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Ring microlasers from conducting polymers

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We demonstrate pulsed, photopumped multimode laser emission in the visible spectral range from cylindrical microcavities formed by conducting polymer thin films deposited around optical fibers. The laser is characterized by narrow emission lines ($\sim 1.5\ \mathrm{cm}^{-1}$), a well-defined excitation threshold, anisotropic emission in both polarization and azimuthal intensity distribution, and high $Q(\geqslant 3000)$, which leads to a low excitation threshold of order 1 nJ/pulse. We observed two different sets of laser modes; these are waveguided ring modes in the polymer film and whispering gallery modes close to the optical fiber surface. [S0163-1829(97)53032-3]

Recent advances in the synthesis of luminescent conducting polymers (LCP) followed by a better understanding of their optical and electronic properties, have provided evidence of optical stimulated emission (SE) in LCP solutions and thin films.[1–4] SE occurs at a relatively high excitation intensity when the optical gain exceeds optical losses due to self-absorption, light scattering caused by imperfections, and other factors. SE is usually accompanied by a dramatic spectral narrowing, as has recently been observed in various conducting polymer films.[2–4] Even though spectral narrowing is one of the main characteristic properties of lasing,[1–2] other phenomena of high optical gain, such as superfluorescence and amplified spontaneous emission.[2–4] may also produce analogous spectral narrowing. Laser oscillations, on the other hand, require a *cavity* to provide optical feedback.[5] The resonant nature of the laser cavity establishes a well-defined spectral mode structure and an associated highly anisotropic (i.e., directional) emission pattern.

In this paper we investigate photopumped lasing in LCP using cylindrical microcavity structures of thin films deposited on glass fibers. Microcavities provide excellent coupling of spontaneous emission into lasing modes, and a high-cavity quality factor Q which consequently leads to low lasing thresholds.[6] Two LCP have been tested: derivatives of poly(p-phenylene-vinylene) (PPV) with lasing in the red, and disubstituted polyacetylene (DPA) with lasing in the green. Multimode, narrow laser lines ($\sim 1.5\ \mathrm{cm}^{-1}$) with low threshold intensities (1 nJ/pulse) have been demonstrated in these structures using pulsed photoexcitation. We note that low lasing threshold is an important criterion in developing electrically pumped plastic lasers.

In our studies we used soluble derivatives of PPV and DPA as gain media; including DOO-PPV (Ref. 3) and PDPA-Si(iPr)$_3$,[7] respectively. Cylindrically shaped thin polymer films were prepared by dipping commercially available optical fibers into saturated chloroform solutions. Thin polymer rings were consequently formed around the glass cylindrical core following fast drying in the air. The estimated thickness d of the deposited polymer film was about 2–3 μm. The self-assembled polymer microstructures in the form of cylindrical microrings are similar to those previously reported in Ref. 8, with deposited films of laser dyes blended in transparent polymers. In the present paper, however, we have exclusively used pristine conducting polymers as lasing media. The excitation source was a Nd: yttrium aluminum garnet (YAG) regenerative laser amplifier producing 100 ps pulses with a repetition rate of 100 Hz. This laser light was either frequency doubled (532 nm), or tripled (355 nm) for pumping the DOO-PPV and PDPA-Si(iPr)$_3$ films, respectively. The pump beam was focused using a cylindrical lens into a 100 μm$\times$5 mm stripe perpendicular to the polymer coated fiber ($\varnothing$100–200 μm); thus only a small fraction of the pump light was absorbed by the polymer film. The pump beam polarization could be rotated to be either parallel or perpendicular to the fiber axis. The light emitted from the excited polymer ring was collected in the plane of the ring with a round lens and spectrally analyzed using a 0.6 m triple spectrometer and a charge-coupled device array with maximum spectral resolution of about $1.5\ \mathrm{cm}^{-1}$.

