Ultrafast studies of stimulated emission and gain in solid films of conjugated polymers

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Abstract

The recent discovery of gain narrowing in conjugated polymers has placed new emphasis on understanding the details of stimulated emission (SE) and gain in these plastic laser materials. In this Letter, the results of ultrafast SE and photoinduced absorption (PA) measurements on films of poly(2-butyl-5-(2'-ethyl-hexyl)-1,4-phenylenevinylene) (BuEH-PPV), a conjugated polymer that demonstrates gain narrowing above threshold, are presented. The ≈ 60 ps SE gain decay time of BuEH-PPV is significantly longer than that of most other conjugated polymers, allowing ample time for lasing to occur. We argue that the existence of gain is limited by a dynamic blue-shift of the PA resulting from interchain interactions.

The photophysics of conjugated polymers is of current interest because the fundamental nature of the primary photoexcitations in this novel class of semiconductors is poorly understood and because of the potential of these materials for applications in lasers and electroluminescent devices. Many conjugated polymers exhibit relatively high photoluminescence (PL) efficiencies with emission that is shifted sufficiently far from the absorption edge that self-absorption is minimal. In such a case, stimulated emission (SE), essential to the development of lasers, would be expected throughout the lifetime of the excited state. Ultrafast spectroscopic studies of poly(phenylene vinylenes) (PPVs) [1–6] and poly(paraphenylenes) (PPPs) [7–9] have revealed that SE gain is readily observed in solutions and dilute blend films; in neat solid films, however, SE gain was either not observed or decayed within at most a few ps. The absence of SE gain results from strong photoinduced absorption (PA) which overwhelms the SE in neat films, but not when the polymer chains are isolated in solution or in dilute blends [1].

The exact nature of the sub-gap PA in conjugated polymers has been a subject of debate; the PA has been assigned to diverse species such as singlet excitons, triplet excitons, individual polarons, and interchain bound polaron pairs (spatially indirect excitons) [10–13]. Whatever the origin of the PA, the absence of observable SE implies that the excited medium does not exhibit gain. Without gain, poly-

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mer lasers and solid state polymer laser diodes are not possible.

The recent observation of lasing in films of conjugated polymers [14–16] demonstrates, however, that these materials can exhibit gain in the solid state without need for dilution. The gain narrowing and other signatures of lasing seen in these experiments depend on two critical factors: the existence of gain from stimulated emission, and confinement of the emitted photons in the excited region of the film. Photon confinement can be provided by one of several means: multiple scattering from titanium dioxide nanocrystals [14], planar waveguide structures [15], or microcavities [16]. Additional work is needed to determine what factors control the magnitude and lifetime of the SE gain in this new class of laser materials, and to reconcile the observation of lasing with the earlier ultrafast studies [1–10], which showed no significant SE gain.

In this Letter, we present the results of femtosecond spectroscopic studies on poly(2-butyl-5-(2'-ethyl-hexyl)-1,4-phenylenevinylene) (BuEH-PPV), a semiconducting polymer in which gain narrowing has recently been demonstrated [15]. We find that in neat solid films of BuEH-PPV (at room temperature) SE gain persists for over 60 ps, providing ample time for the occurrence of gain narrowing and lasing. We discuss the possibility that the discrepancy between the ≈ 60 ps SE gain decay time and the ≈ 900 ps decay of the PL could result from excitation-intensity dependent effects, and then argue that the shorter SE time is due to a dynamic blue-shift of the PA which causes the PA to mask the SE at longer times. The relaxation dynamics of the PA are different from those of the SE and PL, implying that the PA and SE/PL in these materials result from distinct interchain and intrachain electronic excitations formed separately upon photoexcitation.

