

Interchain Excitations in Conjugated Polymers

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The luminescence quantum yield is dramatically increased upon going from films to dilute blends or solutions of a soluble phenylenevinylene polymer. Nevertheless, direct measurements of the decay dynamics of the emissive excitons show that their lifetimes are not very different. Separation of the polymer chains suppresses interchain exciton formation, which otherwise competes favorably with the generation of emissive intrachain excitons in films. We discuss the consequences for the design of polymeric systems for optoelectronics.

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The nature of the photogenerated states in quasi-one-dimensional organic semiconductors is of both theoretical [1–3] and practical interest [4,5]. Recent transient absorption and gain measurements have led to the suggestion that spatially indirect excitons (bound polaron pairs) are the predominant species formed upon photoexcitation of poly(*p*-phenylenevinylene) (PPV) films [6,7]. This species is responsible for the large picosecond photoinduced gap absorption and competes with the formation of the emissive singlet excitons which are responsible for PPV photoluminescence (PL) and electroluminescence (EL) [2]. Based on the requirement of a Coulomb attraction sufficiently large to prevent dissociation, it was speculated that the charges comprising the indirect excitons are on adjacent chains rather than conjugation segments of the same chain [7,8].

In the present paper, we report a test of this hypothesis with an experimental comparison of the photoexcitation dynamics in substituted phenylenevinylene polymer films with those of the same polymer in dilute solution and polymer blends. Specifically, we compare the transient photoinduced absorption (PA), stimulated emission (SE), and PL of the soluble polymer MEH-PPV [poly(2-methoxy, 5-(2'-ethylhexyloxy)-paraphenylenevinylene)] [9] in both films and dissolved in chlorobenzene liquid or polystyrene blends. Our results confirm the assignment of the PA in conjugated polymer films to spatially indirect excitons and show that these photogenerated excitations are interchain species which can be eliminated by preventing chain aggregation. As a practical consequence, the PL yield of the films is nearly an order of magnitude lower than that for solutions or dilute blends. The implications for rational design of polymers to be used in EL devices and solid state lasers are discussed. This underscores the need to understand three-dimensional effects in these quasi-one-dimensional materials.

MEH-PPV was prepared by the dehydrochlorination of 2,5-bis(chloromethyl)-1-methoxy-4-(2-ethylhexyloxy)benzene as described by Wudl and Srdanov [10]. Solutions of 3.3 mg of polymer per mL of chlorobenzene were prepared and placed in a 1 mm path

length cuvette. These had absorbance of ~ 2.8 at 520 nm, the excitation wavelength used for our experiments. A polymer solution containing 6.6 mg of polymer per mL of chlorobenzene was used to spin (at 800 rpm) films of approximately 1900 Å on quartz substrates. Blends of dilute MEH-PPV in polystyrene host were prepared using the method of Hagler *et al.* [11]. Picosecond transient absorption and gain data were recorded using an amplified dye laser apparatus described previously [12]. Subpicosecond excitation pulses of 0.2–0.5 μJ at 520 nm and 540 Hz were used in conjunction with a white light continuum probe produced by self-phase modulation in water. The weak probe transmission through the sample was compared with a reference pulse which did not travel through the sample. The temporal delay between pump and probe pulses was regulated by varying their respective path lengths with a mechanical delay stage. Complementary measurements of the emissive exciton dynamics were made by observing depletion of the steady state PL when a strong subpicosecond probe at 605 nm ($\geq 10\times$ the pump fluence) is used to cause stimulated emission. The exciton dynamics are reflected in the fraction of PL depleted ($-\Delta\text{PL}/\text{PL}$) as a function of pump probe delay. The measured value will be independent of sample thickness as long as the sample is optically thin at the probe wavelength, a condition met in our experiments. This new method has the advantage of measuring the emissive excited state dynamics without interference from spectrally overlapped bleaching recovery or excited state absorption and is analogous to previous stimulated emission “dumping” techniques [13,14]. Time-resolved PL measurements on a longer ($\gg 100$ ps) time scale were done by multichannel time-correlated photon counting using a resistive anode array detector [15] with about 100 ps resolution. The excitation source was a synchronously pumped coumarin dye laser excited by the third harmonic of a mode locked Nd:YAG laser and cavity dumped at 4 MHz. All of the data presented are linear in excitation fluence.