Figure 1 shows the emission spectra of DOO-PPV films coated onto two different optical fibers with outside diameters D of 200 μm (a) and 125 μm (b), respectively, obtained at pumping intensities of order 1 nJ/pulse. In the insets of Fig. 1(a) we show the DOO-PPV polymer repeat unit and, for comparison, the much broader ($\sim 2500\ \mathrm{cm}^{-1}$) photoluminescence (PL) spectrum. The sharp emission lines seen in Fig. 1 appear only above a threshold excitation intensity I_0. Figure 1(b) shows three emission spectra measured below, at, and above I_0. Since the sharp lines are absent at low intensity, they cannot be due to a quantum electrodynamic enhancement of PL in a μcavity.[9] We therefore attribute these lines to laser modes associated with the cylindrical μcavity formed by the thin polymer film. The linewidth of the narrow laser lines was limited by the spectral resolution of the apparatus ($1.5\ \mathrm{cm}^{-1}$). The inset of Fig. 1(b) also shows that the spectrally integrated emission intensity depends nonlinearly on the excitation intensity, and this is another characteristic feature of lasing. We note that I_0, expressed in terms of absorbed energy/pulse, is of order 1 nJ. This I_0 is lower by about three orders of magnitude than that of the spectral narrowing previously observed in flat thin DOO-PPV films.[2]

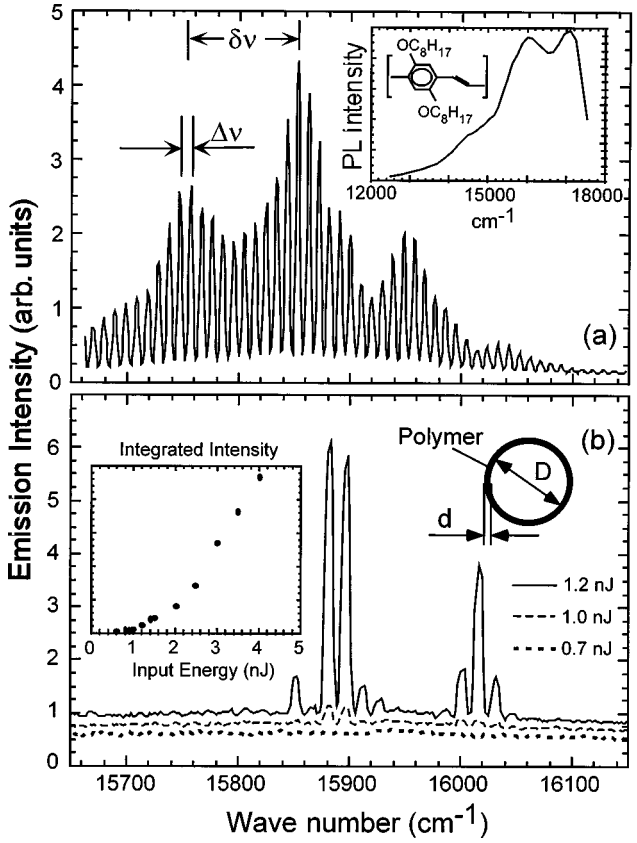

FIG. 1. Laser spectra of DOO-PPV films coated on glass fibers: (a) $D=200\ \mu$m, absorbed energy/pulse=1.5 nJ; (b) $D=125\ \mu$m at various absorbed energies/pulse. Insets in (a) show the polymer repeat unit and for comparison the broad DOO-PPV PL spectrum; insets in (b) show the polymer ring structure (right) and the integrated emission intensity dependence on the absorbed excitation energy/pulse (left).

Another salient characteristic of lasers is the increased directionality of the emission.[5] In the case of microring lasers, we then expect, for excitation intensities $I>I_0$, more light to be emitted into the plane of the ring. We show this property in Fig. 2 by measuring the emission angular dependence using the DOO-PPV coated 125-μm-diam fiber. We introduced a 1 mm pinhole in front of the collecting lens for monitoring the emission intensity at a given angle θ, as shown in Fig. 2, inset. It is seen that the laser emission is concentrated in a small cone of $\Delta\theta\sim 0.03$ rad.[10] We note that the plane of the microring does not coincide with the optical axis of the apparatus and therefore the peak intensity in the angular dependence of Fig. 2 is slightly shifted away from $\theta=0$. From $\Delta\theta$ we can estimate the lateral size ζ of the lasing ring mode: $\zeta\approx\lambda/\Delta\theta\approx 20\ \mu$m, where λ is the emission wavelength (630 nm). ζ is smaller than the size of the excitation length parallel to the fiber (100 μm), indicating that it is limited by inhomogeneity in the polymer film. Further improvements in the film quality may lead to enhanced directionality of the microring laser emission.

The polymer ring laser emission was found to be linearly polarized. Its polarization is parallel to the fiber axis, which is a characteristic property of transverse electric (TE) laser modes. The measured polarization ratio $P=I_{\parallel}/I_{\perp}$ ($I_{\parallel}$ and $I_{\perp}$ are the emission intensities with polarizations parallel and perpendicular to the fiber axis, respectively) was found for $I>I_0$ to be $P>100$. The background PL, however, is characterized by $P\approx 1$ independent of I. We also found that P does not depend on the pump beam polarization.

