

phys. stat. sol. (b) **206**, 131 (1998)

Subject classification: 78.45.+h; 71.35.-y; 78.47.+p; S12

Gain Dynamics in Conjugated Polymers at Room Temperature

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(Received September 1, 1997)

We report on stimulated emission and optical gain in BEH-PPV polymer films at room temperature. Performing femtosecond pump-probe experiments we find very fast (≤ 100 fs) relaxation of excitons within a ladder of vibronic states. From spectra taken at very early times after photoexcitation we identify several vibronic transitions with a linewidth of about 8 nm. Strong coupling of excitons to these vibrations leads to stimulated emission and large optical gain of up to 10^4 cm $^{-1}$. For a pump-probe delay of 200 fs the different transitions are no longer distinguishable due to broadening through spectral diffusion and exciton migration. The lifetime of the optical gain corresponds to the exciton lifetime. Population depletion by stimulated emission leads to a density dependent decay within a few hundred fs up to about 2 ps.

1. Introduction

Widely used as the active material in organic light emitting diodes, the conjugated polymer poly-phenylenevinylene (PPV) and its derivatives have attracted a lot of interest lately as a new semiconducting solid state organic gain material [1 to 5]. Optical gain of $g = 2500$ cm $^{-1}$ was observed in PPV films for exciton densities of 10^{19} cm $^{-3}$ already in 1994 [1]. After a few picoseconds the gain was seen to be replaced by induced absorption in the same wavelength range that persists for several hundred picoseconds. This absorption was assigned to nonemissive spatially indirect excitons and was believed to be an obstacle to the development of solid state PPV lasers.

However, recent reports on lasing action in optically pumped solid state polymers films [2, 6, 7] contained in planar cavities have shown impressively, that sufficiently high optical gain can be achieved and utilized. This is strongly supported by reports on dramatic photoluminescence (PL) line narrowing in a variety of plain PPV derivate films seen above a threshold exciton density of about 10^{17} cm $^{-3}$ [4, 5] and indicative of stimulated emission (SE). The narrow line always occurs at the spectral position of the main vibronic PL peak. Interestingly, the SE linewidth of 7 to 9 nm is much smaller than the spectral width of the excitonic gain, which covers the whole 120 nm broad spectral region of spontaneous excitonic emission. The most straightforward interpretation of these results in terms of amplified spontaneous emission (ASE) can be ruled out since the samples were much thinner than the optical gain length $d_0 = 1/g$. Therefore two different interpretations have been applied. According to Hide et al. [4] the PL line narrowing is completely due to waveguiding effects in the plane of the film that lead to

an increase of the interaction length and therefore to ASE. In contrast, Frolov et al. [5] explain their experimental results by superradiance effects, which, from atomic systems and molecular crystals, are also known to lead to PL line narrowing. Several papers, supporting one or the other explanation for the quite general observation of the narrow SE have been published.

We present a detailed analysis of SE, as well as of absorption changes above and below the excitonic absorption band of BEH-PPV films using femtosecond pump-probe spectroscopy. We show that the optical gain is due to the inversion of several exciton-phonon transitions. At very early times after the fs excitation we find distinct spectral holes indicating that the homogeneous linewidth of the individual transitions is only 8 nm. Gain narrowing, ASE, or superradiance arguments are not needed to explain the origin of the narrow SE spectrum.

2. Experimental

Thin films of the soluble and at room temperature processable PPV-derivative poly(2,5-bis(2'-ethyl-hexyloxy)-1,4-phenylenevinylene)(BEH-PPV) [8] were fabricated by spin coating from xylene solution. The samples were resonantly excited in their absorption edge, using an amplified CPM laser system which provides spectrally tunable light pulses of 100 fs duration. The excitation was varied between 10 $\mu\text{J}/\text{cm}^2$ and 1 mJ/cm^2 . The dynamics of the absorption change and the optical gain were measured in a pump-probe set-up using a broad band (≈ 120 nm) probe pulse. The PL was time resolved using a streak camera with 10 ps resolution.