Figures 1(a)–1(c) present the transient absorption and gain spectra in the solution, blend, and film. In each case,

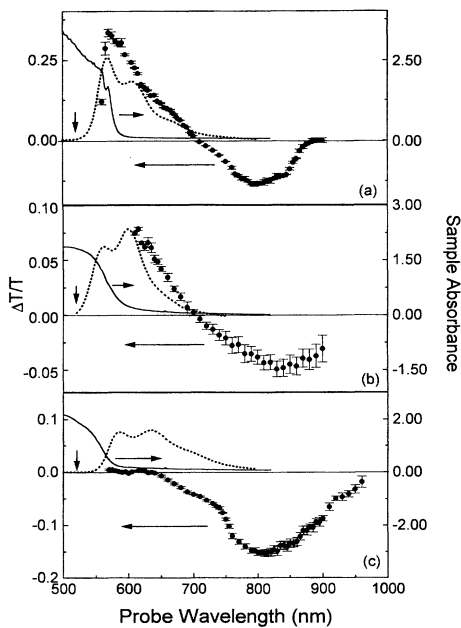


FIG. 1. Time-resolved absorption in MEH-PPV solution, film, and blend. (a) Fractional change in probe transmission $\Delta T/T$ vs probe photon energy at "zero" picosecond pump-probe delay in MEH-PPV solution (\bullet). For reference, the steady state PL (dashed line, arbitrary units) and absorption (solid line, referenced to right axis) spectra are shown. Vertical arrows indicate the excitation wavelength. (b) Data analogous to (a) in MEH-PPV/polystyrene blend. (c) Data analogous to (a) in MEH-PPV film.

there is a large PA in the near infrared (~ 1.4 eV) similar to what is observed in PPV [7,16,17] and methoxy-substituted PPV (M-PPV) films [6]. The solution and blend, however, exhibit a huge increase in probe transmission for wavelengths coincident with the steady state PL spectrum. This occurs in a region with little ground state absorption and is primarily due to probe amplification by stimulated emission of the singlet excitons responsible for PL. The large gain is consistent with observations of photopumped lasing in MEH-PPV [18] solutions. Very little gain is observed at the corresponding wavelengths in the film but the dilute MEH-PPV/polystyrene blend exhibits gain similar to that in the solution. This suggests that diluting blends of emissive polymers in an inert host polymer may be a promising approach to fabricating a photopumped solid-state laser if scattering losses in the host matrix are sufficiently small.

More insight into the reason for the differences between film, blend, and solution is provided by measurements of the decay dynamics of the PA and PL (Figs. 2 and 3). Figure 2 illustrates the transient gain dynamics in solution at several different probe wavelengths. The decay at 690 nm is exponential with ~ 300 ps lifetime, in agreement with that derived from PL measurements of Smilowitz *et al.* [9]. The measured gain dynamics

at bluer wavelengths have a fast (< 10 ps) component in addition, which appears to reflect exciton relaxation. However, a comparison with the transient PL depletion for strong 605 nm probe (Fig. 2) shows that the fast component is, in fact, due to transient bleaching recovery. Even in solution, there must be a fraction of excitations which lead to rapid geminate recombination (i.e., internal conversion to the ground state) prior to forming stable excitons. This rapid internal conversion pathway has been postulated elsewhere as an explanation for the decreasing PL yield at shorter excitation wavelength observed in phenylenevinylene polymers [17], but we believe the dynamics of Fig. 2 to be the first direct evidence.

The blend and film PL depletion are compared with the solution result in Fig. 3. The blend and solution decays are similar with nearly exponential dynamics and lifetime around 300 ps. The film behavior is distinctly different than blend or solution. No SE gain is observed in the film, and the total PL is considerably smaller than that in blend or solution. The emission decay dynamics are also different in that they are nonexponential. This is probably due to increased exciton mobility to quenching defects in the film as has been demonstrated in PPV [19]. The relatively small change in average exciton lifetime cannot, however, account for the large decrease in magnitude of the SE and PL or for the fact that these decreases are observed on a subpicosecond time scale. The difference also cannot be rationalized on the basis of a change in radiative lifetime in going from solution to film because the quantum yield for MEH-PPV emission in solution has been measured by Smilowitz *et al.* [9] to be (55–70)%. To reduce stimulated emission an order of magnitude due to a longer radiative lifetime (smaller emission dipole) in the film would more than double the exciton lifetime while we find it is smaller if anything in the film. These observations require us to invoke a process which competes with the formation of emissive excitons on a subpicosecond time scale in MEH-PPV films.

