Photoexcitations in polythiophene at high pressure

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We report optical-absorption, photoluminescence (PL), and picosecond photoinduced absorption (PA) decay in films of poly-3-hexyl-thiophene at pressures up to 80 kbar. The spectral bands redshift non-linearly with pressure and the PL intensity decreases markedly. Thermochromic transitions are completely inhibited at pressures as low as 14 kbar. The picosecond recovery of the PA decay at high pressure is similar to that of unpressed polythiophene, but has a power-law exponent consistent with more ordered chains at high pressure. These effects suggest changes with pressure in the chain conformation and in the electronic polarizability; no changes in the interchain transfer integral are observed.

I. INTRODUCTION

The unique properties of conjugated polymers such as polyacetylene $(CH)_x$ and related polythiophene (PT) are manifestations of their quasi-one-dimensional (1D) nature.[1] But the influence of neighboring chains may nonetheless play a key role. Recent experiments suggest that neighboring chains may influence the electronic states through (1) the conformational shape of the chain,[2] (2) coupling of dipolar fluctuations[3] (the "solvent effect"), or (3) covalent interchain coupling[4] that allows transfer of the excitation through the interchain transfer-matrix element $t_\perp$.

Although intrachain excitations are the dominant photoexcitations, interchain coupling appears to be important to the survival of long-lived photoexcitations in both $(CH)_x$ (Ref. 5) and PT.[6] Three-dimensional coupling is, of course, important to conductivity studies,[7] since transport over macroscopic distances requires carriers to hop from one chain to another. Recent theoretical studies[8] show that interchain coupling in $(CH)_x$ can destablize 1D excitations such as polarons.

Pressure studies in $(CH)_x$ have focused on the possibility of increasing the interchain coupling $t_\perp$. Optical absorption (OA) studies show a redshift and broadening of the absorption band with increased pressure.[4(a)] Raman-scattering line shapes also broaden under pressure and are accompanied by a decrease in scattering cross section.[9] The results in $(CH)_x$ are explained as an increase in $t_\perp$ with increasing pressure, with very little change in the 1D gap parameters.

Polymers with large sidegroups such as polydiacetylenes (PDA) are not expected to have significant interchain coupling, yet they also show a redshift in OA with pressure.[3] The most common model[3] proposed is that the decrease in electronic energies arises from the "solvent" or "gas-to-crystal" effect familiar in the study of molecular crystals, in which dipole-dipole interactions with the surroundings lower the excited-state energy relative to

the ground state. These interactions increase as the density increases with pressure.[3]

Here we concentrate on soluble poly-3-hexyl-thiophene (P3HT), which has sidegroups of intermediate size. Yoshino *et al.*[2] have recently measured OA and photoluminescence (PL) in polythiophene films and solutions up to 9 kbar. They observed redshifts of the spectral bands in both OA and PL, as well as changes in the PL intensity; they attributed the effects to conformational changes.

In this paper we present OA and PL studies, as well as picosecond photoinduced absorption (PA) in P3HT at pressures up to 81 kbar. We see effects suggestive of both conformational and dipolar coupling changes under pressure, but no evidence of significantly increased covalent interchain coupling $t_\perp$.

II. EXPERIMENT

Films of poly-3-hexyl-thiophene (P3HT) were cast from solution in chloroform on 12-μm Mylar sheets. Small pieces of uniform film thickness (about 2000 Å) were cut to fit in the gasketed chamber of a Piermarini-Block diamond anvil cell. Deoxygenated water was used as the quasihydrostatic pressure medium because in alcohols the samples decomposed upon laser illumination. From our ruby fluorescence linewidths (as in other studies[10]), the pressure inhomogeneity in water was only about 5% at 70 kbar.

An argon laser was used to excite the PL. Transmitted PL was collected by a fiber bundle placed against one of the external diamond faces. The bundle terminated as a line at the entrance slit of a $\frac{1}{4}$-m monochromator. PL spectra were corrected for the grating, fiber, and Si detector optical response, but not for sample transmission.