3. Photoluminescence and Stimulated Emission

Fig. 1a shows the spectral shape of the time integrated PL of a 100 nm BEH-PPV film at room temperature for three different pump fluences and under excitation at 555 nm. The spectra are corrected for reabsorption effects and the linear absorption of the 110 nm thick sample is shown for comparison. The low density PL spectrum (curve i in Fig. 1a) is similar to the one observed in electroluminescence. It exhibits the well-known vibrational structure with a prominent energy spacing of about 150 meV and a distinct substructure. For increasing excitation fluence, the initial 120 nm broad PL spectrum collapses into a 9 nm wide emission line at about 630 nm (curve iii in Fig. 1a). This transition happens, when the excitation reaches about 50 $\mu\text{J}/\text{cm}^2$ analogous to an average exciton density of $n_{\text{eh}} = 5 \times 10^{18} \text{ cm}^{-3}$. The time-resolved PL below and above this threshold intensity is plotted for the position of the narrow line at 630 nm in Fig. 1b. At the excitation fluence, where the narrow line is observed, the decay time decreases drastically from about 60 ps to a time shorter than 10 ps, the time resolution of our streak camera. The rapid decay of the PL is typical for SE.

The narrow emission line that appears for excitation fluences slightly above the threshold is best described by a single Gaussian at 632 nm and a linewidth of about 8 nm, the error in linewidth and center wavelength being less than 0.2 nm. With increasing excitation the SE spectrum broadens remarkably and a clear asymmetry and additional structures develop on the high-energy side. We carefully analyzed PL spectra for nine different levels of excitation and found that all SE spectra can be very accurately fitted assuming three different transitions with a Gaussian shape peaking at $\lambda = 632$, 621, and 609 nm, labeled A, B, and C, respectively. The error in spectral position and

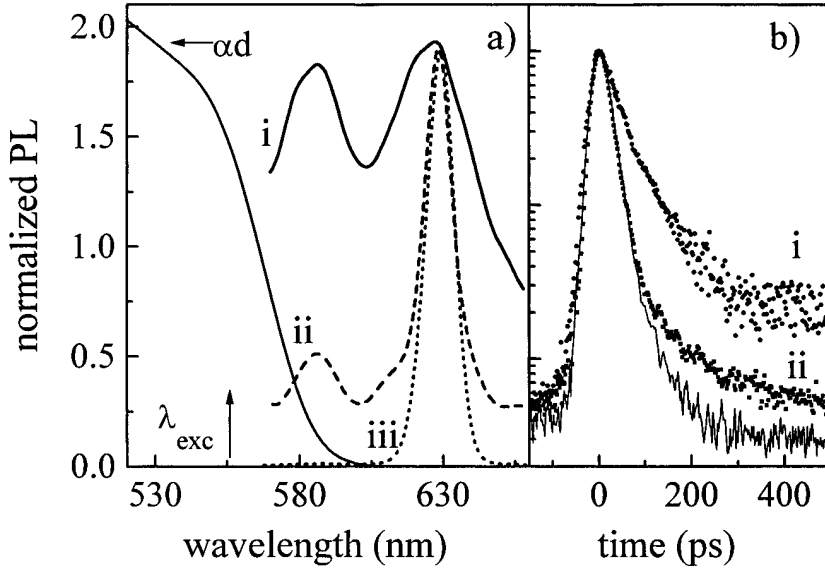


Fig. 1. a) Normalized PL for (i) 30, (ii) 50, and (iii) 120 $\mu\text{J}/\text{cm}^2$ excitation at $\lambda = 555$ nm (indicated by the arrow). The absorption spectrum is plotted for comparison. b) PL decay curves at (i) 30 and (ii) 50 $\mu\text{J}/\text{cm}^2$ excitation. The solid line is the apparatus function of the set-up

linewidth determined for the higher energy transitions is less than 1 nm. Fig. 2a shows the PL spectrum for an excitation of 500 $\mu\text{J}/\text{cm}^2$. The pump fluence dependence of amplitude and linewidth of these three peaks is shown in Fig. 2b and c. For all transitions we find the same qualitative behavior. The amplitude exhibits a sharp threshold with increasing excitation, followed by saturation. Doubling the excitation fluence at the threshold results in an increase of the emission of peak A by more than two orders of magnitude. The strong increase in quantum efficiency is again typical for SE since this very fast recombination channel shortcuts slower nonradiative processes, that determine the quantum efficiency and the kinetics at low excitation densities. The threshold fluence is larger for transitions at higher photon energy. In the unsaturated regime we observe for all three transitions a common linewidth of 8 nm. This linewidth increases to 11 nm at saturation. Above 500 $\mu\text{J}/\text{cm}^2$ the PL efficiency drops and the total spectrally integrated emission becomes constant since absorption bleaching at the excitation wavelength leads to less efficient optical pumping. We would like to point out, that we do not find any signature of superradiance or superfluorescence. We do not observe a quadratic behavior of the PL intensity and no further line narrowing with increasing excitation density. The latter is also expected if ASE determines the linewidth.