Femtosecond pump–probe experiments were performed using the second harmonic of an amplified CPM laser (310 nm, ≈ 100 fs, 0.25 μJ, 1 kHz) to excite the sample and a mechanically delayed white-light continuum generated from the remaining fundamental light to probe the spectral dynamics. For the ≈ 500 μm spot size used here, the excitation density is $\approx 10^{19}$ cm^{-3}. Spectral signals recorded on a CCD array were double-normalized utilizing signal and reference probe beams both with and without the

pump light, as described previously [17]. The data were corrected for a ≈ 2 fs/nm chirp on the continuum (with all reflective optics in the delay line) which was measured assuming an instantaneous rise of the PA of diphenylbutadiene in hexane. The magnitudes of the PA and SE signals at zero time delay ($\approx 10\%$ $\Delta T/T$) were linear with pump intensity. The relative polarization of the pump and probe light was set to the magic angle. Films of BuEH-PPV, synthesized as described elsewhere [18], were drop-cast from o-dichlorobenzene with ≈ 1 μm thickness on sapphire substrates in a N_2 atmosphere (glass substrates led to problems with sample heating under fs UV excitation). The samples were placed immediately in an optical cryostat and kept under dynamic vacuum (≈ 2 mTorr) during the experiments.

BuEH-PPV has such a high luminescence efficiency (PL quantum yield for 430 nm cw excitation is 0.62 in films and 0.75 in tetrahydrofuran solution [18]) that the number of luminescence counts detected on the CCD was greater than the number of counts from the weak continuum probe light in the emission region (500–575 nm), a situation where small fluctuations in the pump intensity produces background changes which are large on the scale of the photoinduced signals. Thus, the SE data (cf. Fig. 2b below) were triple-normalized by rapidly scanning the delay stage to a time before $t = 0$, thereby providing a reference for the luminescent background for each data point. The delay time in physically moving the stage produced better normalization for early time delays and resulted in poorer S/N for delays greater than ≈ 50 ps. Longer time PL measurements used a streak camera with a ≈ 25 ps instrument response and 440 nm fs pulsed excitation from the second harmonic of an unamplified Ti:Sapphire laser.

Fig. 1 presents the ground state absorption (dashed curve), PL (solid curve), and molecular structure of BuEH-PPV. The absorption band (onset near 500 nm) and PL spectrum are similar to those of unsubstituted PPV, indicating that the alkyl side-groups added to improve solubility do not significantly alter the electronic structure. Thus, we believe the results presented here are general to the class of PPV-related materials. The time dependence of the spectrally integrated PL is shown in Fig. 2a; the thin solid line is a fit to the instrument rise and a single

exponential decay with a time constant of 914 ps. The high PL quantum yield and correspondingly long PL decay time compared to other substituted PPVs are likely the result of reduced interchain interactions caused by the presence of the alkyl side-chains [19]. The measured PL decay and quantum yield predict a radiative lifetime of ≈ 1.5 ns for this material. This prediction is consistent with radiative lifetime estimates for several PPVs, and suggests that the emission has little, if any, contribution from aggregate species [20].

The gain spectrum and transient absorption spectrum of BuEH-PPV films immediately following photoexcitation are displayed as the circles in Fig. 1. In the 520–620 nm region, the probe undergoes an increase in transmission, corresponding to strong SE gain. To the red of 620 nm, the nascent excited state spectrum shows a broad PA extending well into the near IR. Although qualitatively similar to that observed in films of other conjugated polymers [1–11], the PA is both broader and red-shifted in BuEH-PPV. This difference likely originates from the decreased interchain interactions in BuEH-PPV compared to other substituted PPVs. Also unlike that observed in other conjugated polymers, the nascent excited state spectrum of the BuEH-PPV film is very similar to that observed for isolated BuEH-PPV chains in solution.