For OA measurements, the monochromator was illuminated by a tungsten lamp; a 100-μm pinole at the exit of the monochromator was imaged on the sample. A different method was used for the data at high temperatures (the data of Fig. 5). The sample was fixed to a dia-

mond face with vacuum grease. Light from a tungsten lamp was brought to the cell from the monochromator via the fiber. To block stray light, an Al foil aperture was placed between the sample and the diamond. A heater surrounding the cylinder of the diamond anvil cell controlled the temperature to within $5°$; the temperature was measured by a thermocouple placed between the anvil supports.

For the picosecond PA measurements, we used two synchronously pumped dye lasers for pump and probe beams focused to 100 μm and overlapped on the sample in the pressure cell. The pump-beam photon energy was fixed at 2.15 eV, while the probe beam was tuned to cover the spectral range 1.2 to 2.15 eV. Changes ΔT in the probe transmission T were measured as a function of the probe delay t. The PA was measured for delays between about 50 ps and 3 ns. ΔT was measured at 10-MHz modulation using a fast lock-in amplifier, a tuned preamplifier, and a Si detector. The sensitivity $\Delta T/T$ of this system was 3×10^{-6}.

III. RESULTS

The OA and PL bands redshift monotonically with pressure (spectra at 0 and 61 kbar are shown in Fig. 1). The OA band shifts rigidly at the lowest pressures, but some broadening is observed at 20 kbar. As seen in Fig. 1, the PL spectrum also redshifts with pressure.

The pressure-induced redshifts in the OA and PL bands are shown in Fig. 2. The gap energy E_g is taken as the extrapolation of the absorption edge to zero absorbance. At the lowest pressures, the shift is

$$dE_g/dP = -10 \text{ meV/kbar} ,$$

smaller than the shift in (CH_x) (-17 meV/kbar),[4(a)] and
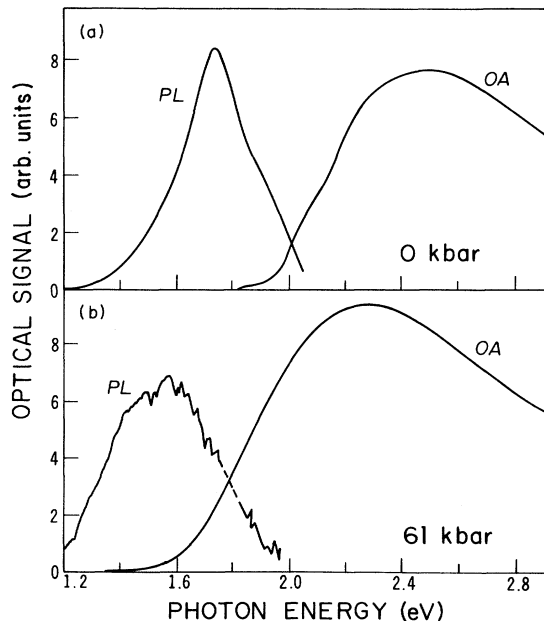

FIG. 1. Optical-absorption and PL spectra: (a) at ambient pressure and (b) at 61 kbar.
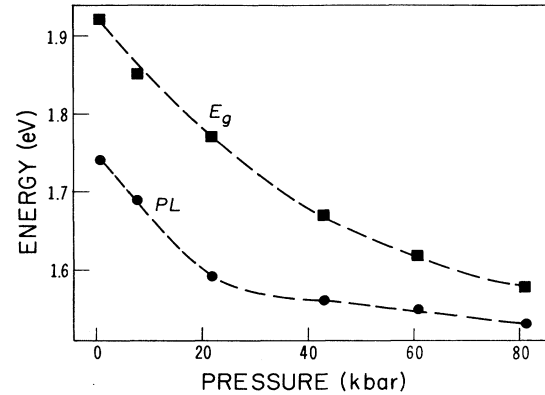

FIG. 2. Shift of the optical-absorption onset and PL band center energies with pressure up to 80 kbar; the lines are guides to the eye.

about the same shift as in polydiacetylenes.[3(b),3(c)] The overall shift is sublinear in pressure, similar to $(CH)_x$ [Refs. 4(a) and 11] and other polymers.[4(b),3(b)] For the PL the energy of the center of the PL band at half-maximum is plotted; the vibronic contributions[12] are not clear at room temperature. Above 20 kbar (Fig. 2), E_g redshifts more than the PL band center, probably due in part to inhomogeneous broadening. Note from Fig. 1 that the separations of the PL peak and the absorption peak remain roughly the same between 0 and 61 kbar.