The data summarized in Fig. 2 reflect the successive inversion of different optical transitions. Transition A obviously exhibits the lowest excitation density necessary for inversion. Once the pump fluence reaches the threshold for SE, that is when the rate for SE becomes larger than the rate for nonradiative trapping processes, this narrow emission line dominates the PL spectrum because of the much higher radiative efficiency. The SE linewidth of 8 nm corresponds to the (homogeneously broadened) linewidth of this optical transition. With increasing pump fluence gain saturation sets in. In an inhomogen-

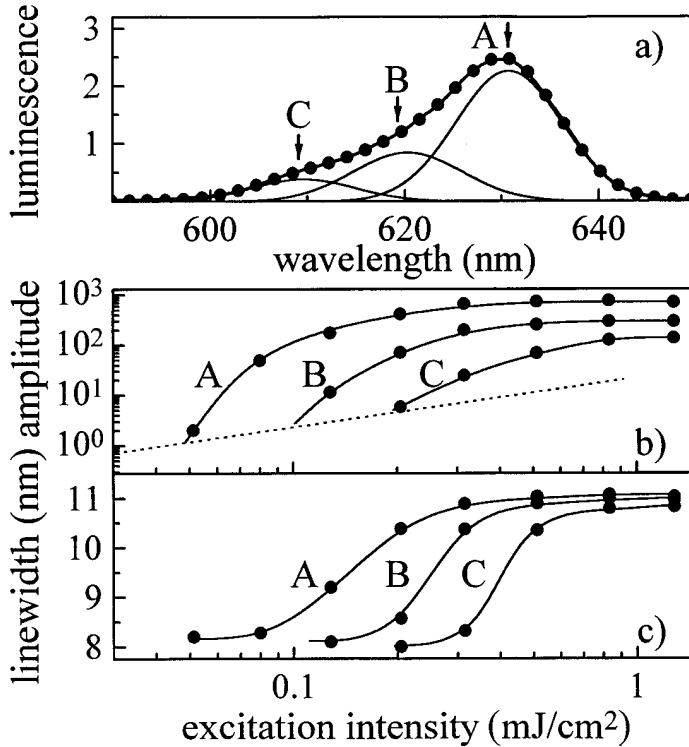


Fig. 2. a) Spectrum of the time integrated SE (PL) for $500 \mu\text{J}/\text{cm}^2$ excitation. Dots and thin lines represent a fit to the lineshape as explained in the text. b) Amplitudes of peaks A, B, and C as a function of excitation fluence. c) FWHM of peaks A, B, and C as a function of excitation fluence

eously broadened system this process is accompanied by an increase in the observed linewidth since nearby transitions will also contribute until finally the SE linewidth corresponds to the combined homogeneous and inhomogeneous linewidth of the transition (11 nm). The same is true for transitions B and C the only difference being that the pump fluence necessary for inversion of these transitions is slightly higher. Stimulated emission of energetically higher transitions is observed when the optical gain of the preceding transition saturates.

4. Optical Gain and Nonlinear Absorption

4.1 Spectra for temporal pump-probe overlap

Fig. 3 shows the absorption changes observed in a pump-probe experiment on a 190 nm thick sample. We plot the relative absorption bleaching ($\Delta\alpha/\alpha$) in the spectral region of the excitation wavelength (555 nm) as well as the net optical gain ($\Delta\alpha d - \alpha d > 0$) observed in the transparent region of the sample. The spectra are shown at zero time delay between pump and probe pulse and for various excitation intensities. First, we would like to comment on the magnitude of the optical gain. A maximum gain of 0.185 translates into a gain coefficient of almost 10^4 cm^{-1} . This is comparable to or even high-