The most striking feature of Fig. 1 is the strong SE gain between the absorption edge and 620 nm.
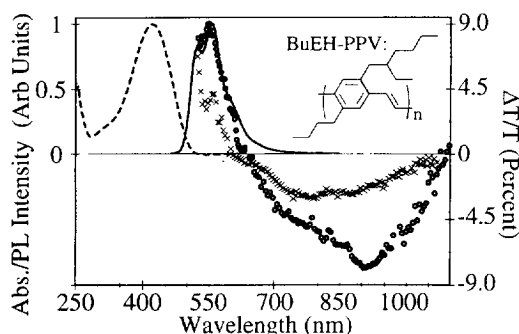

Fig. 1. Fractional change in probe transmission ($\Delta T / T$) versus photon energy for BuEH-PPV films at 'zero' time delay (circles, right axis) and 30 ps time delay (crosses, right axis) following 310 nm photoexcitation. For reference, the steady-state PL (solid curve, arbitrary units) and absorption (dashed curve, arbitrary units) are also shown. Inset: chemical structure of BuEH-PPV.
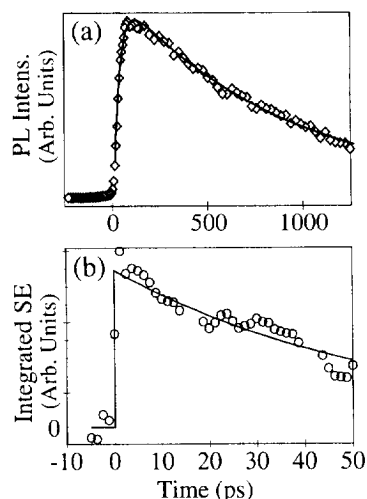

Fig. 2. (a) Spectrally integrated PL decay of a BuEH-PPV film excited at 440 nm recorded on a streak camera (diamonds) and fit to the instrument rise followed by exponential decay (solid curve). (b) Decay of the SE spectrally integrated from 525–575 nm (circles) and fit to 60 ps exponential decay (solid curve).

This result stands in marked contrast to poly(2-methoxy-5-(2'-ethylhexoxy)-phenylenevinylene) (MEH-PPV), where no SE was observed in neat solid films [1,13]. The entire SE band appears instantaneously within our instrumental resolution (≈ 250 fs), and is notably similar to the steady-state PL spectrum. This extremely rapid development of the equilibrium emission spectrum indicates that any relaxation processes associated with formation of the light-emitting excitations (e.g. binding of carriers to form excitons and/or relaxation of the lattice following polaron or exciton formation) occur very rapidly, evidently at times $\leqslant 100$ fs [4,6,21].

Although qualitatively similar to the steady-state PL, careful inspection indicates that the nascent SE gain is slightly blue-shifted from the steady-state PL. The SE undergoes a red shift over the first ≈ 10 ps following photoexcitation. Dynamic Stokes shifts, where the transient PL takes a similar time to evolve into the steady-state PL, have been observed in PPP [8] and other PPV [6,21] derivatives. Previous discussions of the transient PL have assigned the red shift to energy transfer through an inhomogeneous density of states [6]: the above band gap excitation produces luminescent species on both shorter (higher

energy) and longer (lower energy) conjugated segments. Energy transfer from shorter to longer segments during tens of ps would then result in the dynamic PL Stokes shift. This explanation is also plausible for the Stokes shift in BuEH-PPV. We note, however, that structural relaxation processes such as phenyl twisting motions also take place on this time scale and could be responsible for the observed red shift.

The crosses in Fig. 1 show the excited state spectrum of BuEH-PPV 30 ps after photoexcitation. As is clear in this figure, SE gain is still prominent even at this later time delay. The dynamics of the SE gain are explored in Fig. 2, which compares the spectrally integrated decay of the PL (part a, upper panel) to the time evolution of the SE spectrally integrated from 525–575 nm (part b, lower panel). The integrated SE gain data are available only for the first 50 ps, where the normalization procedure described above is effective. The solid curve in Fig. 2b is a single exponential fit to the data with a decay time of 60 ps. The exponential fit is chosen simply to characterize the SE gain lifetime; no physical model is implied. In fact, by the arguments presented below, we expect that the SE gain decay is likely not truly exponential. The lifetime of SE gain in BuEH-PPV, at least 60 ps, is one of the longest observed in any conjugated polymer: In earlier studies of neat films of other PPVs [3–5] and PPPs [7,9], the gain decayed in just a few ps. Recently, a 240 ps SE gain decay was reported for poly(2,5-dioctyloxy-p-phenylenevinylene) (DOO-PPV), another polymer like BuEH-PPV that demonstrates gain narrowing [22].

