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Optical gain at room temperature in PPV-related materials

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Abstract

Recently π-conjugated semiconductor polymers have been proposed as laser-active media. In order to achieve lasing, it is essential to observe optical gain in these materials. By using nanosecond pulses from a Q-switched Nd:YAG laser and the variable stripe length (VSL) method the steady-state photoluminescence (PL) spectra was measured for various soluble alkoxy derivatives of poly(*para*-phenylenevinylene) neat films. The PL emission is red-shifted from the absorption and shows an exponential growth characteristic of a net gain coefficient. The results show evidence of stimulated emission (SE) which is largely due to intrachain singlet exciton recombination processes and its spectral shift is sidegroup dependent. The VSL method resolves the optical gain spectra as well as its shape in the visible spectral range. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

In the last years conjugated polymers have stimulated the research activities in developing efficient electroluminescent devices [1]. However, nowadays π-conjugated semiconductor polymers have become interesting materials because they combine the optical and electronic properties of semiconductors with the ease of processing and the mechanical properties of polymers [2,3]. Being promising material for new solid-state lasers, due to their strong photoluminescence (PL) efficiency, which can be chemically tuned to cover the complete visible spectral range [4,5]. This strong PL emission normally is red-shifted with respect to the broad absorption band and stimulated emission (SE) is expected during the lifetime of the photoexcited states in this spectral region [6]. In order to achieve lasing, it is essential to observe optical gain in the material.

Ultrafast recombination processes of the photoexcited states in these polymers are well known (few ps) [7–9]. Many authors have studied the exciton dynamics (ps resolution) [10], and the factors influencing the SE [11] and/or photoinduced absorption (PA) [12], difficulties in the observation of SE in PPV films have contributed to the controversy [13]. However, the exact spectral signatures of photo-excitations in PPV have remained unclear because of their overlapping spectral features in the visible spectral range.

During the chemical processing the alkyl sidegroups are added to improve the PPV solubility and the polymer aggregation. As a consequence, the electronic structure of the polymer changes due to a different conjugation length. Since the PL emission is mainly produced from long conjugation segments, the PPV derivatives give rise to higher densities of intrachain emitting species for lasing. However, the alkyl radicals can also provoke conjugation breaks: then a transfer of charge

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inside the polymer dissociates the exciton and quenches the PL. Another signature comes from the photo-oxidation [14] responsible for quenching the PL by carbonyl substitution of the vinyl double bound [15].

This work presents evidence of optical gain due to SE using the variable stripe length (VSL) method. In these experiments, the steady state of the PL intensity is measured as a function of the length of a focused stripe on the sample. The results show the first direct evidence of the spectral shape of the optical gain in the visible spectral region and provide values for the gain coefficient for several alkoxy substitute PPV films.

2. Experimental

Gain measurements were performed in several PPV-related materials, using methoxy ethyl-hexyloxy (MEH), bi-ethyl-hexyloxy (BEH) and methoxy (M) as alkyl groups. The elemental unit structure of the polymer is shown in the inset of Fig. 1(a). In this case the liquid solution of the polymer was dissolved in xylene to reach desirable viscosity and then was spin coated on silica glass substrates to obtain ~100 nm polymer film thickness.

The active part of the sample was photo-excited by the higher harmonics of a Q-switched Nd:YAG laser (6–8 ns pulses at 10 Hz repetition rate). MEH and BEH–PPV samples were photo-excited with the 532 nm line, whereas for the sample M–PPV the line of 355 nm was used. In the VSL experiment, the laser beam is focused on the sample by using a cylindrical lens to form a narrow rectangular stripe. by means of a telescope, the beam is focused on the sample with dimensions of 56 μm width and 0.06–2 mm variable length (Table 1). The emitted light (i.e.,

