of the studied DOO-PPV films. Due to stimulated emission, a featureless band at ~630 nm with a characteristic bandwidth of ~10 nm appeared at the threshold excitation intensity I_A. At $I > I_A$, the spectral narrowing process continued and resulted in the formation of numerous randomly positioned spectral lines with linewidths on the order of 0.1 nm. The latter process could be observed only at excitation intensities greater than a second threshold intensity I_B (see Fig. 9), provided that the excitation stripe width was small ($a < 100$ μm) [41]. For $I > I_B$, the emission spectra were typically dominated by a few strong, "super-narrowed" lines, as shown in Fig. 9(b). The position and strength of these lines appear to be random and different for different excited areas of the same film. We note, however, that the phenomenon of spectral "super-narrowing" could not be seen unless a thin stripe-like excitation area was used [41].

We found that the ASE model (as well as superfluorescence [12]) cannot adequately describe this laser-like phenomenon; its possible origins have been discussed elsewhere [41], [42]. We also observed similar effects in blends of laser dyes and nonabsorbing scatterers (SiO_2 nanoballs) [42]. However, "super-narrowing" was not detected in the same blends without the scatterers. This led us to conclude that narrow lines may routinely appear in stimulated emission spectra of high gain media, if there is sufficiently strong light scattering in these media. The origin of such a scattering mechanism in polymer films is currently unclear. It has been speculated, however, that polymer optical losses ($\alpha_{\rm res}$) are partly due to scattering rather than absorption [14]. Light scattering in this case may provide not only optical losses, but also a form of optical feedback similar to that of random lasers [43]–[45].

It has been argued that very strong scattering is required for random lasing. In fact, lasing was predicted to occur only if the scattering length l^* is on the order of λ [46], [47]. In our case, $l^* \gg \lambda$, even if we attribute $\alpha_{\rm res}$ of ~30 cm^{-1} solely to a scattering process. We speculate, however, that even weak scattering may produce sufficient optical feedback to cause the appearance of random resonances in the stimulated emission spectrum of a high gain medium. In the case of thin stripe excitation, this process may resemble the mechanism of distributed feedback [42], in which we envision weak backscattering occurring repeatedly along the entire length of the excitation stripe. Such backscattering is speckle-like and therefore wavelength-selective, where the selection process is largely random and determined by the structural arrangement of the scatterers inside the excitation volume. This, in part, has been confirmed by the emission spectra shown in Fig. 10, which were obtained from a uniform DOO-PPV film for different stripe lengths L. As L increases, numerous narrow lines appear in the spectrum shortly after the onset of stimulated emission. It can be seen that the entire length of the excitation stripe participates in the formation of these narrow lines. Also, I_B decreases as L increases, which is consistent with the DFB model [32]. The observed resonances are, therefore, macroscopic and may be used to characterize the morphology of the specific excited area.

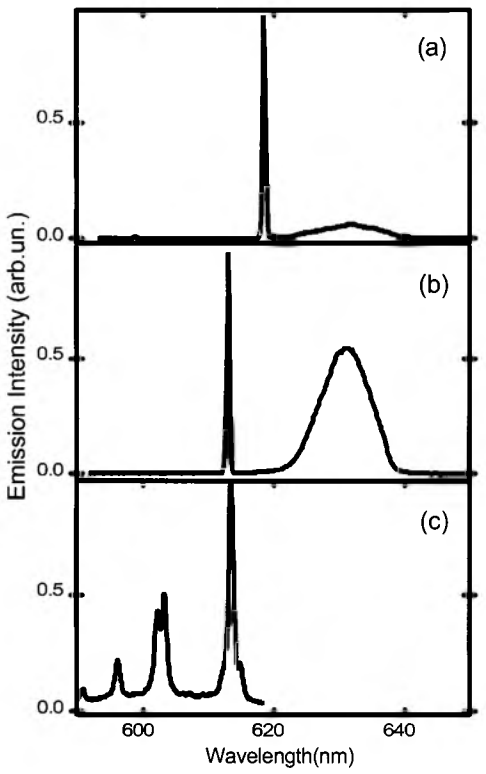

Fig. 11. Emission spectra from a DOO-PPV film excited (a) with 90-μJ pulses at 563.5 nm and (b) with 12-μJ pulses at 559 nm. (c) Spontaneous Raman scattering spectrum of a DOO-PPV film measured using 752-nm excitation and plotted versus wavelength assuming hypothetical 559-nm excitation.