Basic theory predicts that the time decay of the SE and PL should be the same and equal to the lifetime of the excited state [23]. Why, then, does the SE in BuEH-PPV (although relatively long-lived compared to other conjugated polymers) decay so much more rapidly than the PL (Fig. 2)? One possibility lies in the fact that due to experimental limitations, the excitation densities used in the measurement of the SE decay are several orders of magnitude larger than those employed in determining the PL lifetime. Thus, the discrepancy between the measured PL and SE decay times could actually reflect different excited state lifetimes under the different excitation conditions. Several mechanisms for decreasing the lifetime of the emissive excited species

with increasing excitation intensity are known, including loss of population due to stimulated emission [24] and direct interaction between adjacent excitations (e.g., exciton–exciton annihilation) [7,8,25]. We first consider the intensity dependent mechanisms, and then discuss the possibility that the difference in the PL and SE lifetimes results not from an excitation density effect but from dynamic changes in the spectral overlap between the SE and the PA.

One argument that has been previously proposed to explain changes in the PL lifetime with excitation intensity is exciton–exciton annihilation [7,8,25]. We note, however, that in other PPVs, the effects of exciton–exciton annihilation are only beginning to become significant at the $\approx 10^{19}$ cm^3 excitation densities used in the present pump–probe experiments [25]. Thus, while it is possible that such a mechanism turns on at lower excitation densities in BuEH-PPV, it does not seem likely that this type of concentration-dependent mechanism is consistent with the observed decrease in lifetime of over an order of magnitude (from 900 ps to ≈ 60 ps). Exciton–exciton annihilation would also not explain the non-uniform decrease of the SE band with time (as seen in the transient spectrum at 30 ps delay presented in Fig. 1). In addition, we observe a linear intensity dependence for both the SE signal and the magnitude of the bright fluorescence background in the pump–probe experiment. Finally, stimulated fluorescence depletion experiments on MEH-PPV performed under excitation conditions quite similar to those of our experiments on BuEH-PPV showed no significant decrease in the excited state lifetime [1,13]. Thus, we conclude that exciton–exciton annihilation is not likely as the explanation for the observed difference in the PL and SE decay times.

Another possible mechanism for decreasing the PL lifetime at high excitation intensities comes from loss of population due to stimulated emission, a phenomenon which has been previously observed in dye solutions [24]. In this effect, some of the spontaneously emitted fluorescence passes through an excited region of the sample and stimulates further emission, leading to a loss of population on the time scale over which the light takes to propagate through the sample. Given the short gain lengths recently measured for optically excited BuEH-PPV [15], this type of scenario could explain the observed discrep-

ancy between the measured PL and SE decays. Moreover, this type of effect would be expected to deplete the gain at the peak of the emission maximum prior to the rest of the emission band, consistent with the transient spectrum at 30 ps displayed in Fig. 1. Because of the directional nature of the stimulated emission and its dependence on pumping geometry, an expected signature of this effect would be the measurement of different decay dynamics for different directions of the probe light [24]. However, no changes in lifetime were observed for two different probing geometries. Furthermore, we note that these effects in the dye solutions were only observed at excitation intensities several orders of magnitude higher and in samples several orders of magnitude thicker than those used in our pump–probe experiment, and that no signs of gain narrowing were observed under pulsed fs excitation.

Assuming, therefore, that the lifetime of the excited species remains on the order of 900 ps during the course of fs experiments reported here, then the more rapid SE gain decay *must* result from a competing PA which appears on the ≈ 60 ps time scale in the emissive spectral region. This PA could result either from an excitation which takes ≈ 60 ps to form or from a dynamic blue-shift of the near IR PA which requires ≈ 60 ps to mask the SE. If this is the case, then understanding the origin of this interfering PA is the key to controlling the gain and to lowering the threshold for lasers which use semiconducting polymers as the gain media. The rest of this paper explores the ramifications of this explanation for the difference between the SE and PL decay times.