Our deduction of a separate pathway is corroborated by the data in Fig. 3 that compare the dynamics of the stimulated emission and transient PA documented in Fig. 1. The situation is uncomplicated in blend and solution with the PL and PA decays being exponential and indistinguishable, the PA clearly being due to emissive excitons. We note that the spectral position of this absorption is close to one of those calculated by Leng *et al.* for singlet exciton absorption in PPV [20]. The close correspondence of PA and SE dynamics in solution and blend would tend to rule out large intersystem crossing yields to form triplet states, which are known to absorb as well in this region [21].

In the case of the film, the ratio of PA to SE is at least an order of magnitude higher than in the blend or solution. Moreover, the PA and PL decay nonexponentially, and their dynamics do not match each other as has been

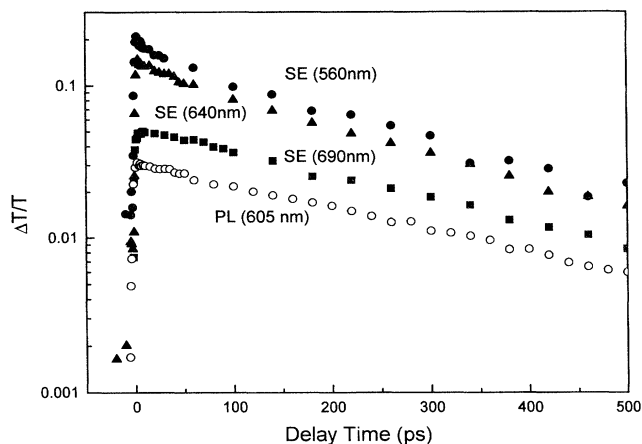


FIG. 2. Transient decay dynamics for MEH-PPV in solution. Stimulated emission decay at several wavelengths (solid markers) compared with PL depletion measurement at 605 nm (open circles) as described in text.

observed in PPV [7,20], monomethoxy-PPV [6], and polythiophene [22] where the PA has been ascribed to a distinct species, spatially indirect excitons (bound polaron pairs) [6,7]. This type of excitation with charge transfer character is typical of aggregated organic molecules, and there is a large literature on exciplex ("excited complex") formation in aromatic crystals [23]. Alternative explanations for the PA such as singlet and triplet excitons, bipolarons, and separated polarons were ruled out in previous work [6,7] on other phenylenevinylene polymers. We believe MEH-PPV films should exhibit similar behavior and that the picosecond PA is also due to spatially indirect excitons. The fact that these do not appear in solution or dilute blends where the polymer chains are isolated suggests that

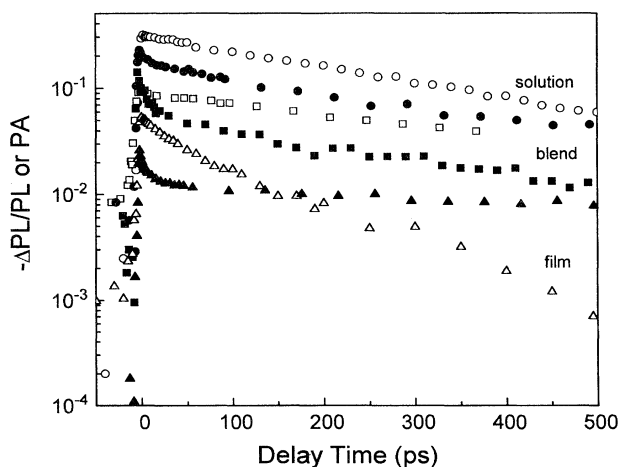


FIG. 3. Comparison of transient decay dynamics for MEH-PPV solution, blend, and film. Decay of PL depletion at 605 nm (open markers) and the PA at 800 nm (solid markers) plotted for film (\blacktriangle), blend (\blacksquare), and solution (\bullet) cases.

these excitons are an *interchain* species. This is consistent with the requirement that the (presumably delocalized) charges forming the indirect excitons be sufficiently close to have large binding energy. If confined on separate conjugation segments of the same chain, the charges would be tens of angstroms apart, whereas adjacent chains are only spaced by a few angstroms. Moreover, the observed absorption has frequency in accord with that calculated by Mizes and Conwell (~ 1.4 eV) for bound *interchain* polaron pairs [8]. The formation of these nonemissive interchain excitons competes with emissive intrachain exciton formation and reduces the gain and PL almost an order of magnitude. This has prescriptive significance for the design of LEDs and platelet lasers to be based on conjugated systems. In particular, dispersing chains in inert matrices or designing ordered polymers with large separations between the electronically active backbones should suppress interchain exciton formation and improve efficiencies. This may be related to the observed enhancement in electroluminescence with increasing alkyl substituent length in poly(3-alkylthiophenes) [24].