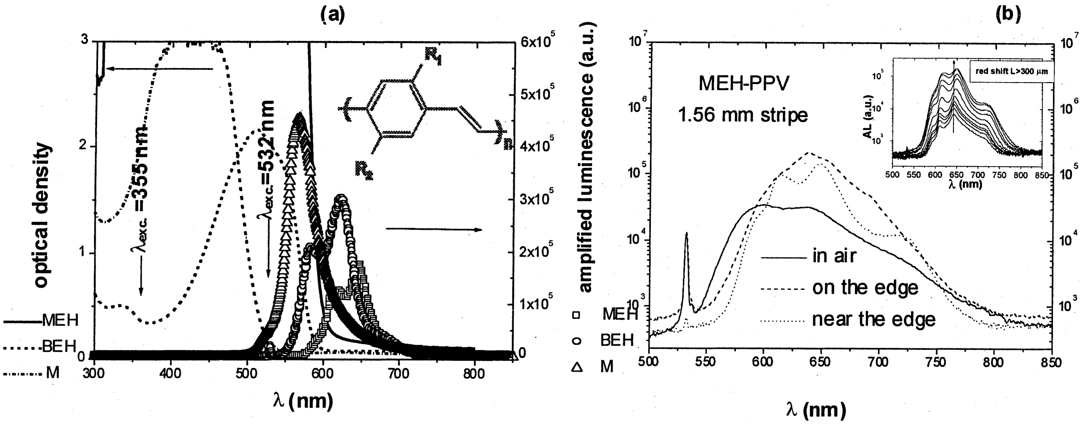

Fig. 1. PL signal of PPV related materials (a) with its linear absorption and (b) photo-oxidised MEH–PPV for comparison. PPV molecular unit is shown in the inset of (a). PL growth when increase the stripe length and the red-shift of the signal are shown in the inset of (b).

Table 1
Experimental parameters and results for the studied PPV polymers

Polymer sample	Stripe lengths (μm)	Excitation energy (kW cm^{-2})	PL peak (nm)	Gain coefficient (cm^{-1})
MEH–PPV	56–2123	740	660	71
BEH–PPV	56–1564	267	625	148
M-PPV	56–727	88	571	273

amplified luminescence) at right angles in the direction of the stripe, is collected for different stripe lengths. The laser spot on the sample was carefully positioned to avoid the scattering from the edge roughness of the glass substrate. In all cases PL measurements were performed with the sample kept in vacuum (5×10^{-3} Torr) at room temperature. The PL of the MEH–PPV sample was also measured at atmospheric pressure in air in order to know the photo-oxidation process on the PL emission.

In these experimental conditions the PL intensity along the focus axis is related with the optical gain by the relationship [16]:

$$I_{\mathrm{AL}} = \frac{I_{\mathrm{SP}}}{gL}(\mathrm{e}^{gL} - 1), \qquad (1)$$

where I_{AL} and I_{SP} are the amplified and spontaneous emission, respectively. The net gain coefficient is g and the experimental variable stripe length is L. The gain coefficient and spontaneous emission can be calculated by fitting the experimental data to Eq. (1) using the Levenberg–Marquardt algorithm [17]. However, the gain saturation limits the stripe length domain L for which the amplification of the spontaneous emission grows exponentially. In this case, saturation effects seem to be produced for $gL > 2$ faster than in bulk semiconductors ($gL > 5$) [18] but similar to semiconductors quantum dots ($gL > 2$) [19].

3. Results and discussion

Fig. 1(a) shows the absorption bands and the PL yield for the different alkoxy groups showing a spectral shift (Table 1, column 3), indicating the produced change in the conjugation length of the polymer chain. This fact opens the possibility of chemical tailoring to tune the band gap along the visible spectrum. This result indicates that lower excitation produces higher density of emitting species, due to a lesser efficiency to dissociate the excitons and lowering the species that quench the PL. In this way, Fig. 1(b) shows the PL signal of the photo-oxidized MEH–PPV sample. The formation of a carbonyl ($\mathrm{C=O}$) in the vinyl double bound breaks the conjugation pathway of the exciton along the polymer chain, that can be appreciated by the decrease of the PL efficiency at lower energies. Moreover, the observed red-shift from the absorption band reveals a migration of excitons before recombination. This suggests that PL yield is mainly due to radiative decay of intrachain singlet exciton species. The inset of Fig. 1(b) shows the growth of the PL when the stripe length is increased and the red-shift of the signal when $L > 300$ μm. This effect is due to the saturation process and the luminescence is no longer amplified. The signature of the phonon replica that strongly influence the optical gain spectra is also apparent on the PL signal.

Fig. 2 shows the results of the fitting from Eq. (1) for some wavelengths, which correspond to the spectral position of the maximum gain coefficient, as can be seen gain saturates for $L > 400$ μm for MEH and BEH–PPV samples. However, for M-PPV with better efficiency, gain saturates for $L > 200$ μm, as is shown in the inset of Fig. 2. The fit at 720 nm (open square) corresponds to $g = 0$, that is only spontaneous emission. The higher the optical gain coefficient, the faster gain saturation was observed. Then, using ns-pulses which take too long to resolve the emissive processes in these polymers, is not possible to observe the line narrowing of the PL signal that it is essential for lasing. However, gain dynamic measurements, on BEH–PPV similar sample using 100 fs-pulses from a colliding pulse mode-locking (CPM) laser have shown such line narrowing. An initial 200 nm broad luminescence evolves into a 9 nm narrow peak characteristic of the SE [20].