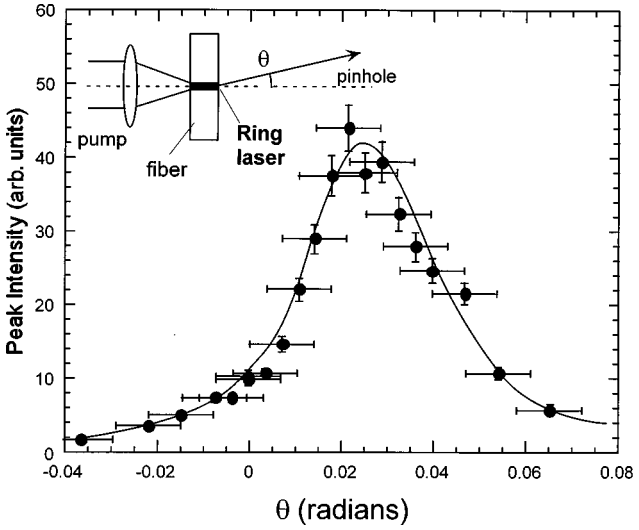

FIG. 2. Intensity angular dependence of the DOO-PPV 125 μm ring laser emission. The inset schematically shows the experimental setup.

The spectral peak of the polymer ring laser (Fig. 1) is at the maximum of the optical gain spectrum, $\gamma(\lambda)$, which is close (but not equal) to one of the PL sideband peaks [Fig. 1(a), inset]. We note that lasing occurs at λ where $\gamma(\lambda)$ exceeds the optical losses; this condition is given by[9]

$$\gamma \geqslant \frac{2\pi n_p}{\lambda Q}, \tag{1}$$

where n_p is the polymer index of refraction and Q is the cavity quality factor. Q is usually used to characterize the quality of a resonator mode and is defined as 2π times the number of optical cycles required for the cavity mode field to decay to $1/e$ of its initial value.[5] There are three contributions to Q: $Q_{\rm abs}$ is the absorption limited quality factor given by $2\pi/\alpha\lambda$, where α is the absorption coefficient; $Q_{\rm scat}$ is determined by scattering losses in the polymer film and its surface due to imperfections; and $Q_{\rm cav}$ is the cavity finesse determined by the μcavity geometry. These Q's are added as follows:

$$Q^{-1}=Q_{\rm abs}^{-1}+Q_{\rm scat}^{-1}+Q_{\rm cav}^{-1}. \tag{2}$$

For cylindrical μcavities, $Q_{\rm cav}$ is in the range of 10^4-10^8.[6] $Q_{\rm scat}$ strongly depends on the polymer film quality and in principle, may be made so large as to eliminate the $Q_{\rm scat}^{-1}$ contribution in Eq. (2); however, it is the least controllable parameter. $Q_{\rm abs}$ is estimated for our DOO-PPV films from $\alpha(630\ {\rm nm})\approx 30\ {\rm cm}^{-1}$, to be of order 10^3-10^4.[11] Since $Q_{\rm abs}^{-1} \gg Q_{\rm scat}^{-1}$ for our films, then from Eq. (2) $Q\approx Q_{\rm abs}$.

The value of Q can be directly obtained from the cavity resonance line halfwidth $\Delta_{1/2}\nu$ below the laser threshold using the relation: $Q=\nu/\Delta_{1/2}\nu$, where $\nu=c/\lambda$. However, none of the resonance lines are observed below the lasing threshold [Fig. 1(b)]. In this case the maximum value of $\Delta_{1/2}\nu$ can be estimated from the separation $\Delta\nu$ between neighboring

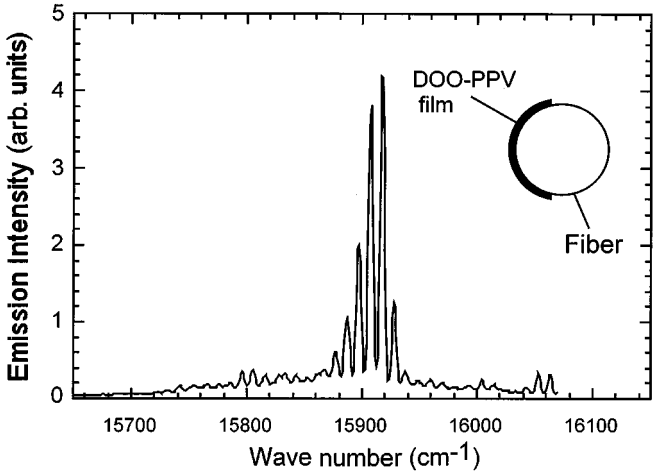

FIG. 3. Laser spectrum of a 200-μm-diam fiber coated with DOO-PPV film on one side, as shown in the inset.