B. Amplified Raman Scattering

Another phenomenon which results in narrow laser-like lines even in the absence of an optical cavity is the resonant amplification of the most strongly coupled Raman modes in the gain medium [48], [49]. Fig. 11(a) and (b) demonstrate this type of optical amplification in a thin film of DOO-PPV. The excitation source for these measurements was a Raman-shifted 100-ps pulsed laser tuned at (a) 563.5 nm and (b) 559 nm, respectively, both of which cover the long-wavelength tail of the polymer absorption band. In both cases, the regular ASE band centered at ~630 nm did not shift with the excitation wavelength. However, a very intense, narrow emission line appeared in both cases on the high energy side of the ASE band. We determined the width of this sharp line to be less than 0.3 nm. Its position shifted by 4.5 nm (143 cm^{-1}) when the excitation wavelength was tuned from 559 to 563.5 nm, thus exactly corresponding to the energy difference of the excitation lasers. This fact clearly demonstrates the presence of the Raman gain in the DOO-PPV films.

In order to identify the active Raman mode participating in the optical amplification, we measured the off-resonance, spontaneous Raman scattering response of DOO-PPV at low excitation intensities. The resulting Raman scattering spectrum shown in Fig. 11(c) reveals strong Raman active lines at 968, 1171, 1285, 1313 and 1584 cm^{-1}, respectively. The latter mode is the strongest and therefore is the most likely candidate to be amplified by the gain medium at high excitation intensities. Indeed, as seen in Fig. 11(c), we obtained excellent spectral overlap between the positions of the Raman mode at 1584 cm^{-1} and the narrow line in Fig. 11(b). This demonstrates that we may use luminescent π-conjugated polymer thin films as inexpensive laser Raman-shifters for spectroscopy [50].

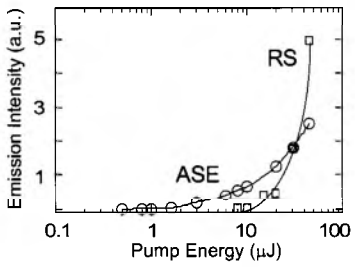

Fig. 12. Emission intensity versus excitation pulse energy of the ASE band and amplified 1584 cm^{-1} Raman scattering mode in a DOO-PPV film for 563.5-nm excitation.

We measured the emission intensity versus the excitation intensity for a DOO-PPV film excited at 563.5 nm (Fig. 12). It is seen that the threshold excitation intensity for Raman gain is about one order of magnitude higher than that of the ASE, occurring at 8 and 0.5 μJ, respectively. The resonant Raman amplification reveals, however, a higher slope efficiency compared to that of ASE. At the highest used excitation intensities, it is therefore possible to generate emission where Raman scattering is dominant. In this case, a narrow laser-like emission line is realized in the polymer films with no optical cavity, in addition to a residual smaller and much broader ASE band.

IV. Summary

We have observed and studied various regimes of stimulated emission produced by optical pulsed excitation of π-conjugated polymer films. Multimode lasing was demonstrated in various cylindrical microcavities, including self-assembled microrings on optical fibers and metal wires, and patterned microdisks. Such microcavities were shown to possess a high Q factor, limited by intrinsic losses of the polymer gain medium. This high Q value, however, depends on the excitation pulsewidth and decreases for longer excitation pulses. Operating micro-LED's were fabricated using microring and microdisk configurations with the goal of producing laser emission using current injection. In the absence of a laser cavity, thin polymer films were shown to exhibit two unusual regimes of stimulated emission, in which narrow lines appeared in the ASE spectrum. One of these regimes was associated with the optical feedback induced by random light scattering inside the films, whereas the other regime was found to be due to amplified Raman scattering.

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