ELSEVIER

Synthetic Metals 84 (1997) 663-664

SYNTHETIC METALS

# Observation of stimulated emission and ultrafast transient absorption dynamics from a novel alkyl-substituted PPV

Benjamin J. Schwartz,[a] Fumitomo Hide, Mats R. Andersson,[b] Alan J. Heeger

*Institute for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, CA 93106-5090, USA*

[a]Permanent address: *Department of Chemistry and Biochemistry, University of California , Los Angeles, CA 90095-1569, USA*

[b]Permanent address: *Chemistry Department, Chalmers Inst. of Tech., Göteborg, Sweden*

**Abstract**

Ultrafast transient absorption, stimulated emission (SE), and photoluminescence (PL) measurements were performed on solid films of the conducting polymer: poly[2–butyl–5–(2'–ethyl–hexyl)–1,4–phenylenevinylene] (BuEH-PPV). The ground state absorption and luminescence of BuEH-PPV are similar to those of unsubstituted PPV, indicating that alkyl substitution does not significantly alter the electronic structure of the ground state. The PL lifetime and PL quantum yield of BuEH-PPV, however, are ≥ 900 ps and over 0.6, respectively. These numbers are nearly 3 times longer and higher than those for unsubstituted PPV. Moreover, BuEH-PPV exhibits a strong, relatively long-lived SE (≥ 60 ps). The SE decays more quickly than the PL due to an interfering photoinduced absorption which undergoes a dynamic blue-shift to mask the SE at later times. These observations taken together offer a prescription for controlling the excited state electronic structure of conjugated polymers, and open the possible production of optically or electrically pumped solid polymer lasers.

*Keywords:* time-resolved fast spectroscopy; photoinduced absorption spectroscopy; stimulated luminescence; photoluminescence; poly(phenylene vinylene) and derivatives; lasers

Although many conjugated polymers are highly luminescent, the development of polymer lasers has been hindered by the lack of stimulated emission (SE) in these materials. Ultrafast spectroscopic studies have revealed that SE is readily observed in polymer solutions and dilute blend films; in neat solid films, however, SE is either not observed or decays within at most a few ps.[1-4] The absence of SE results from a 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, clearly the result of interchain interactions.[1]

In this paper we present the results of femtosecond spectroscopic studies on a new semiconducting polymer, poly(2–butyl–5–(2'–ethyl–hexyl)–1,4–phenylene vinylene) (BuEH-PPV). We find that SE in neat solid films of BuEH-PPV at room temperature persists for over 60 ps, making this, to our knowledge, the longest SE lifetime observed for any conjugated polymer. We discuss the implications for the possible production of solid-state polymer laser diodes.

Femtosecond pump-probe experiments were performed using the second harmonic of an amplified CPM laser (310 nm, ~100 fs, 0.3 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. Films of BuEH-PPV, synthesized as described elsewhere,[5] were drop-cast from *o*-dichlorobenzene with ~1 μm thickness on sapphire substrates in a $N_2$ atmosphere. The samples were placed immediately in an optical cryostat at room temperature and kept under dynamic vacuum (~2 mTorr) during the experiments.

Fig. 1 presents the ground state absorption (dashed curve), photoluminescence (PL) (solid curve), and molecular structure of BuEH-PPV. The inset in Fig. 1 shows the time dependence of the spectrally integrated PL measured on a streak camera; 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 (0.62

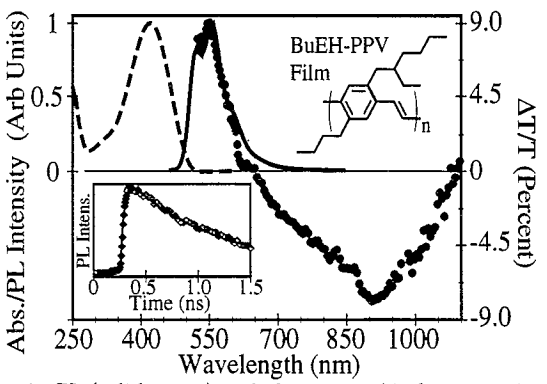


Fig. 1. PL (solid curve) and absorption (dashed curve) (arb. units); fractional change in probe transmission at "0" delay (circles, right axis). Inset: PL decay (symbols) and fit (solid).

in films, 0.75 in solutions) 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 bulky alkyl side-chains.[6]

The gain spectrum and transient absorption of BuEH-PPV immediately following photoexcitation are displayed as the open circles in Fig. 1. In the 520-620 nm region, the


*PII* S0379-6779(96)04098-2

probe undergoes an increase in transmission, corresponding to strong SE gain. To the red of 620 nm, the nascent excited state spectrum consists of a broad PA extending well into the near IR. Although qualitatively similar to that observed in other conjugated polymers,[1–4] the PA is broader and is red shifted in BuEH-PPV. This difference is also likely related to the decreased interchain interactions in BuEH-PPV compared to other substituted PPVs.