Transient PL on a longer time scale (Fig. 4) shows that, while the PL decay in solution is exponential, the PL in the film has a long tail extending to tens of nanoseconds. The film PL spectrum at long delays is, however, identical to that at minimum delay and must also be due to singlet excitons. Clearly, these excitons result from a delayed formation process since it is unlikely that a subset of the excitons would live longer in the film than in solution. Based on the absence of intensity dependence to the dynamics, that delayed formation process is geminate, and we believe it is due to a small amount of reformation of emissive intrachain excitons from the interchain excitons [19,25]. This is qualitatively consistent with the extremely long lifetime to the tail of the film PA and the excitation wavelength dependence of the long-lived tail PL with respect to the early PL [25]. It is also supported by the complete

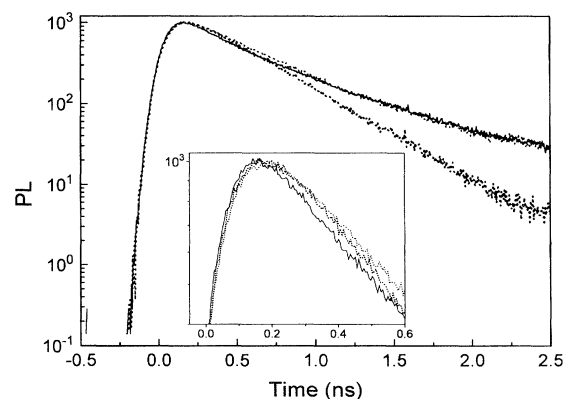


FIG. 4. PL decay dynamics in MEH-PPV solution, blend, and film on a longer time scale. Inset is an expanded view of the first several hundred picoseconds.

absence of such a tail in the solution. We note that while the blend dynamics tend to follow the solution at short times (Figs. 3 and 4, inset), the long tail is also observable in the blend, and we attribute it to small amounts of aggregation. These aggregation effects are also evident in the long tail at the red edge of the blend absorption spectrum and the slight reduction ($\sim 2\times$) of the SE to PA ratio relative to solution. The slow recombination behavior may also depend on the aggregate size since we are unable to exactly model the blend PL from a simple linear combination of the solution and film results. As an aside, we point out that the essentially exponential behavior for the PL decay observed in blend and solution could not result from intrachain diffusive recombination of separated carriers, which has more complex dynamical behavior as is observed for charge soliton pair recombination in *trans*-polyacetylene [26]. This observation argues for a substantial binding energy E_b for MEH-PPV emissive excitons ($E_b \gg kT$), at least in isolated chains.

In summary, we have compared the film, and solution and dilute blend behavior, of the soluble conjugated polymer MEH-PPV. With isolated chains dissolved in chlorobenzene or a polystyrene host matrix, the picosecond PL, stimulated emission, and PA dynamics match and obey a simple exponential decay law. All are due to intrachain singlet excitons, which are formed in high quantum yield. In films where the chains aggregate, the PL and gain are decreased by an order of magnitude while the PA decay no longer matches that of the PL. These observations reflect the fact that PL and PA are due to different species, the latter being caused by a large quantum yield (perhaps as high as 0.9) [7] of nonemissive excitons analogous to charge transfer exciplexes in organic crystals. These do not appear in solution because the charges comprising them are on separate chains. We demonstrate dramatic enhancement of emission yields compared to those of a neat film when interchain charge transfer is reduced by dilution of conjugated polymers in blends. In fact, quantitative comparison of gain in solution and blends indicates that the blends should be capable of photopumped laser action. We predict similar enhancement of emission yields by chemical design of relatively crystalline emissive polymers with large interchain spacers. To this end, theoretical work which considers the three dimensionality of conjugated polymers in films is required to better understand the energetics of these interchain excitons and its dependence on chain packing.

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