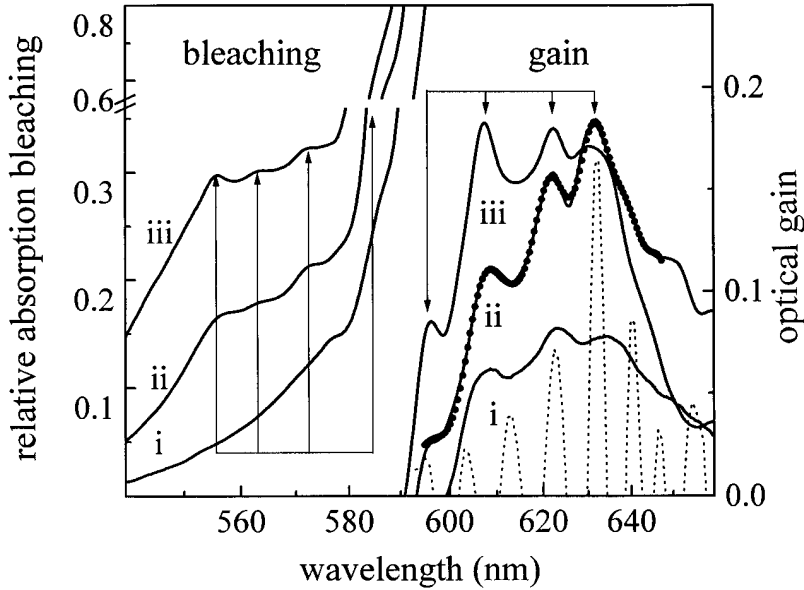


Fig. 3. Spectra of the relative absorption bleaching ($\Delta\alpha/\alpha_{\text{lin}}$) and of the corresponding net optical gain ($\Delta\alpha - \alpha_{\text{lin}}$) for (i) 0.1, (ii) 0.4, and (iii) 1 mJ/cm² excitation. The data are shown for vanishing pump-probe delay. The thin dotted line corresponds to the negative second derivative of curve i in Fig. 1 and dots represent a fit to the gain spectrum as explained in the text and assuming a FWHM of 8 nm

er than in inorganic semiconductors and by far the largest value reported for a semiconducting polymer up to now. We measured similar gain coefficients in 110 nm and 500 nm thick samples, showing that the gain is an intrinsic material parameter and does not depend on the sample thickness. For excitation densities up to $3 \times 10^{19} \text{ cm}^{-3}$ the gain increases linearly with the exciton density and we find a SE cross-section of $2 \times 10^{-16} \text{ cm}^2$. The gain spectra exhibit several peaks. While for lower excitation intensities, the gain is largest around 620 to 630 nm, it eventually saturates at this wavelength and peaks at 609 and 595 nm. These findings are in very good agreement with the results of the PL lineshape analysis. We find that the three major gain peaks at 632, 621 and 609 nm correspond exactly to transitions A, B, and C observed in the single-beam PL experiments (see Fig. 2). Indeed, these transitions can also be seen in the low-density PL far below the threshold for SE. The dotted line in Fig. 3 shows the inverse second derivative of the low-density PL spectrum. Peaks correspond to substructures of the main vibrational PL peak (curve i in Fig. 1a). The low-density PL spectrum is very accurately described by a sum of several transitions located at the spectral position given by the second derivative, if one assumes a Gaussian linewidth of (11 ± 1) nm. Noteworthy, by decreasing the linewidth to (8 ± 1) nm, we also get excellent fits to the optical gain spectra. As an example we show the fit to the optical gain at 0.4 mJ/cm² excitation as dots in Fig. 3. This is again in good agreement with the PL lineshape analysis. The same homogeneous linewidth of 8 nm is observed in the gain spectra at zero time delay and in the unsaturated SE spectra. The linewidth of 11 nm found in the saturated SE regime (see Fig. 2c) as well as in the low-density PL is additionally influ-

enced by inhomogeneous broadening of the system. Assuming a Gaussian lineshape we get from deconvolution an inhomogeneous broadening of about 7.5 nm.

Absorption bleaching (left side of Fig. 3) is observed at the position of the exciting laser ($\lambda = 555$ nm) and in a broad spectral region that covers more than 180 meV around this wavelength. Several vibronic transitions can be distinguished in the region below the excitation wavelength. Since all four transitions display mirror-symmetry with respect to their appearance in absorption and emission and their energy positions correspond approximately to the ones observed in [9, 10] we assign them to vibronic transitions. The fact, that the relative bleaching is always largest at the exciton ground state (580 nm) and is larger for higher excitation (as high as 0.8), reveals very fast (<150 fs) energy relaxation of excitons excited at 555 nm. Note that the ground state is only slightly shifted from the zero-phonon emission line, indicating a Stokes-shift due to structural relaxation of only a few nm. This is in agreement with the results from site-selective spectroscopy [9, 10]. With increasing excitation (curves i to iii) states that are higher in energy become more and more occupied and the corresponding gain increases accordingly.

We also observe bleaching at photon energies above the excitation. This is due to the fact, that, in addition to the occupation of the different states, the spectra reflect simultaneous blocking of different transitions (excited exciton states) because of their common molecular ground state.