Fig. 2 displays the early time spectral dynamics of the SE; the SE undergoes a red shift over the first ~10 ps following photoexcitation. Similar dynamic Stokes shifts,

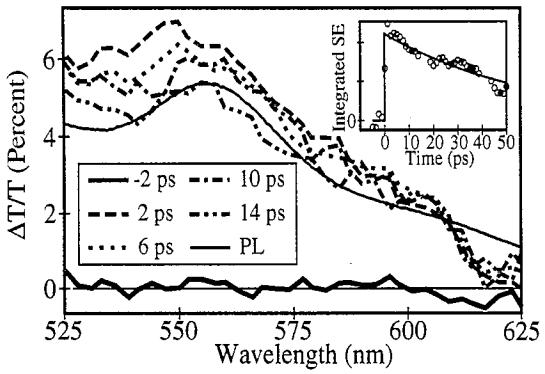


Fig. 2. Early Time SE dynamics of BuEH-PPV following 310 nm photoexcitation. The steady state PL (thin solid curve, arb. units) is shown for reference. Inset: Integrated SE decay.

where the transient PL takes a similar time to evolve into the steady-state PL, have been observed in other conjugated polymers,[7,8] but this is the first observation of this phenomena in a semiconducting polymer via SE. Previous discussions of the transient PL have assigned the red shift to energy transfer through an inhomogeneous density of states:[7] the above band gap excitation produces luminescent species on both shorter (higher energy) and longer (lower energy) conjugated segments. Energy transfer from the shorter to longer segments during tens of ps would then result in the observed dynamic PL Stokes shift. This explanation is certainly plausible for the observed Stokes shift in BuEH-PPV. However, structural relaxation processes such as phenyl twisting also occur on this time scale and could be responsible for the observed red shift.

The inset in Fig. 2 displays the time evolution of the SE, spectrally integrated from 525-575 nm. The solid curve is a single exponential fit to the data with a decay time of 60 ps. *This represents the longest SE decay time observed in a conjugated polymer by nearly an order of magnitude:* the SE observed in neat films of other polymers decays in just a few ps.[1-4] Measurements of the short-lived SE in PPV showed that the SE decay time decreased as the pump energy was increased above the band edge, and that the SE completely vanished for sufficiently blue excitation.[4] For the BuEH-PPV experiments reported here, the 4.0 eV photon energy of the pump light is nearly 1.5 eV larger than the band gap. Thus, if BuEH-PPV behaves similarly to PPV as expected from their similar electronic structures, the SE decay time should be much longer than 60 ps for near band edge excitation.

Why does the SE in BuEH-PPV (although relatively long lived compared to other conjugated polymers) decay so much more quickly than the PL? Since the excited states that produce the PL live for 900 ps, the more rapid SE decay must result from an interchain masking PA which appears on the 60 ps time scale in the emissive spectral region. Investigation of the near-IR PA decay dynamics shows a clear blue-shift: the PA decays more quickly in the red than the blue.[9] Photoexcitation on the initially separated polymer chains produces the red shifted PA, but then excited state interchain interactions bring the chains closer together, causing the blue shift of the PA which covers the SE (as is the case at early times in other conjugated polymers). The use of bulky, rigid side groups should reduce interchain interactions over the entire excited state lifetime and thus improve the SE.

In summary, we have measured the transient absorption and emission dynamics of a new conjugated polymer, BuEH-PPV. Unlike other substituted PPVs, room temperature films of BuEH-PPV show strong SE, even when pumped significantly above the band gap. 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. This relatively long SE time has important implications for the construction of polymer lasers. Recent work has demonstrated lasing from conjugated polymer films via photon confinement by the introduction of scatterers.[10] Since the SE time in such scattering media is usually on the order of tens of ps, a material like BuEH-PPV could be incorporated directly into a scattering polymer laser diode without need for dilution.[11]

Acknowledgment: This work was supported by the National Science Foundation. M.R.A. thanks the Swedish Natural Science Research Council for support. The authors thank Dr. U. Lemmer for many valuable discussions, and Scott Crooker for assistance with the streak camera measurements.

## References

[1] M. Yan, L. J. Rothberg, E. W. Kwock and T. M. Miller, *Phys. Rev. Lett. 75*, 1992 (1995).
[2] W. Graupner, G. Leising, G. Lanzani, M. Nisoli, S. De Silvestri and U. Scherf, *Phys. Rev. Lett. 76*, 847 (1996).
[3] T. Pauck, R. Hennig, M. Perner, U. Lemmer, U. Siegner, R. F. Mahrt, U. Scherf, K. Müllen, H. Bässler and E. O. Göbel, *Chem. Phys. Lett. 244*, 171 (1995).
[4] M. Yan, L. J. Rothberg, B. R. Hsieh and R. R. Alfano, *Phys. Rev. B 49*, 9419 (1994).
[5] M. R. Andersson *et al.*, manuscript in preparation.
[6] E. G. J. Staring, R. C. J. E. Demandt, D. Braun, G. L. J. Rikken, Y. A. R. R. Kessener, T. H. J. Venhuizen, H. Wynberg, W. ten Hoeve and K. J. Spolestra, *Adv. Mat. 6* 934 (1994).
[7] R. Kersting, U. Lemmer, R. F. Mahrt, K. Leo, H. Kurz, H. Bässler and E. O. Göbel, *Phys. Rev. Lett. 70*, 3820 (1993).
[8] G. R. Hayes, I. D. W. Samuel and R. T. Phillips, *Phys. Rev. B 52*, R11569 (1995).
[9] F. Hide, B. J. Schwartz, M. A. Diaz-Garcia and A. J. Heeger, *Chem. Phys. Lett, 256*, 424 (1996).
[10] B. J. Schwartz, F. Hide, M. A. Diaz-Garcia and A. J. Heeger, submitted.
[11] F. Hide, M. Diaz-Garcia, B. J. Schwartz, M. Andersson, Q. B. Pei and A. J. Heeger, submitted.