The integrated PL efficiency decreases markedly with pressure, as shown in Fig. 3. By 80 kbar, the PL efficiency dropped to about 3% of its ambient value. No significant hysteresis in pressure cycling was observed in the absorption or PL spectra, nor in the PL efficiency.

The picosecond PA decay at 80 kbar pumped at 580 nm and probed at 950 nm is shown on a log-log scale in Fig. 4 (solid line). The magnitude of the picosecond PA signal, $\Delta T/T \sim 10^{-4}$ to 10^{-3} at zero delay, is very similar at high pressure to that in unpressed P3HT.[6(c)] The PA
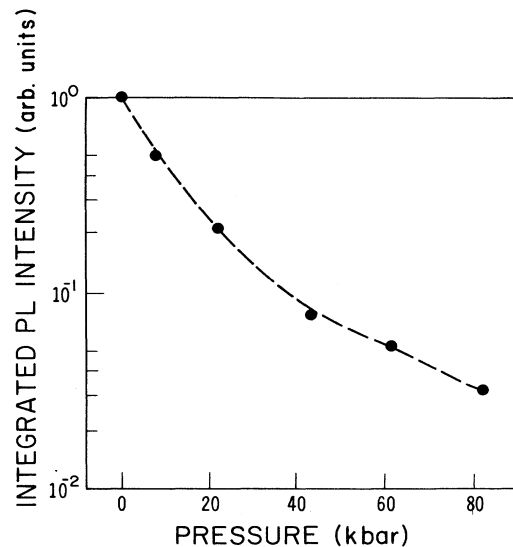

FIG. 3. Decrease of the integrated PL intensity with pressure up to 80 kbar; the line is a guide to the eye.
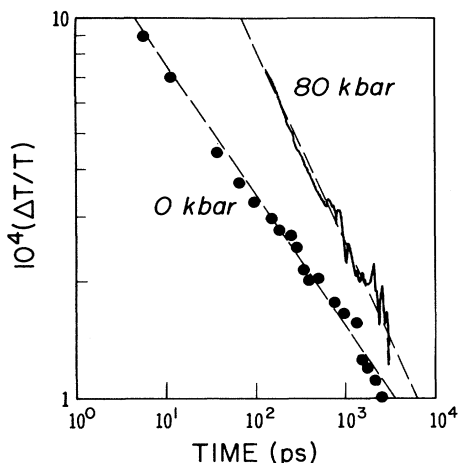
FIG. 4. Picosecond PA decay in P3HT at 80 kbar, probed at 950 nm (solid line) compared to that in PT at ambient pressure, probed at 585 nm (squares). The lines are a fit with power-law decay $t^{-\alpha}$; $\alpha=0.3$ for PT and $\alpha=0.5$ for PT for P3HT at 80 kbar.

at 80 kbar shows a power-law decay $t^{-\alpha}$, with $\alpha=0.50\pm0.03$. The exponents do not change over the probe spectral range from 1.2 to 2.15 eV. In contrast, at ambient pressure the PA decay is significantly slower: $\alpha=0.37$ in P3HT,[6(c)] $\alpha=0.22$ in poly(3-octyl)thiophene (P3OT),[6(c)] and $\alpha=0.3$ in electrochemically coupled PT (Ref. 13) (decay also shown for comparison in Fig. 4).

To investigate the role of pressure in inhibiting rotational defects, we also studied the temperature dependence of the OA at different pressures. At ambient pres-
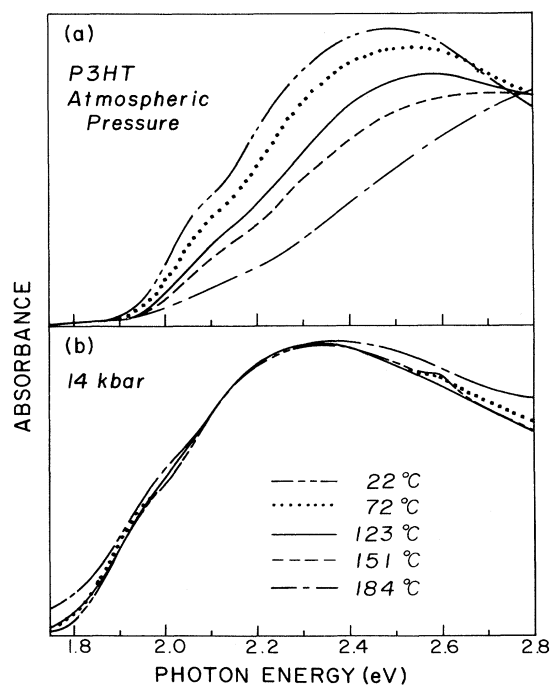