On the other hand, the better fit of the gain spectra is accomplished on the high energy side; this result can be related with the PA band observed by several authors on the lower energy side [10,11]. This result could explain the loss of gain observed in the photo-oxidized MEH–PPV (right-hand side of Fig. 2) and some blue-shift of its PL signal (Fig. 1(b)). As a consequence of the above results, the shape of the gain spectrum will shows similar features as the PL one, as the main signature of the SE. The plot in Fig. 3 corroborates this

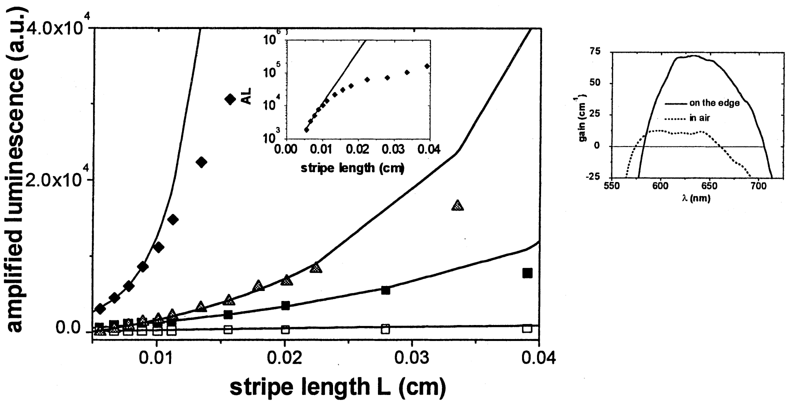

Fig. 2. Fit results from Eq. (1) using 8 stripe lengths, 720 nm (open square) and 624 nm (solid square) from MEH–PPV, 624 nm (solid triangle) from BEH–PPV and 565 nm (solid diamond) from M–PPV. The former is plotted in semilog scale in the inset. The next to the Fig. 2 show the loss of gain in the photo-oxidised MEH–PPV.

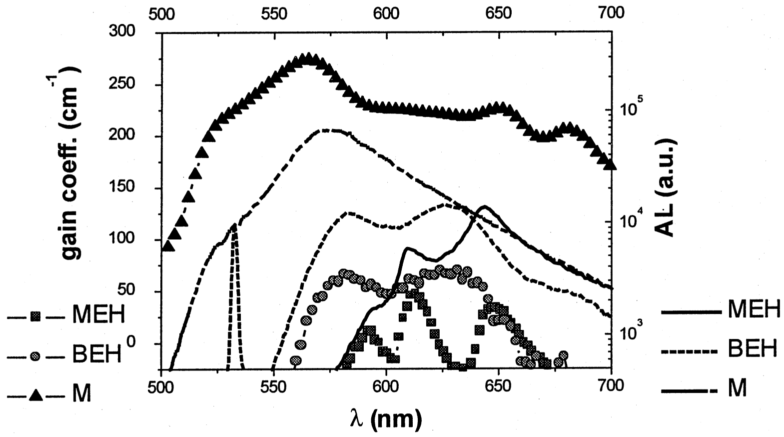

Fig. 3. Gain spectra (left axis and symbols) and PL signal (right axis and lines) for the studied polymers. Laser scattering is apparent in the BEH PL signal at 532 nm.

behavior for the PPV polymers, where the PL run parallel to the gain spectra, accounting for the population inversion responsible for the SE to achieve lasing. Some $g < 0$ is observed in the MEH sample indicating the absence of such inversion.

Then, the VSL method reveals two important conclusions. Firstly, it demonstrates the increase of the gain coefficient for different alkoxy radicals (Table 1, column 4). Secondly, it opens the possibility to chemically control the photo-excited radiative species by tuning the polymer band gap by sidegroup substitution.

4. Conclusions

This work presents for the first time the shape and spectral range of the optical gain for several polymers of the PPV family, by using the VSL method that controls the excitons density, which otherwise are difficult to measure because of the fast gain saturation effects in these high efficient polymers. Gain spectra show the same signature as PL emission corroborating the production of SE. The results confirm the potential application of these polymers as excellent candidates for solid-state lasers, whose band gap can be chemically tuned.

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