We begin by exploring the dynamics of the PA. Fig. 3 presents the PA decay dynamics in BuEH-PPV at several probe wavelengths on short (ps) and long (hundreds of ps) time scales. The entire PA appears instantaneously within the time resolution of our apparatus. Within the first 3 ps (part a, left panel), the PA decays uniformly across its spectrum to roughly half its initial value. The PA then shows a wavelength-dependent subsequent decay at longer times (tens to hundreds of ps) and persists to times past 0.5 ns, the longest investigated in this study (part b, right panel). The ≈ 3 ps decay is not readily evident in this longer time scan due to convolution with the much larger step size. The instantaneous appearance of the entire PA suggests that it results
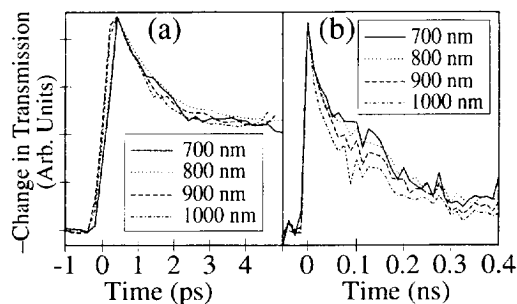

Fig. 3. Spectrally integrated (over 40 nm) PA dynamics of BuEH-PPV films on short (left panel, part a) and long (right panel, part b) time scales for several central wavelengths, normalized to the same maximum amplitude for better comparison: 700 nm (solid curves), 800 nm (dotted curves), 900 nm (dashed curves) and 1000 nm (dot-dashed curves). The y-axis is *negative* fractional transmission change.

from species created directly upon photoexcitation. Thus, triplet absorption is largely eliminated since intersystem crossing takes place at much longer times [10]. The uniformity of the early PA decay reveals that there is no overlap between the PA and the SE at early times: the measured SE gain would show an increase in intensity on the same time scale as the PA decay if the PA and SE spectrally overlapped. This leads to the conclusion that the SE/PL and PA dynamics are unrelated, even in the first few ps following photoexcitation. It is, therefore, natural to assign the SE/PL and at least some of the PA to different electronic species created directly upon photoexcitation.

This assignment of the PA and PL to separate excitations is not new [1,5,9–13], but remains controversial in light of recent proposals that both result from bound intrachain singlet excitons [2,3]. This assignment is based on the fact that for a few polymers, the decay of the PL appears to follow the time derivative of the decay of the PA [2,3]. While it is not clear that such a relationship should even be expected to hold (except in the trivial case of exponential dynamics where the decay is identical to its own derivative), it is evident from Fig. 2 and 3 there is no such relationship between the PA and PL/SE for BuEH-PPV. Moreover, given the rapid ≈ 3 ps change observable in PA, we would have expected to see identical dynamics in the PA and SE if they resulted from the same species (as is the case in

solution) [1,3]. Since the SE in BuEH-PPV does not show the large initial decay present in the PA and the dynamics of the SE/PL and PA differ only in the solid film and not in solution, some fraction of the PA in the film must result from an interchain electronic species (e.g. where opposite charges are on different chains) [1,5,9–13].

The observed PA dynamics (Fig. 3) result from a superposition of contributions from both emissive (intrachain) and non-emissive (interchain) excitations. When the chains are isolated in solution, BuEH-PPV (like most conjugated polymers) shows PA and SE/PL, spectrally separated, which decay with identical dynamics. Thus, the emissive species give rise to excited state absorption which must decay with the same dynamics as the PL. This is also true in solid films: some fraction of the observed PA results from the (intrachain) emissive excitations and hence must decay on the same time scale as the PL. Only the interchain excitations give rise to the difference in dynamics between the SE and PA in the film. We therefore assign the features of the transient spectroscopy of BuEH-PPV films as follows: photoexcitation produces both intrachain and some interchain excitations, the former give rise to the measured SE/PL and some fraction of the PA, and the latter produce the remainder of the PA dynamics. The intrachain excitations are formed hot, cool during the first tens of ps (causing the small dynamic Stokes shift) and then live for ≈ 900 ps (Fig. 2a).