FIG. 5. Optical-absorption spectra of P3HT from 22 to 194 °C (a) at ambient pressure and (b) at 14 kbar.

sure the well-known thermochromic effect[14] is seen [Fig. 5(a)], in which the absorption shifts to higher energies with increased pressure. The effect is due to the reversible conversion of planar, rodlike chains to twisted chains at higher temperatures. At 14 kbar [Fig. 5(b)], however, the OA does not show any temperature shift up to the highest temperature measured, 184 °C (near the ambient-pressure melting point), where only a slight irreversible broadening occurs.

IV. DISCUSSION

In these highly anisotropic conjugated polymers, a dominant effect of hydrostatic pressure should be to decrease the interchain separation. This could cause changes in interchain coupling, the solvent effect, and in the chain conformation.

In $(CH)_x$ the redshift in OA is accompanied by a broadening of the band, which is well explained theoretically by an increase in interchain coupling.[4(a)] But in our case, the OA band shifts rigidly without broadening except at the highest pressures where the shifts are smallest. Perhaps the most convincing evidence against large changes in the magnitude of $t_\perp$ in P3HT comes from the lack of significant change in the picosecond PA intensity and in its overall picosecond decay. If $t_\perp$ had increased greatly, we would expect at high pressure to see an increase in the fraction of long-lived polaronic excitations[6,13] that escape fast geminate intrachain recombination,[5,6] but at high pressure the size of the long-lived picosecond PA signal $\Delta T/T$ is very similar to that in unpressed PT. Only the power-law exponent changes in the PA (Fig. 4) at high pressure, suggesting that the recombination is still limited by the diffusion of 1D polaronic excitations.[6,13] With large interchain coupling, we would expect very different photoexcitations and relaxation pathways. But we observe no new dynamics in the PA decay probed in the gap (down to 1.2 eV), which suggests that no new photoexcitations have been created at high pressure. Although P3HT chains appear to stack in sheetlike structures with the backbones on top of each other,[6(c)] lifetime studies of long-lived (millisecond) excitations[6(c)] indicate that the alkyl sidegroups do decrease the interchain coupling compared to unsubstituted polymers, and our results suggest the sidegroups also prevent a significant increase in $t_\perp$ with pressure.

The dipolar or "solvent" effect was the explanation given for the pressure-induced spectral redshift in polydiacetylenes[3] in solutions and films (where the neighboring chains play the dielectric role of the solvent). The initial pressure shift in P3HT is comparable to the shift in polydiacetylenes.[3(b),3(c)] This effect may have a significant role in the pressure redshift of P3HT. But we have recently shown from resonant Raman scattering at high pressure that the solvent effect alone cannot describe the OA pressure redshift in polydiacetylene 4-butoxy-carbonyl-methylurethane (4BCMU), because it does not predict a parallel softening of the distribution of resonant Raman phonons, which we observe.[15] In addition, we observe a dramatic change in the exciton lifetime in 4BCMU at high pressure,[16] which is explained by confor-

mational rather than solvent effects. In P3HT, the solvent effect certainly cannot account for the dramatic decrease in radiative recombination (Fig. 3).

On the other hand, PL efficiency and spectral shifts depend strongly on conjugation length N, which can reflect the actual chain length or the shorter length of uninterrupted π conjugation. The electronic energies vary with N as

$$E(N) = E_\infty + A/N . \tag{1}$$

This energy dependence has been observed in polyenes,[17] polydiacetylenes,[18] and recently in thiophene oligomers[19] for N between 4 and 24 (i.e., one to six rings). The PL efficiency η is greatest for shortest N, in polyenes and other polymers. In polydiacetylene crystals with planar chains, no PL is detected.[20] On the other hand, in PT and polydiacetylene in good solvents, the chains are randomly coiled and the PL is quite strong. η increases strongly with temperature for P3HT in *solution*,[21] and the activation energy was interpreted as the energy required to create a rotational defect; in this model the rotational defect is a PL recombination center. On the other hand, in polythiophene *films* η decreases with increasing temperature, as is common for other solids, but the decrease is only a factor of about 2 between 20 and 300 K.[12] This weak temperature dependence probably results from two nearly canceling effects as the temperature is increased: an increasing (activated) nonradiative recombination rate and a parallel rising density of rotational defects which act as radiative centers.