Changing the pump wavelength 559 nm we found no considerable change in the position of the main peaks in the gain and bleaching spectra. We therefore believe that the contribution of stimulated Raman processes to the observed gain spectra is small.

4.2 Gain and bleaching dynamics

The temporal evolution of absorption bleaching and optical gain is shown in Fig. 4 for an excitation fluence of $400 \mu\text{J}/\text{cm}^2$. Spectra of the relative absorption change and of the corresponding optical gain are plotted for three different characteristic delay times ($\Delta\tau = 0, 300$ fs, and 30 ps). We find that for a delay of 300 fs, the different transitions are no longer distinguishable due to broadening caused by spectral diffusion and exciton migration. In addition, an induced absorption feature, centered around 590 nm affects the spectrum. After 30 ps (shaded curves in Fig. 4) most of the carriers have recombined due to SE. The remaining excitons are concentrated around 580 nm, the corresponding gain at 630 nm. We still observe about 15% of the initial bleaching and gain.

We find that absorption bleaching and optical gain display the same kinetics. After a fast (some hundred fs) density dependent decay, the decay time slows down to about 2 ps. We assign this behavior to the population depletion by SE. The same 2 ps decay time is found for the induced absorption around 595 nm. We, therefore, assign this feature to an excited state absorption that occurs from the occupied single exciton state.

After 5 ps bleaching and gain show a plateau, for which we find no considerable decay for times up to 200 ps. This long lifetime (≥ 1 ns) cannot be explained by the low-density exciton lifetime of 60 ps measured by time-resolved PL. Our results indicate that the long-lived component of the absorption bleaching is not due to free excitons, but rather due to localized excitons. Apparently, part of the initially excited “hot” excitons are able to move to potential minima where they have a much longer lifetime than free excitons.

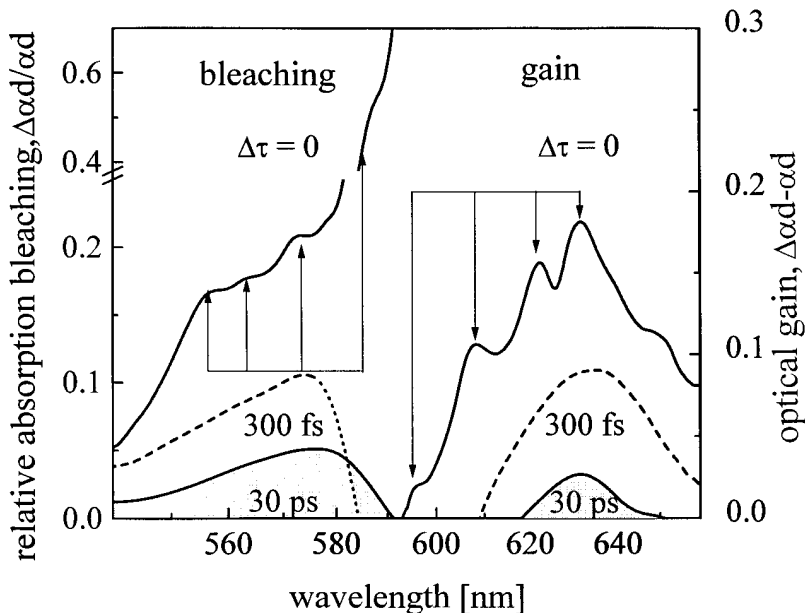


Fig. 4. Spectra of the relative absorption bleaching $\Delta\alpha/\alpha_{\text{in}}$ and the corresponding optical gain ($\Delta\alpha - \alpha_{\text{in}}$) measured for three different time delays between pump and probe pulse, $\Delta\tau = 0$, 300 fs, and 30 ps and for an excitation fluence of $400 \mu\text{J}/\text{cm}^2$

5. Summary

In conclusion, we have demonstrated spectral hole-burning in the absorption and gain region of the conjugated polymer BEH-PPV. We show that there is a common homogeneous (8 nm) and inhomogeneous (7.5 nm) broadening for various excitonic vibronic transitions in absorption and emission below and above the threshold for SE. Strong coupling of excitons to high-energy vibrations results in high optical gain of up to 10^4 cm^{-1} in a spectral region where the material is transparent. The lifetime of the gain corresponds to the density-dependent exciton lifetime. A long lived component ($>1 \text{ ns}$) is assigned to localized excitons. Induced excited state absorption, which is observed energetically above the stimulated emission, does not significantly influence the optical gain in the transparent region.

Acknowledgements The authors like to acknowledge ONR through the MURI Center (CAMP) and NSF for support.

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