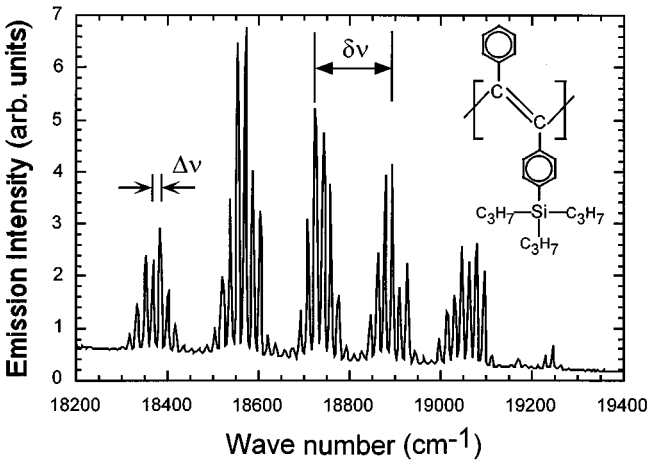

FIG. 4. Laser spectrum of PDPA-Si(iPr)$_3$ films coated on a 125-μm-diam fiber. The polymer repeat unit is also shown in the inset.

laser modes, since $\Delta_{1/2}\nu < \Delta\nu/2$; otherwise no separate laser lines would be observed. We then obtain from Fig. 1(a) $\Delta_{1/2}\nu < 5\ \mathrm{cm}^{-1}$ and using $\nu = 16\,000\ \mathrm{cm}^{-1}$ we estimate $Q \geqslant 3\times10^3$ for the DOO-PPV ring laser.

We can also determine Q from I_0. γ is given by σN, where σ is the optical gain cross section and N is the average number density of photogenerated excitons. Using Eq. (1) at threshold we get

$$Q = \frac{2\pi n_p}{\sigma N_0 \lambda}, \tag{3}$$

where N_0 is N at threshold. For DOO-PPV films, $n_p \sim 1.7$ (Ref. 11) and $\sigma \sim 10^{-15}$ cm^2.[3,12] N_0 can be approximated by $N_0 \approx N_p/V$, where N_p is the total number of absorbed photons per pulse at I_0 and V is the volume of the lasing microring. This assumption is justified in our case, since the exciton lifetime in DOO-PPV is 240 ps (Refs. 3 and 12) and this is longer than the excitation pulse duration (100 ps). For the 125-μm-diam fiber we estimate $N_p = 3\times10^9$ and $V \approx 10^{-7}$ cm^3. Using Eq. (3) we then obtain $Q \approx 5\times10^3$, in agreement with the other two estimates. Since all three separate Q estimates are close to each other, we conclude that Q is in fact limited by self-absorption.

The polymer layer acts as a waveguide forming a ring resonator around the glass fiber. The resonant frequencies ν_m for the waveguided laser modes (WM) are given by[8]

$$\nu_m = \frac{mc}{\pi D n_{\mathrm{eff}}}, \tag{4}$$

where m is an integer, c is the speed of light in vacuum, and n_{eff} is the effective refraction index in the cylindrical waveguiding film. n_{eff} in turn, is determined[13] by the thickness d, and the refraction indices of the polymer n_p and fiber n_g (=1.46). For a relatively thick polymer film, as in our case, n_{eff} may be approximated[14] by $n_{\mathrm{eff}} \approx n_p\ (1 - d/D) \approx n_p$. Using this approximation in Eq. (4), we calculate the intermodal spectral spacing, $\Delta\nu = \nu_m - \nu_{m-1} = c/\pi D n_p$, to be 9.4 and 15 cm^{-1} for the 200- and 125-μm-diam fibers, respectively. These values are in good agreement with the experimental $\Delta\nu$ in Fig. 1, which are 9.5 and 15.2 cm^{-1}, respectively.