Some insight into the role of rotational defects in the radiative process may come from a consideration of the energies of the lower excited states $2A_g$ (radiatively forbidden) and $1B_u$. Theory predicts that with increasing N, the $2A_g$ state crosses below $1B_u$,[17,22] which should decrease the PL as excitations can thermalize (with a parity change) to the lower forbidden state at large N. Recent calculations[23] have shown that when thiophene chains are twisted, the $2A_g$ state again becomes the higher state, which would increase the PL.

Because of repulsion between the sidegroups and the sulfur atom, the lowest energy of a *single* chain of the alkylthiophenes is not planar.[24] While coils and screws are improbable in the solid because they cannot pack efficiently, the ring angles probably fluctuate along the chain to relieve to some degree the steric interactions. In addition, disorder in the sidegroups themselves can disrupt the chain planarity.

Since the planar chain occupies the least volume, this form is favored at high pressure. As Yoshino *et al.*[2] recently suggested, pressure can increase the chain planarity in P3HT as the packing density increases, and hence also increase the average conjugation length $\langle N \rangle$. An increase in planarity would both contribute to the redshift in the electronic energies and decrease the PL intensity. The fact that the PL efficiency recovers as the pressure is decreased shows that the changes are reversible (as expected for conformational changes) and are not due to the creation under pressure of permanent nonradiative

traps in the sample.

The absence of the thermochromic effect at high pressures (Fig. 5) shows that pressure does inhibit rotational defects that are otherwise easily produced thermally at relatively low temperatures. The thermochromic transition temperatures from 100 to 200 °C imply barriers against rotation of about 30–40 meV, consistent with calculated energies[25] for $\pi/2$ rotations in *isolated* chains. The inhibition of the thermochromic effect at 14 kbar shows that the barrier against rotation is greatly increased with moderate pressures.

Pressure-induced conformational changes do not imply that the sample as a whole becomes more homogeneous under pressure; indeed; we see that the PL and OA bands broaden with pressure (Fig. 1). This broadening probably arises from topological defects and amorphous regions, grown in the sample, whose local order cannot be improved as much with pressure. As the pressure increases, the PL decreases as $\langle N \rangle$ increases, and the PL comes more and more from these exceptionally twisted chains, whose energies lie higher in the distribution of electronic energies because of their shorter N. This causes the PL to approach the broadened band edge as the pressure increases (Fig. 2).

The picosecond decay exponent α can also be an indication of increased local order, associated with an increase in $\langle N \rangle$ in the pressed sample, as rotational defects are pressed out. An exponent α of $\frac{1}{2}$ is predicted theoretically[26(b),26(c)] for 1D diffusion-limited recombination on uniform chains and is observed at short times in trans-$(CH)_x$ and other polymers.[26(b)26(c)] α less than $\frac{1}{2}$ observed at longer times can be explained by the presence of disorder.[26(b),26(c)] For example, in trans-$(CH)_x$ at 300 K, a crossover from $\alpha = 0.5$ to 0.37 occurs at about 50 ps.[26] At 80 kbar we observe $\alpha = 0.50 \pm 0.03$ into the nanosecond time range (Fig. 4), suggesting that for purposes of 1D diffusion P3HT at high pressure may be more ordered than unpressed trans-$(CH)_x$ and unpressed polythiophenes ($\alpha = 0.2$ to 0.4).[6(b),6(c),13]

In summary, conformational changes are clearly evident in the suppression of the thermochromic effect with pressure, and are the most likely explanation for the decrease of the PL intensity. While the OA and picosecond PA results seem to rule out a significant increase in the interchain covalent interaction in P3HT, it is likely that both the dipolar "solvent effect"[3] and conjugation length effects contribute to the redshift. The faster decay of the PA at high pressure is consistent with an increase in chain planarity with pressure.

ACKNOWLEDGMENTS

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