The ≈ 3 ps uniform PA decay is quite similar to that previously observed in a PPP derivative, and has been assigned to an interchain hopping process [9]. It is also possible that this fast decay may reflect some loss of excited population via an excitation-density dependent mechanism like those discussed above, a situation which will be greatly clarified by future intensity-dependent studies. Alternatively, the PA in excited phenyl-substituted polyenes undergoes a uniform initial decay which has been assigned to vibrational cooling [26]. By analogy, the latter could also explain the ≈ 3 ps decay in Fig. 3a.

Over the next ≈ 100 ps, the PA decays more quickly in the red than the blue (Fig. 3b), indicating a dynamic blue-shift. This dynamic blue-shift of the PA easily explains the differences between the '0' ps (circles) and the 30 ps (crosses) transient spectra presented in Fig. 1. During the first 30 ps, the PA

absorption maximum has shifted significantly toward the blue, as has the turnover point where the PA overwhelms the SE. The shape of the SE gain is also altered at these later times as a result of the overlapping PA which masks the longer wavelength portion of the SE more strongly than the shorter wavelength portion. This dynamic blue shift of the PA could likely be the result of structural relaxation that brings the chains on which the interchain excitations reside closer together until their configuration more closely resembles that of other substituted PPV derivatives where the PA overlaps the SE completely even from time zero. Thus, a blue-shift of the PA resulting from interchain relaxation can explain the ≈ 60 ps decay of the SE gain (Fig. 2b).

If this explanation is correct, then these observations provide a prescription for preparing new films of lasing conjugated polymers with longer-lived SE gain. The interchain structure of such films should start with the proper chain separation and orientation so that the interchain PA does not overlap the SE. This occurs naturally in BuEH-PPV as demonstrated by the strong resemblance of the initial PA in films and solutions and the fact that the PA is significantly red-shifted from that observed in other PPVs. Once the chains start in the proper configuration, it is advantageous to avoid any dynamic changes in the interchain structure. This can be accomplished via synthesis by making the polymer sufficiently rigid that structural relaxation around the interchain excitation does not subsequently mask the SE (e.g. using bulky, rigid side-groups or via cross-linking). An alternative method for controlling interchain packing is to vary the solvent from which the films are spin-cast. Recent work has demonstrated gain narrowing from MEH-PPV films spin-cast from tetrahydrofuran [15], while neither lasing nor SE gain are observed from MEH-PPV films cast from chlorobenzene [1,13,15]. Clearly, more work needs to be directed at studying the role of chain packing on both the ultrafast photophysics and lasing behavior of this class of materials.

Finally, we note that none of the above results allow us to comment on the binding energy of either the intrachain species responsible for the SE or the interchain species responsible for PA. We have used the word 'excitation' in the discussion above because the arguments apply equally well whether or not the

excitations are charged polarons or neutral excitons with binding energy large compared to kT.

In summary, we have measured the transient absorption and emission dynamics of BuEH-PPV, a conjugated polymer which shows low-threshold gain narrowing. Unlike most other substituted PPVs, films of BuEH-PPV show strong SE gain, even when pumped significantly above the band gap. The differences in the decay dynamics of the PL/SE and PA imply that they arise from distinct intrachain and interchain excitations, respectively. Even though the PL of BuEH-PPV takes ≈ 900 ps to decay, the SE decays in ≈ 60 ps because of a dynamic blue-shift of the PA on this time scale. It is this relatively long persistence of the SE gain that allows BuEH-PPV to serve as the low-threshold medium in optically pumped polymer lasers [15]. With the understanding that the gain is controlled the interplay between the PA and SE, further increases in SE gain lifetime and magnitude should be possible, leading to lower lasing thresholds and eventually to the development of polymer diode lasers.

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