In addition to the waveguided modes (WM) in the polymer film, the cylindrical glass fiber may also support whispering gallery modes (WGM) propagating close to the fiber surface.[5] The resonant frequencies ν_k of the WGM in the absence of the polymer film are given by $\nu_k = kc/\pi D n'_{\mathrm{eff}}$, where k is the primary mode number and $n'_{\mathrm{eff}} = n_0 = \sqrt{n_g^2 - 1}/\tan^{-1}\sqrt{n_g^2 - 1}$.[5] When the polymer film is deposited on top of the glass fiber, n'_{eff} increases and since $n_g < n_p$, the WGM become lossy. In order to show that WGM may exist in our geometry, we coated only one side of the 200 μm fiber with DOO-PPV. As seen in Fig. 3, lasing could be still obtained from this ''one-sided'' structure. However, due to a lower Q value and limited WGM penetration into the polymer film, the corresponding I_0 in this case is an order of magnitude higher than that of the complete ring. As shown in Fig. 3, the WGM of the incomplete ring resonator are characterized by a larger $\Delta\nu$ (=10.4 cm^{-1}), from which we find that $n'_{\mathrm{eff}} = 1.53$; this value is in agreement with theory since $n_0 < n'_{\mathrm{eff}} < n_p$.

The fiber WGM are not dominant in the complete ring resonator, since WM in the film have higher Q. However, WGM in the fiber are able to modify Q_{cav} of the primary WM in the polymer ring. Q_{cav} increases whenever the frequencies of WM and WGM are in resonance, i.e., $\nu_m \approx \nu_k$, whereas Q_{cav} decreases if the corresponding frequencies are detuned from each other. As a result, Q_{cav} is periodically modulated in ν with a period $\delta\nu$ determined by the relation

$$\delta\nu = \Delta\nu \frac{n_{\mathrm{eff}}}{\Delta n_{\mathrm{eff}}}, \tag{5}$$

where $\Delta n_{\mathrm{eff}} = n_{\mathrm{eff}} - n'_{\mathrm{eff}}$ is the difference between n_{eff} of the WM and WGM, respectively. It is indeed seen in Fig. 1 that the equally spaced laser modes are periodically modulated in intensity. We conjecture that this intensity modulation can be explained by the variation of Q versus ν caused by resonances between WGM and WM. From Fig. 1 we find $\delta\nu = 94\ \mathrm{cm}^{-1}$ for the 200-μ-diam fiber and 140 cm^{-1} for the

125-μm-diam fiber. From $\Delta\nu$ measured separately for WM and WGM (Figs. 1 and 3, respectively) we calculate $\Delta n_{\text{eff}} = 0.17$. Using Eq. (5) we obtain, in agreement with the experiment, $\delta\nu = 94$ and $150\ \text{cm}^{-1}$ for the 200 and 125 μm fibers, respectively.

Microring lasers were also made from PDPA-Si(iPr)$_3$, which has a broad PL spectrum peaking at $19\,000\ \text{cm}^{-1}$ (~ 530 nm).[7] Figure 4 shows a multimode laser spectrum of a DPA ring formed around a 125-μm-diam fiber; the polymer repeat unit is shown in the inset. We note that I_0 here is larger than I_0 for DOO-PPV by an order of magnitude. We measured $\Delta\nu$ at the red end of the spectrum ($18\,500\ \text{cm}^{-1}$) to be $16.7\ \text{cm}^{-1}$, which according to Eq. (4) corresponds to $n_{\text{eff}} = 1.53$. We also measured $\Delta\nu = 16.0\ \text{cm}^{-1}$ at the blue end of the spectrum ($19\,000\ \text{cm}^{-1}$) leading to $n_{\text{eff}} = 1.59$. For thick films $n_{\text{eff}} \approx n_p$ and thus, using the measured laser mode structure, it is possible to accurately determine the absolute value and frequency dispersion of n_p. Similar to DOO-PPV (Fig. 1), the mode structure in Fig. 4 is periodically modulated; this may be also attributed to the resonant coupling between WM and WGM in the ring cavity.

In summary, we have demonstrated multimode red and green lasing from cylindrical microcavities of thin conducting polymer films deposited on optical fibers. The laser emission is characterized by the following properties: (i) drastic spectral narrowing, where a single mode linewidth is less than $1.5\ \text{cm}^{-1}$; (ii) a well-defined threshold excitation intensity for lasing; (iii) a high degree of polarization above the threshold; and (iv) increased azimuthal directionality. The observed threshold excitation intensities for these microlasers are orders of magnitude smaller than those of spectral narrowing previously reported in flat thin films. This is a promising step towards developing electrically pumped plastic lasers.

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